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Pollution and risk assessment of potential hazardous elements in a shooting range soils (NW Spain)

Contaminación y evaluación de riesgo de elementos potencialmente peligrosos en suelos de un campo de tiro (NO España)
Contaminação e avaliação de risco de elementos potencialmente perigosos en solos dum campo de tiro (NO Espanha)

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ABSTRACT

Pollution at shooting ranges is an issue of growing importance. Accumulation in soils of potentially harmful elements (PHEs) from ammunitions used is a major environmental risk. The total and available (extraction with 0.01 M $CaCl_2$ and DTPA) content of As, Cd, Cu, Ni, Pb, Sb and Zn were evaluated in 10 soils from a shooting range for military use (León, Spain). The results showed that, among the studied pollutants, Pb is the element present in highest concentration (13.83-4451.57 mg kg^{-1}), followed by Sb (1.80-96.10 mg kg^{-1}), Cu (4.50-88.52 mg kg^{-1}), As (13.24-62.47 mg kg^{-1}), Zn (13.31-46.19 mg kg^{-1}), Ni (11.53-46.30 mg kg^{-1}) and Cd (0.30-1.00 mg kg^{-1}). The strong soil acidity, its medium organic matter content and low proportion of clay, favor a high availability of these PHEs, particularly Pb and Cu. Although impact mitigation measures, such as collecting cartridges whenever a round of shots is fired in the shooting range, the pollution assessment indicates that performances should improve in the berm. The application of organic amendments, or nanomaterials, could help reduce the PHEs availability and avoid the contamination of adjacent areas.

RESUMEN

La contaminación en los campos de tiro es una preocupación de creciente importancia. La acumulación en los suelos de elementos potencialmente peligrosos procedentes de las municiones utilizadas supone un gran riesgo ambiental. Se evaluaron los contenidos totales (As, Cd, Cu, Ni, Pb, Sb y Zn) y disponibles (extracción con $CaCl_2$ *0,01 M y DTPA) en 10 suelos de un campo de tiro de uso militar (NW de España). Los resultados mostraron que el mayor contenido es el de Pb con mayor concentración (13,83-4451,57 mg kg*$^{-1}$*), seguido del Sb (1,80-96,10 mg kg*$^{-1}$*), Cu (4,50-88,52 mg kg*$^{-1}$*), As (13,24-62,47 mg kg*$^{-1}$*), Zn (13,24-46,19 mg kg*$^{-1}$*), Ni (11,53-46,30 mg kg*$^{-1}$*) y Cd (0,30-1,00 mg kg*$^{-1}$*). La fuerte acidez de los suelos, el contenido medio de materia orgánica y la baja proporción de arcillas favorecen la elevada disponibilidad de estos elementos, en especial de Pb y Cu. A pesar de que en el campo de tiro se realizan medidas de mitigación de impacto, como la recogida de los casquillos cada vez que se efectúa una ronda de disparo, la contaminación detectada indica que se deberían mejorar las actuaciones en la berma de llegada. La aplicación de enmiendas orgánicas, o nanomateriales, podría ayudar a reducir la disponibilidad de los elementos potencialmente peligrosos, evitando así la posible contaminación de áreas adyacentes..*

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RESUMO

A contaminação em campos de tiro é uma questão de importância crescente. A acumulação nos solos de elementos potencialmente perigosos (EPP) das munições utilizadas representa um elevado risco ambiental. O conteúdo total e disponível (extração com 0,01 M $CaCl_2$ *e DTPA) de As, Cd, Cu, Ni, Pb, Sb e Zn foi avaliado em 10 solos de um campo de tiro militar (León, Espanha). Os resultados mostraram que o chumbo é o elemento contaminate que apresenta uma concentração mais elevada (13,83-4451,57 mg* kg^{-1}*), seguido de Sb (1,80-96,10 mg* kg^{-1}*), Cu (4,50-88,52 mg* kg^{-1}*), As (13,24- 62,47 mg* kg^{-1}*), Zn (13,32-46,19 mg* kg^{-1}*), Ni (11,53-46,30 mg* kg^{-1}*) e Cd (0,30-1,00 mg* kg^{-1}*). A elevada acidez do solo, o conteúdo de matéria orgânica e a baixa proporção de argila favorecem uma grande disponibilidade destes EPP, particularmente Pb e Cu. Embora existam medidas de mitigação do impacto (por exemplo, a recolha de cartuchos), após a prática de tiro, a avaliação da contaminação indica que essas medidas devem de ser melhoradas na berma. A aplicação de corretivos orgânicos ou nanomateriais poderá eventualmennte contibuir para a redução da disponibilidade dos EPPs, de modo a evitar a contaminação das áreas adjacentes.*

