Special Series

Per- and polyfluoroalkyl substances (PFAS) exposure through munitions in the Russia–Ukraine conflict

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EDITOR'S NOTE:

This article is part of the special series "Consequences of Modern Warfare on Ecology and the Environment." The series presents a collection of views from global experts on the broad environmental science and policy challenges raised by ecocide as a result of war, providing data-driven, science-based insights that inform our understanding of the environmental impacts of war, and how they may be documented, characterized, and responded to.

Abstract

Considered contaminants of emerging concern, per- and polyfluoroalkyl substances (PFAS) are a class of toxic, manufactured chemicals found in commercial and consumer products such as nonstick cookware, food packaging, and firefighting foams. Human exposure to PFAS through inhalation and ingestion can cause a variety of harmful effects and negative health outcomes. Per- and polyfluoroalkyl substances possess high polarity and chemical stability, enabling them to resist degradation in most environmental conditions. These characteristics allow PFAS to be mobile in soil, air, and water, and bioaccumulate in living organisms. Due to their thermally resistant chemical properties, PFAS are used as binders in polymerbonded explosives (PBX) and in various components of munitions. Thus, when munitions are detonated, PFAS are released into the environment as aerosols and can deposit in the soil, surface water, or biota. Air emission modeling suggests that ground-level and airborne detonation of munitions can increase PFAS deposition both locally and long range. Further, if industrial facilities with PFAS are damaged or destroyed, there is greater potential for environmental degradation from increased release of PFAS into the environment. As a consequence of their persistent nature, PFAS can remain in an environment long after armed conflict, indirectly affecting ecosystems, food sources, and human health. The toxic contamination from munitions could present a greater hazard to a larger population over time than acute detonation events. This article discusses methods for estimating war-related damage from PFAS by exploring predictive modeling approaches and postwar ground validation techniques. Integr Environ Assess Manag 2022;00:1-6. © 2022 The Authors. Integrated Environmental Assessment and Management published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Munitions; PFAS; Russia–Ukraine conflict

INTRODUCTION

Known as "forever chemicals," per- and polyfluoroalkyl substances (PFAS) are a class of toxic, manufactured chemicals found in various commercial and consumer products such as nonstick cookware and food packaging, firefighting foams, and munitions (Cousins et al., 2019). Perand polyfluoroalkyl substances have variable solubility and mobility based on their chemical properties (Bolan et al., 2021; Popek, 2018; Teunen et al., 2021); however, PFAS are generally resistant to environmental degradation; mobile in air, soil, groundwater, and surface water; and able to bioaccumulate in living organisms (Abunada et al., 2020). Due to their recalcitrance, PFAS are now ubiquitous contaminants found in the environment, wildlife, aqueous biota, and humans (Abunada et al., 2020; Banzhaf et al., 2017; Cousins et al., 2019). Air and dust inhalation and ingestion are the main routes of exposure for humans (Agency for Toxic Substances and Disease Registry [ATSDR], 2021; Lloyd, 2021; Tavasoli et al., 2021). Human exposure has

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been linked to endocrine disruption, immunotoxicity, and certain types of cancer (Abunada et al., 2020; DeWitt et al., 2019; Fenton et al., 2020). Significant attention has been given to PFAS in aqueous firefighting foams (AFFF) used by military forces; however, PFAS are used in other military applications, to include military munitions. Although use of PFAS in military munitions is well known, quantification of environmental damages from the detonation of munitions during conflicts, such as the Russia–Ukraine conflict, are not well understood.

PER- AND POLYFLUOROALKYL SUBSTANCES IN MILITARY MUNITIONS

Per- and polyfluoroalkyl substances, typically fluoropolymers, are used in munitions for their ability to withstand high temperatures and pressures. Known applications of PFAS in munitions include use as binding agents and as oxidizers in flares and ignitors when high energy output is required (Olsavsky et al., 2020). Although the use of PFAS in munitions varies, approximately 20% of the US military's most used munitions contain appreciable PFAS content. The fraction of PFAS found in each type of munition also varies but typically accounts for approximately 1%-3% of the munition's net explosive weight. The US military is actively researching changes in perfluorinated chemical structure during detonations at 430 °C-730 °C; however, PFAS are thermally resistant below 1100 °C, indicating a significant fraction of PFAS in munitions is likely to be aerosolized after detonation, not destroyed (Olsavsky et al., 2020). Additionally, the instantaneous detonation of munitions can occur in several ways, including surface-level, below-ground,

