# Advances in the area of greener munitions and energetics

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***Abstract:*** *The paper provides an overview of the lessons learned in Romanian MoD while trying to reduce the environmental impact of the armament systems, in the context of fast changes in legislative, social and technological challenges. Legislative risks and drivers, steps to be followed and relevant aspects regarding available solutions for reducing the environmental impact of munitions are discussed.*

***Keywords:*** *environmental impact; heavy metals; toxicity; energetic materials; munitions*

## 1 Drivers demanding for Greener Munitions

Firing of conventional munitions has an important effect on the environment, which manifests mostly in the firing position (direct action of gases over the operators and nearby personnel; deposition of incomplete burn products on the soil; atmospheric pollution; direct action of the shock wave against operators, nearby personnel and structures; noise pollution) or in the target position (explosion effect; unexploded ordnance; fragments from projectiles, fuses, etc., resulted from firing; soil, water and air contamination; noise pollution). Other important negative effects are generated during manufacture and disposal of the munitions, but these are easier to control and mitigate.

In the last two decades we assisted to stronger and stronger trends, which are driving increased pressure on users and manufacturers of energetics and munitions to approach the improvement of the environmental impact of their products, starting with compliance with the national and international applicable regulations.

The complexity of environmental legislation regarding manufacture, use and waste treatment is expanding rapidly around the world, but especially in EU and US. REACH, RoHS, and other directives are introducing more and more restrictions and disclosure regulations. In parallel, the enforcement agencies and NGO's are stepping up surveillance as they become more aware on how to enforce regulations so they are active in exposing violations.

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Nations are increasingly concerned about environmental, health, and safety aspects incurred by the use and disposal of these materials, and they are willing to support higher acquisition costs for environmentally friendly ordnance that can diminish the costs related to the management of training ranges and disposal actions. In the public sector, we can see increased efforts to update the purchasing policies by taking into account the environmental impact of the products. The best example is the EU Ecolabel scheme aiming at highlighting products that have a reduced environmental impact throughout their entire life cycle, from the raw material to production, use and disposal.

In this context, of fast changes in legislative, social and technological challenges, numerous countries and organizations have acknowledged the environmental impact of military activities and dedicated a lot of effort towards its assessment and mitigation. Munitions were blamed as the main vector for spreading dangerous chemicals in the environment, varying from heavy metals to complex organic molecules, thus the concept of Green Munitions (or Greener Munitions) being introduced and developed in MoDs and industry.

In Romania, the National Defence Strategy adopted in the last years urged the RO MoD and the defence industry to adapt and comply to EU legislation, to prevent pollution and optimize the waste management, to extend their efforts to re-establish and preserve the environment, to encourage and promote less pollutant activities and technologies and to reduce negative impact of military activities on the environment. In this context, the RO MoD has decided to improve its knowledge, procedures and tools for the environmental management in order to diminish the consequent impacts.

The involvement in the excellent collaborative work performed within European Defence Agency - EDA-GEM2 project Environmentally Responsible Munitions – ERM (Ad Hoc project led by UK and supported by other six nations: NL, PT, GE, FR, NO and RO) greatly contributed to a better understanding of this area.

## 2 Impact of legislation on ammunition production, use and disposal

National legislation is usually defined by: Laws, Decrees, Decisions of the Government, Orders of the Ministry/Agency of Environment, Standards or Regulations. A synthesis of the provisions regarding the maximum allowable concentrations for substances of interest should be used for the comparative evaluations after field and laboratory experiments. Regarding the European legislation, the first to be mentioned is the Directive 2000/76, which has direct implications upon incineration installations of ammunitions and EM, requiring the use of a series of filtration and purification systems for gases resulted in the process. The Directive is based on an integrated approach, containing both provisions concerning the maximum permissible air emissions and maximum allowable values for water emissions. The incineration or co-incineration installations have to be approved and operation approval is given by the competent authorities only if it satisfies the 76 Directive requirements. The Directive requires installations equipped with special monitoring system of the plant parameters and emissions values. The fulfillment of 76 Directive provisions makes EM's incineration process very expensive, so many demil agencies are starting to re-evaluate the possibility of recovery and reuse of EM.