KEY WORDS
Military manoeuvre field, soil contamination, availability, lead, geoaccumulation, risk assessment

PALABRAS CLAVE
Campo de maniobras, contaminación, disponibilidad, plomo, geoacumulación, evaluación de riesgo

PALAVRAS-CHAVE
Campo de tiro, contaminação, disponibilidade, chumbo, geoacumulação, avaliação de risco

1. Introduction

Soil degradation is a major concern for humanity as this environmental component provides important services to humans due to its functions as food producers and pollutant filters. In the European Union, the main causes of soil degradation are sealing, erosion and local and diffuse contamination, causing a steady deterioration of its functions (EEA 2015; Keesstra et al. 2012; Brevik et al. 2015).

Soil can be degraded by the accumulation of potentially harmful elements (PHEs) to such levels that they may be toxic to soil organisms. Therefore, this form of chemical degradation causes partial or total loss of soil productivity.

Military training camps are used in all countries for the preparation of armies to defend their countries. However, they represent a hotspot of land degradation at local and regional levels due to: i) accumulation of PHEs from ammunitions, mainly Pb and Sb; ii) erosion and vegetation loss caused by troop movements or heavy vehicles and iii) habitat fragmentation (Althoff et al. 2007; Wang et al. 2014; Guemiza et al. 2015).

The ammunition used is composed mainly of Pb and Sb (± 95 % by weight) and Cu-Zn (± 5%), but can contain varying amounts of elements, such as Cd, Cr or Ni (Bannon et al. 2009; Evangelou et al. 2012; Islam et al. 2016). When the ammunition reaches the soil, usually fragmented, its surface weathers slowly; favoring the release of the elements of which it is composed (eg. Pb^0 to Pb^{2+}). This implies an increase in the availability of these elements for organisms and an ecological risk to the ecosystems in which they live.

The use of extracting agents [e.g. $CaCl_2$, DTPA, NH_4NO_3, low molecular weight organic acids (LMWOAs)] can help identify the pollution risk caused by PHEs indicating their availability, which completes the information obtained from the analysis of total content (Naidu et al. 2008; Anjos et al. 2012).

Moreover, there are other methods to assess the effects of natural and anthropogenic factors on the PHEs concentration in soils: 1) qualitative or statistical (Principal components analysis (PCA), factor analysis or cluster analysis); 2) quantitative, such as the use of indices to assess contamination at a known scale (pollution factor, enrichment factor, geoaccumulation index, risk assessment methods, etc.) or in graphical form by performing distribution maps (Geographic Information System) (Jensen and Mesman 2006; Wu et al. 2014; Islam et al. 2016; Zhou et al. 2016).

Although in recent years several authors have begun to study the contents and effects of ammunition components other than Pb and Sb) such as, Ni or Cd (Bannon et al. 2009; Evangelou et al. 2012; Sanderson et al. 2012b), the existing information still remains scarce.

Therefore, the objectives of this study were: i) to determine the total and available contents of As, Cd, Cu, Ni, Pb, Sb and Zn in an active military firing range, ii) to assess the degree of contamination and iii) to evaluate the potential ecological risks that the ammunition degradation generates in soils.

2. Material and methods

2.1. Study area

The shooting range and training center of El Teleno (León, Spain) is a facility of the Spanish Ministry of Defence, where army training exercises are carried out (42º 20’ 28” N, 6º 16’ 15” W). It is an area of 6100 ha divided into three different zones: one for artillery projectile fall, one where manoeuvres are carried out, one where the artillery settlement and observatories are located and another one where the exercises are carried out.

The geology of the area consists mostly of orthoquartzite, sandstones and black slate. Its average altitude is 1100 m. (a.s.l.), and its average annual temperature and precipitation are 10.5 ºC and 700 mm. It has a Mediterranean climate with dry warm summers and mild winters (classified as Csb by Köppen-Geiger system) (Forteza et al. 1982; Spanish Ministry of Defence 2007).