and airborne explosions. Munitions can also be destroyed during a slow open burn, for example, if an ammunition cache or a vehicle carrying munitions catches fire. Each of these destruction mechanisms occurs under varying conditions and will affect how PFAS within the munition moves into the environment. For example, buried munition detonations will create more particulate matter than surface-level explosions (Aurell et al., 2015), which will affect the distance that aerosolized PFAS will travel from the explosion. Given these considerations, release of PFAS into the environment due to munition definition can be considerable, especially when large quantities of munitions are detonated over long timescales.

MOVEMENT AND FATE OF PFAS POSTDETONATION

The movement and fate of PFAS postdetonation is also an area of research (Olsavsky et al., 2020). Figure 1 depicts the probable transport of PFAS after detonation and their fate in several compartments. Published studies have explored chemical and particulate dispersion patterns after detonation of surface-level and buried munitions (Aurell et al., 2015; Kim et al., 2016); however, available studies of PFAS aerosol dispersion have been limited to industrial factories with elevated stacks (D'Ambro et al., 2021; Kim et al., 2016; Shin et al., 2011). These studies suggest that PFAS may be directly inhaled by those in the vicinity of the detonation. Per- and polyfluoroalkyl substances air emission studies also suggest that contaminant accumulation in soil or water bodies may occur locally and at greater distances because of long-range atmospheric transport

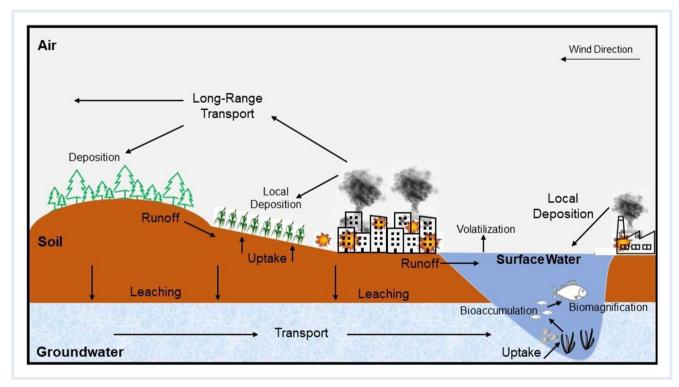


FIGURE 1 Probable transport and fate of per- and polyfluoroalkyl substances (PFAS) postdetonation

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(D'Ambro et al., 2021; Thackray et al., 2020). In addition to air emissions, shrapnel and unexploded ordnance can contain PFAS, which can leach into soil or enter water through runoff. Estimated half-lives in surface water of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are 41 and 92 years, respectively (Agency for Toxic Substances and Disease Registry [ATSDR], 2019, 2021; National Toxicology Program, 2016; Sellers et al., 2020). Due to various capacities of soil binding, retardation, and absorption, leaching varies by PFAS, with short-chain PFAS being more mobile than long-chain (Bolan et al., 2021). Shorter chain PFAS contaminants in soil can also more easily leach into the vadose zone and contaminate groundwater (Abunada et al., 2020).

Widespread dispersion of PFAS from munition detonation can increase exposure and opportunities for ingestion by organisms at all trophic levels in the food web. This increased exposure also facilitates biomagnification, as the concentration of PFAS will increase in organisms found at the highest trophic levels (Alcaraz et al., 2011; Andres et al., 1999; Kim et al., 2015). Bioaccumulation of PFAS in blood and liver, even with minimal exposure to PFAS over long time frames, can be harmful—even if individuals are no longer actively exposed (ATSDR, 2019). An example of the harmful impacts from aerosolized PFAS may be observed in Ukrainian agriculture. Once water or soil is contaminated, livestock and crops can be exposed to PFAS through uptake or ingestion. If undetected in soil, PFAS in harvested crops can be transported great distances from the location of initial munition detonation (MacDonald, 2022). To support farming operations, farmers often must travel farther distances to sell produce (Dathan, 2020; MacDonald, 2022). Before this conflict, Ukraine provided 10% of global wheat and 14% of corn exports (Dathan, 2020). Further, as a result of the resistant nature of PFAS in soil, remediation is costly and time consuming. For example, soil in France and Germany is still contaminated by WWII munitions, with 2000 tons of unexploded bombs and munitions found yearly (Knolle, 2021).