The provisions of other EU regulations were analyzed as they may affect the future use of certain chemicals in the manufacturing process of EM and ammunitions.

What we concluded after the EDA-ERM experience was that the most important legislative drivers in EU, in this area, are the REACH for the manufacture, the waste directive and the air quality directive for disposal and the national provisions regarding thresholds concentrations of different contaminants in air, water and soils for the use of munitions. An EDA study on Ammunition non-EU Dependencies [1] revealed that basically for all infantry, tank and artillery ammunitions there are major non-EU dependencies generated by environmental legislation and especially by REACH.

ECHA (European Chemicals Agency - Helsinki, Finland) is the EU agency that administers the registration, evaluation, authorization and restriction of chemicals. SVHC (Substance of Very High Concern) chemicals, which are listed by the agency, have to be authorized by the ECHA before production, import or use inside the EU. Member states, ECHA or the European Commission may propose a substance to be identified as a SVHC. At this point, more than 140 substances are on this list, including some very important chemicals for the ammunition industry, such as 2,4-dinitrotoluene, di-butyl-phthalate, di-isobutyl-phthalate or bis-(2-ethylhexyl)phthalate. The SVHC list is amended continuously and a substance which is once on the list will be always on the list. The substances identified in the SVHC list are eventually included in Annex XIV of the REACH Regulation and once included in that annex, they cannot be placed on the market or used after a date unless the company is granted an authorization. For example, at this point 2,4-dinitrotoluene, di-butyl-phthalate or lead and other 20 compounds used in ammunitions are on this authorization list.

In RO, a review of the ammunitions in use and their components revealed the following substances of concern from the perspective of the EU and national legislation: Pb compounds (picramate, oxides, azide, styphnate); Sb compounds; Ba compounds; Hg compounds; Sr compounds; W; Potassium nitrate; Potassium chlorate; Ammonium perchlorate; Phthalates (dioctyl and dibutyl); Halogen-compounds (carbon tetrachloride, hexachloroethane, hexachlorobenzene); DPA and nitroso/nitro derivatives; Centralites; NC; TNT; DNT; RDX; PETN; EGDN; NG.

## 3 Ways to make munitions greener

There are numerous ways to reduce the environmental impact of military training, such as the use of greener materials, replacement of toxic compounds from ammo parts, smart range management to control contamination and ease of remediation, extensive use of self-destruction mechanisms, practice with non-pollutant blank ammunition, detection and disposal of unexploded ordnance (UXO), and others.

An important phase of the process should be the acknowledgement of the significant environmental problems raised by the legislative or social drivers and the development of a coherent assessment process for the evaluation of environmental impacts. This could involve for the MoDs to enforce specific environmental policy for the development of new munitions, for the periodic T&E phase, or the procurement phase. There are European countries, such as UK [2], which have successfully developed and applied environmental management systems and assessment methodologies to assist MoDs in the identification, characterization and prioritization of the environmental impacts and risks, related to the manufacture, use and disposal of ammunitions and energetics.

The legislative targets and drivers should be very well defined, which involves a thorough study of the national and international legislation regarding the environmental provisions in manufacture, use and disposal.

Secondly, an inventory of all the munitions in use and their main constituents should be performed, conducting to the selection of "problematic" ingredients that could be the source of pollution/health issues and could make the object of replacement and subsequent redesign of the system.

The third phase, and maybe the most difficult, is the development of the theoretical and experimental tools for the assessment of the environmental impact in very specific situations. If we are to refer just to the use of the ammunitions, a proper assessment involves the following: calculus and/or measurement of the combustion products and residues released in the environment, measurement of deposition rates, and evaluation of short/long term effects, persistence, transport, eco-toxicity and toxicity.