In the manoeuvres area there is a 300 m x 90 m shooting range for lightweight and portable arms. It has an arrival berm of about 5-7 m high and firing positions 100, 200 and 300 m away. The facility lacks vegetation cover in more than 50% of its surface and is also scarce in the rest of the field, which is mostly formed by low-growing ericaceous plants.

According to information provided by the Ministry of Defence, an environmental management system has been carried out for several years and consists of collecting cartridges after the manoeuvres and occasional sieving in the berms.

2.2. Surface soil sampling

For the selection of the sampling areas, the methodologies used in Etim and Onianwa (2012) and Rodríguez-Seijo et al. (2016a, b) were adapted: three zones at different heights of the arrival berm (S1-S3), seven at different distances from the arrival berm (10 m, 50 m, 100 m, 150 m, 200 m, 250 m and 300 m) (S4-S10) were chosen (**Figure 1**). A control area (S11) was located in a dryland pasture, about 5 km from the shooting range, following the methodology described by Etim and Onianwa (2012) to avoid the influence of military activities. In each zone, different horizontal sectors were selected and, in each of them, three sampling points spaced 20 m apart. Three topsoil samples (0-15 cm) were taken in each of them with an Eijkelkamp sampler and stored in polythene bags.

To obtain a representative sample of each sector, nine samples were taken in each, mixed and homogenized to form a composite sample, from which three subsamples were obtained for the corresponding analysis.

The composite samples were air-dried, sieved through a 2 mm-sieve and homogenized. Three subsamples per sector were finally used for all of the analytical measurements, meaning that all of the analyses were performed in triplicate.

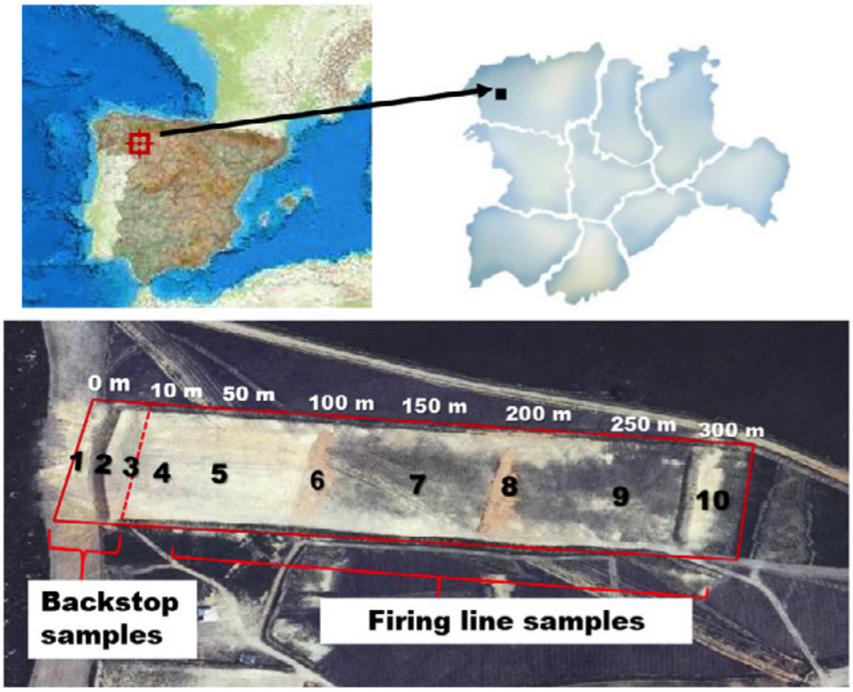

Figure 1. Schematic representation of the configuration of the shooting range and sectors of soil samples.

2.3. Physicochemical analyses

The soil texture was determined by the pipette method (Gee and Or 2002). Soil pH was determined with a pH electrode in a 2.5:1 water/soil ratio. Organic matter (OM) was determined following the Walkley and Black (1934) procedure. Total Kjeldahl-N was determined according to Bremner and Mulvaney (1982). Exchangeable cations (Al^{3+}, Ca^{2+}, K^{+}, Mg^{2+} and Na^{+}) were extracted with 0.1 M $BaCl_2$ (Hendershot and Duquette 1986). The analyses were performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin Elmer Optima 4300DV). The iron (Fe), manganese (Mn) and aluminium (Al) oxide contents were extracted with the dithionite–citrate method (Sherdrick and McKeague 1975; US Soil Conservation Service 1972).