QUANTIFYING PFAS FROM MUNITIONS IN THE RUSSIA–UKRAINE CONFLICT

An estimation of war-related damage from PFAS released during the Russia–Ukraine conflict could be ascertained from a combination of predictive modeling and postwar onground validation techniques. For predictive modeling, a multistep process can be used, beginning with estimating the quantity of PFAS released by military munition detonations, predicting how PFAS moves through the environment postdetonation, and then predicting the fate of PFAS after movement in several compartments—soil, groundwater, surface water, and biota. For postwar model validation, on-ground sampling and analysis can be used to help quantify PFAS in each compartment. The analysis can be strengthened by a comparison with known, or estimated, background PFAS concentrations in each area analyzed (where available). The estimated quantity of PFAS released by munitions to the natural environment in Ukraine during the conflict initiated in 2022 could be modeled using a combination of several factors, to include the number of munitions detonated, the type of munition, the PFAS content in each type of munition, the location of detonation, and how the munition is detonated. As mentioned, munitions normally detonate in one of three ways: airborne explosion (i.e., at some distance above the ground), at ground-level on impact, or beneath the ground level (i.e., buried; Aurell et al., 2015). Each detonation method should be considered an instantaneous occurrence, as the detonation happens in a fraction of a second. Given these factors, PFAS emissions from a single munition detonation, or grouping of munitions detonated in the same vicinity, can be modeled as:

Note: For instantaneous detonations, the time of detonations could be assumed to be 1 s.

The number of actual detonations versus the number of munitions fired should also be considered in estimating an emission rate. Compared with an approximately 5% failure rate in modern US weapons, Soviet weapons are estimated to have up to a 60% failure rate (Stewart, 2022). If munitions fail to detonate, then a much smaller amount of PFAS (perhaps none) will be released to the immediate area.

Due to their recalcitrance, PFAS released from munitions may not chemically transform or degrade at detonation temperatures (Olsavsky et al., 2020). Perfluorinated substances can be found within particulates or in a gaseous state; however, PFOA and PFOS, which are ionic, are more likely to be found in particulate matter (Ahrens, 2011; Ge et al., 2019). Therefore, PFAS released can conservatively be assumed to all be emitted to the atmosphere as an aerosol, and the emission rate determined in Equation (1) can be used in dispersion models to determine aerosolized PFAS dispersion patterns (D'Ambro et al., 2021). Other factors such as meteorological data, atmospheric stability, wind speed, and wind direction need to be considered for accurate dispersion modeling (Cooper & Alley, 2010). Of note, PFAS released from munitions destroyed during an open burn, which typically occurs at lower temperatures over a period of minutes or hours (i.e., not instantaneous; Longendyke et al., 2022; Olsavsky et al., 2020), should be considered separately in dispersion models, as should unexploded ordnance.

Once emitted into the atmosphere, PFAS can disperse both locally and globally (D'Ambro et al., 2021; Shin et al., 2011); dispersion modeling can estimate the fraction of PFAS that stays locally or regionally in Ukraine versus the amount dispersed to more distant locations. The most likely compartment aerosolized PFAS will deposit is surface soil, especially in more rural areas. From there, PFAS can transfer to groundwater and subsequently to drinking water, crops,

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and biota (Paustenbach et al., 2006). A fraction of emitted PFAS will also deposit onto surface water and be transported further from the source (Davis et al., 2007; Galloway et al., 2020). Therefore, PFAS dispersion models need to incorporate accurate geographic information for the detonation area.

After deposition, the PFAS can be modeled as partitioning into soil, groundwater, and/or biota using a combination of approaches. Sima and Jaffé (2021) reviewed PFAS models used for the soil-water environment, finding that sorption isotherms (i.e., linear, Freundlich, or Langmuir) are commonly used for modeling PFAS soil sorption. Further, models have recently been proposed to quantify subsequent PFAS leaching from the vadose zone to groundwater, to include surfactant-induced flow models and ratelimited, nonlinear adsorption models (at the soil-water interface; Guo et al., 2022). In principle, these approaches could be used in conjunction to model how PFAS released from munitions are transported through the air, then to soil and groundwater.