Once the problems identified, the replacement of hazardous compounds and redesign of the munitions can be taken in account. This issue made the object of many recent scientific publications the synthesis and characterization of new energetic materials (EMs) as replacements in primers, igniters, boosters, main charges or propellants. But not only the explosive substances are to be blamed for the environmental impact. Plasticizers and stabilizers are sometimes far more dangerous if released in larger quantities or under the form of more toxic combustion products. Also, a lot of work was dedicated to replacement of toxic heavy metals in the ammunitions parts that are released in the environment by abrasion, projectiles, combustion/detonation or as UXO. But often the replacement of "dangerous" components in the ammunition does not guarantee a lower environmental impact. It involves redesign of the system and can produce other hidden impacts, such as energy consumption and supplementary emissions of potentially hazardous chemicals.

Alternatives to the replacement of the energetic or metallic components may be the improvement of the fuse systems (to reduce UXOs rate), the design for disposal coupled with recover and reuse techniques, extending the use of training dummies and smart range management.

# 4 Analysis techniques for environmental impact assessment

One difficult step in the environmental impact assessment related to the use of ammunitions is the measurement of the combustion products and residues released. Usually, gaseous products and solid residues are to be determined. CO, CO2, NOx, HCN, NH3, PHA, dioxins, metals, PM2.5 and PM10, unburned EM, are often monitored.

## 4.1. Live measurement of combustion products and residues

Maybe the most challenging task is the live measurement of combustion products and residues. In the case of pyrotechnic items and small arms ammunition, this can be performed in indoor shooting ranges/labs with total containment of the products and residues in closed vessels, usually plastic (PE) containers or bags. The gaseous products can be analyzed using FTIR, chemo-luminescence (for NOx) or electrochemical sensors mounted directly inside the recipient. The aerosols can be collected using specialized pumps with particle counter systems and porous filters, while the solid residues deposited in the recipients are washed with distilled water and analyzed by AAS or ICPMS. The fumes collected on glass fiber can be analyzed for metal content by the same techniques or by SEM-EDX, when morphological characterization is also performed.

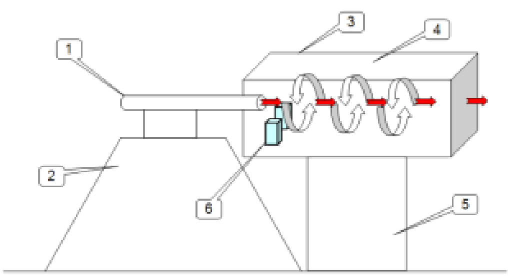


**Figure 1:** Experimental setup: 1. Lab weapon; 2. Weapon support; 3. Frame; 4. LDPE membrane; 5. Support; 6. Electrochemical detectors

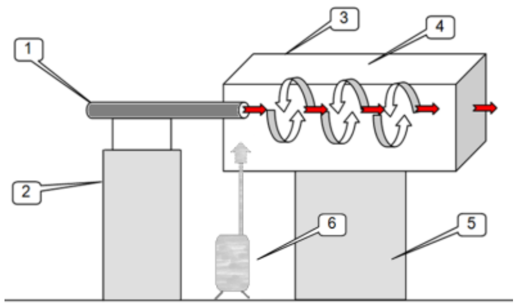


**Figure 2:** Experimental setup: 1. Lab weapon; 2. Weapon support; 3. Frame; 4. LDPE membrane; 5. Support; 6. Specialized sampling pump with glass-fiber filters

Studies performed at Military Technical Academy (MTA) during the EDA-ERM project on several 9x19 mm ammunitions using experimental setups according to figures 1 and 2 showed that even combustion of simple base propellants is not always ideal and can produce high concentrations of CO, NOx and unexpected dangerous gaseous products, such as HCN and NH3, probably due to the DPA stabilizer (table 1).

Regarding the metal residues/fumes, AAS and SEM-EDX measurements performed on four types of ammunitions, including ammunitions with composite Cu bullet and Sinoxid/Sintox primers, revealed high concentrations of Pb and/or Cu in the residues for all types (figures 3 and 4). The metal composition of residue indicates that composite Cu bullets are not entirely greener as they generate high quantities of Cu, which is equally dangerous for the environment (same threshold values with Pb for soils) but much safer for the human health (almost 3 orders of magnitude higher threshold values compared with Pb).

**Table 1:** Gas concentrations measured for typical 9x19 ammo

| Ammo<br><br>Gas | FMJ-SINOXID<br>Concentration<br>[mg/g propellant] | FMJ-SINTOX<br>Concentration<br>[mg/g propellant] |
|---|---|---|
| CO | 484.52 | 450.60 |
| $CO_2$ | 248.27 | 236.07 |
| NO | 9.46 | 7.86 |
| $NO_2$ | 1.57 | 1.51 |
| $NH_3$ | 7.56 | 6.01 |
| HCN | 4.32 | 2.97 |

It is also noticeable the large concentration of lead residue produced by the ammunitions with lead bullet and lead-free primer, this indicating that a large amount of the lead residue is generated through the erosion of the exposed back of the bullet.

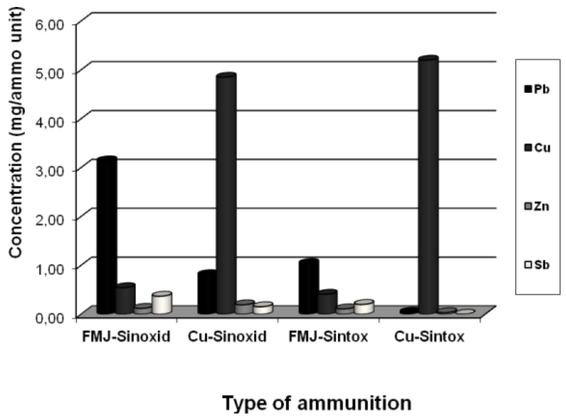


**Figure 3:** Metallic residues by AAS

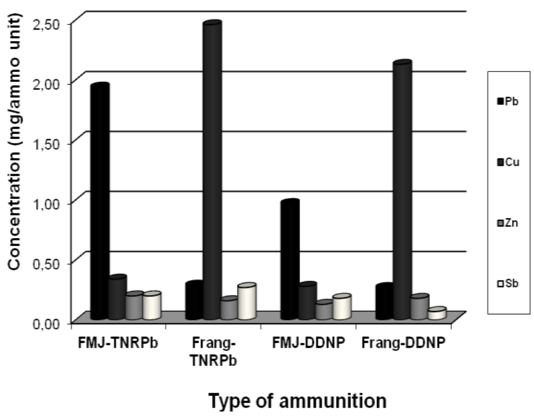


**Figure 4:** Metallic fumes by SEM-EDX

The morphological analysis of the metallic fumes using SEM showed that the vast majority of the particles have diameters in the range 0.1÷0.7 µm, which are considered very dangerous for the accumulation in the respiratory tract.

The study also revealed that over 90% of the solid residue (50 to 100 mg per ammo unit) is composed by unburned or partially burned propellant and that is a serious source of contamination especially for the outdoor firing ranges where the cleaning up of the deposits is not possible.

Other research teams [3] evidenced that replacing the lead core of the bullets with other harder materials, like tungsten or steel, could produce higher emissions of copper due to the abrasion with the bore.

For large caliber and large pyrotechnic items, live measurement of the combustion products and fumes is almost impossible because measurements have to be performed with real life weapons in open firing ranges and they are too dependent on the weather (temperature, wind speed, wind direction, humidity). On the other hand, the rapid spread of products into the atmosphere gives little sample uptake for any further analysis.

However, it is possible to simulate the real firing conditions through burning large caliber propellants for the obtainment of combustion products (solid and gaseous) in special designed ignition chambers in which the pressure can be fitted to match cannons or mortars.

The solid residues spread on the soil can also be collected and analyzed according to the procedures described by Walsh et al. [4], preferable after deposition on snow.

MTA performed the analysis of the emissions for the 12 kg HCH type RO smoke candle LF-12 and determined maximum aerosol concentration (photometrical), gaseous emissions (electrochemical sensors) and metal content in the fumes (SEM-EDX). The results are given in tables 2 and 3.