Per- and polyfluoroalkyl substances are transported from groundwater to crops via irrigation (Lee et al., 2014). Uptake of PFAS from crops and subsequent impacts on human health can be estimated using identified human health toxicity reference values (RfDs) for known PFAS (Brown et al., 2020). Per- and polyfluoroalkyl substances are also known to bioaccumulate in aquatic species, and bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) have been established for several taxonomic classes (Burkhard, 2021). The BCFs and BAFs can be leveraged to estimate the increase in PFAS found in aquatic species, particularly in areas with a large number of detonated munitions.

A significant challenge with the aforementioned predictive modeling approaches is available data. Accurate open-source data concerning munitions used in Ukraine will likely be challenging to find and, to date, are not readily available. Although military intelligence agencies may closely monitor the conflict, on-ground postwar surveys are likely needed to identify more detailed information concerning munitions used, especially in more war-ravaged areas. One way to begin to estimate the impact and approximate number of munitions detonated is to use satellite imagery (e.g., Landsat) to examine prewar and postwar destruction. Coupling these imagery data with available reports concerning the conflict (e.g., type of military unit and intensity of fighting) can provide a rough estimate of the munition type and quantities used in a given area.

Modeling approaches to estimating the fate of PFAS in soil, water, and biota should be validated through on-ground sampling and analysis when practical postconflict. Table 1 provides current USEPA analytical methods for quantifying PFAS in major compartments. Further, Schroeder et al. (2021) provide an example study for sampling contaminated soil and groundwater from aerosolized PFAS that can apply to PFAS emitted from munition explosions.

Another method to quantify PFAS in biota are biomonitors, which quantitatively assess alterations to the environment

 TABLE 1 US Environmental Protection Agency analytical methods for quantifying per- and polyfluoroalkyl substances (PFAS)

Compartment	Quantitative methods
Water	Surface water or groundwater concentrations (EPA draft method 1633)
	Drinking water (EPA method 537.1)
Soil	Sediment analysis (EPA draft method 1633)
Biota	Crops or processed food (FDA C-010.02), fish tissue (EPA draft method 1633)
Air	Gaussian dispersion modeling (EPA Other Test Method-45)

using biological systems on a temporal or spatial scale (Markert et al., 2003). Biomonitors, such as caged bivalves, can be transported to detonation areas, where they can detect and quantify PFAS in water and sediment (Zhou et al., 2008). Biomonitor PFAS concentrations can be used to validate BAFs used in models. The BAFs can be determined using the ratio between steady-state chemical concentration in biota and water (L/kg; see equation below; Gobas et al., 2009).

$$\mathsf{BAF} = \frac{C_{\mathsf{PB}}}{C_{\mathsf{PM}}},\tag{2}$$

where C_{PB} is the PFAS concentration in biota (µg/kg), and C_{PM} the PFAS concentration in surrounding mediums (µg/L).

Further, PFAS concentrations found in soils and bioindicators (e.g., soil microinvertebrates, earthworms, etc.; Dahiya et al., 2022) in munition fallout areas should be compared with PFAS concentrations in nearby areas that experienced fewer, or no, munition detonations. Doing so can help parse out prewar ubiquitous, background PFAS concentrations versus PFAS from wartime munitions and strengthen understanding of war-related PFAS impacts. Drinking water should also be monitored to determine changes in PFAS concentrations, although baseline prewar drinking water quality data in some areas of Ukraine may be limited (Ober et al., 2022).

It is important to note that the ongoing protection of human life during the Russia–Ukraine conflict is of paramount importance. However, the release of PFAS during the war, unfortunately, will create aftereffects on human health that could be increasingly impactful years in the future. Therefore, quantifying the amount of PFAS released from munitions through predictive modeling and postwar onground validation approaches is needed.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

AUTHOR CONTRIBUTIONS

Lauren A. Koban: Conceptualization; Writing—original draft preparation. Andrew R. Pfluger: Conceptualization; Writing—reviewing and editing; Visualization.

DATA AVAILABILITY STATEMENT

Data are available on request from corresponding author Lauren A. Koban (lkoban@gmu.edu)

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