**Table 2:** Aerosols and gases from LF 12 smoke candle

| Atmospheric cond. | | | LF-12 aerosols | Gas emissions Max. conc. (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|
| Wind (m/s) | Temp. (°C) | Humidity (%) | Max. conc. (particles/cm$^3$) | HCN | NO | $NO_2$ | CO | $Cl_2$ |
| 2÷4 | 28.5 | 61 | 4.3 x $10^6$ | 4.7 | 3 | 0.5 | 61 | 0.9 |

**Table 3:** Relative concentrations of elements (wt. %) in LF-12 aerosols

| Elements | C | Al | Zn | Ba | Pb |
|---|---|---|---|---|---|
| Relative conc. (wt. %) | 55.24 | 15.47 | 23.24 | 3.80 | 2.25 |

The measurements revealed the presence of dangerous gaseous products, such as CO, HCN, NOx and Cl2 but also the presence of Pb and Ba compounds in the aerosols, due to the use of Pb3O4 and Ba(NO3)2 oxidizers in the igniter.

## 4.2. Characterization of soil contamination

During the last decades, numerous countries have performed the characterization of contamination sources from the use of ammunitions in various ranges for live-fire training or testing. By far, the Technical Co-operation Program (TTCP) program [5] run by United States, Canada, UK, Australia and New Zealand, have brought the greatest contribution to the development of protocols for EMs contaminated sites characterization. Their investigations regarding EM residues in soils at training ranges showed that TNT and its degradation products (A-DNT), RDX, HMX and AP are the usual contaminants for the impact areas. They also showed that about 99.997 % of the EM is transformed to non-hazardous compounds if high order detonation occurs, indicating that UXOs and low order detonations are the main cause for the site contamination. Another important contribution of the TTCP work was the development of multi-increment sampling strategy and also the validation of environmental military threshold values for explosives in soils, a valuable instrument in the context of absence of corresponding national legislation.

But while contaminations in the impact areas are dominated by high explosives, and this contamination can be greatly reduced by UXOs collection and disposal, the contamination in the firing area is dominated by unburned propellants (DNT, NC and NG) and heavy metals from primers and abrasion.

A study performed by MTA during the EDA-ERM program in the Artillery Testing Range of the RO Armed Forces, using modern multi-increment sampling and composite sampling techniques, indicated soil and vegetation contamination, especially with Pb and Cu in the firing line areas (table 4). The contamination was limited to the upper layer of the soil (50 cm) as indicated by the depth core samples collected down to 3 m and the aquifer analysis did not evidence any transport of the contaminants.

Related to soil contamination, aside for the degree of contamination, “fate and transport” studies are equally important as they indicate how a contaminant behave in a specific environment as a result of its potential to be transported, or transformed and transported, and finally being accumulated in some media.

**Table 4:** Soil concentrations at artillery systems firing line

| | Hg | Cu | Pb | Zn | Sb | Cd | Cr | Ni |
|---|---|---|---|---|---|---|---|---|
| Average on hot spot samples (mg/kg) | 0.16 | *1,482.50* | *356.78* | 164.00 | 2.33 | 0.59 | 43.26 | 31.31 |
| Average on composite samples (mg/kg) | 0.12 | *331.04* | 127.78 | 102.88 | 1.74 | 0.50 | 39.44 | 29.21 |

During the last decade, extensive studies were performed regarding fate and transport of munitions contaminants shifting the general opinion about the “greenness” of consecrated explosives [6-11]. Thus, nowadays TNT and HMX are regarded as greener explosives due to their lower solubility and biodegradability (TNT) compared to RDX.

Performing toxicity and exposure assessment for the potential contaminants is another difficult task as the toxicity data for energetics and munitions components are not easily available.

## 5 Green options for munitions in design and manufacture

Obviously, the first option in our mind for making munitions greener is the replacement of harmful compounds. EMs and especially nitro-compounds, lead compounds and AP were the first to blame for spreading dangerous chemicals in the environment. Lately, a number of publications were dedicated to the synthesis and characterization of greener alternatives to primary and secondary explosives as well as oxidizers for composite propellants. Those were discussed in detail in reputed publications by Klapoetke [12], Talawar [13] and finally by Brink [14] so these will not make the object of our discussion.

What we concluded from our experience in the EDA-ERM project was that there are very few options for the replacement of the consecrated explosives that are really taken in account by the industry. For example, the lead azide and lead styphnate are still produced and used in detonators and primers because their overall quantity/manufacturer is limited and part of it could be exempted on the basis of defense applications. So, basically the pressure for the replacement of lead compounds is generated mostly by the users and range holders.

One of the main concerns of the industry nowadays is related to the replacement of phthalates and stabilizers, which are requested in large quantities and are no longer available in Europe due to REACH. Sebacates, adipates and terephtalates are investigated as replacements as they are not yet on the SVHC list.

Regarding the replacement of RDX in explosive formulations, in spite of numerous new candidates presented by the academia, the industry prefers to reorient towards HMX, which is regarded now as a greener alternative due to its lower solubility. So the focus is on new binders systems which could diminish HMX sensitivity and could assure convenient and safe recovery of the original crystals. Thermoplastic elastomers could represent a solution but the recovery of the explosive will finally involve the use of solvents and the overall greenness of the process could be compromise.

Starting from the principle of polymers used in pharmaceutical application for controlled drug release, MTA performed preliminary studies regarding the synthesis of “smart copolymers” based on copolymers of acrylic acid and alkyl-acrylates, which are insoluble at neutral or acidic pH, but can dissolute in water at 30-40 °C and basic pH values. The results obtained so far are promising as copolymers soluble at pH greater than 10 and insoluble at lower pH values were obtained. This “on demand” water solubility could be used for the incorporation of explosive crystals as well as for controlled recovery of the explosive while maintaining its original morphology.

Considering that the UXOs are responsible for the majority of the environmental impacts, and the average dud rate is 5%, another serious alternative to the replacement of the harmful EMs is the improvement of the fuse systems and the addition/improvement of self-destruction mechanisms to existing fuses in order to reduce or eliminate the UXOs.

Regarding the reduction of heavy metals contamination, having in mind that sampling and chemical analyses are very expensive, we concluded that we could significantly reduce that cost by knowing what we are looking for and where we have to look. Especially for small arms training ranges, we concluded that the best option available at this time, considering also the shortcomes of the proposed alternatives, is to adopt smart range management systems. Databases containing information about the chemical content of ammunition (warheads, propellants, fuzes) could be linked to a range registration database comprising the reports of the users, with the type/number of ammunition used and the number of lost duds. Thus, an image of the identity and distribution of contaminants from munitions is supplied in order to develop a proper monitoring strategy and remediation measures.

# 6 Conclusions

The excellent collaborative work performed within the EDA-GEM2 project Environmentally Responsible Munitions – ERM greatly contributed to a better understanding of the area of greener energetics and greener munitions in the Romanian MoD. The lessons learned by performing the study on legislative impacts and drivers revealed that the industry and the users are not always looking for the same solutions when looking for greener products. While MoDs are mostly interested by controlling, monitoring and reducing range contamination with explosives and heavy metals, the manufacturers issues are more related to the provisions of the EU regulations regarding the restriction in use of some chemicals listed as substances of very high concern.

Development of analysis procedures and infrastructure for the assessment of environmental impact of munitions is always a difficult task especially when live measurements are to be performed. The main solutions for the live detection of combustion products and residues and typical results were discussed here.

Studies regarding the characterisation of soil contaminations usually target the impact areas for contamination with EMs, while contamination with heavy metals and propellants of the firing line areas is equally important.

Besides the replacement of harmful explosives from the energetic formulations, which is always regarded as the first option, there are also some other options to consider for reducing the environmental burden related to the use and disposal of munitions, which could be faster implemented by the users and manufacturers.

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