2.4. Total and extractable PHEs content

The pseudototal As, Cd, Cu, Ni, Pb, Sb and Zn contents were determined following acid digestion with a mixture of HNO_3 and HCl (1:3 v/v) in teflon bottles placed in a microwave oven (200 ºC, 9 bar, 33 min) (Arenas-Lago et al. 2015). In all of the extracts, the PHEs concentrations were analysed by ICP-OES (Perkin Elmer Optima 4300 DV apparatus). The overall accuracy and precision of the analytical procedures for total contents were verified through the analysis of three standard reference materials (San Joaquin 2709a, Montana I Soil 2710a and Montana II Soil 2711a). Spikes and duplicates were also used as part of our quality control. Blank determinations were also performed in triplicate throughout all the experiments. Recoveries for Cd, Cu, Ni, Pb and Sb were 98-104%. Recoveries for As were 84%.

In order to determine the extractable PHE contents in the soils the two most widely used methods were selected. Soil samples were extracted with an acidified 0.01 M $CaCl_2$ solution (1:10 w/v soil to extractant ratio, 2 h shaking) (Houba et al. 2000), representing the total dissolved content, and with DTPA (0.005 M DTPA + 0.1 M TEA + 0.01 M $CaCl_2$) (1:2 w/v soil to extractant ratio, 2 h shaking) in accordance with Lindsay and Norwell (1978), indicating the available content. The PHEs concentrations were determined by ICP-OES.

2.5. Assessment of soil contamination and ecological risks

In this study, two indices to assess the degree of contamination were used, as well as an index to assess the ecological risks that PHEs concentrations generate globally. To this end, the background levels selected were those defined by FOREGS (2005) for topsoils in Europe as there are no defined background values for the soils from the study area. The background values used for As, Cd, Cu, Ni, Pb, Sb and Zn were 9.88, 0.284, 17.3, 37.3, 32.6, 1.04 and 68.1 mg kg^{-1}.

The Geoaccumulation index (Igeo) was introduced by Müller (1969). It is an index that considers the anthropogenic values and influence of natural activities in the background values (Zhou et al. 2016)

(Eq.1) $$I_{geo} = \log (C_n / 1.5 \times B_n)$$

where C_n is the concentration of each element measured in each soil, and B_n is the corresponding background value. The constant 1.5 was introduced to compensate for the possible background modifications caused by lithogenic variations. **Table 1** shows the classification for I_{geo} values (Zhou et al. 2016).

The Enrichment Factor (EF) is commonly used to characterize the level of soil contamination by PHEs. It takes into account the anthropogenic sources and it is calculated versus a reference element (Al, Fe, Mn, Sc or Ti). In this case, Fe is used to standardize the values considering 19,600 mg kg^{-1} as a background level (FOREGS 2005). EF is calculated using **Equation 2**, whose results allow us to classify soils into 5 different categories (**Table 1**):

(Eq.2) $$EF = (C_i / Fe_i) / (C_r / Fe_r)$$

where C_i is the concentration of the examined metal in the contaminated soil, C_r is the concentration of the examined metal in the control soil (S11), Fei is the concentration of the reference element (Fe) in the contaminated soil sample and Fer is the concentration of the reference element (Fe) in the control soil sample (S11).

In this work, Fe was used as a reference element for the standardization following the criteria of Daskalakis and O'Connor (1995), and Acevedo-Figueroa et al. (2006). They indicated that (1) the geochemistry of Fe and many trace metals are similar both in oxic and anoxic conditions; (2) its geochemistry is similar to that of many trace metals and (3) its natural sediment concentration tends to be uniform. As a result, there are five categories defined for the different EF values.

Although both I_{geo} and EF are good tools for assessing the pollution levels of an individual element, neither of them can evaluate the contamination caused by different PHEs simultaneously (Yang et al. 2015). For this reason, in this work the joint pollution caused by the different PHEs was evaluated by applying an ecological risk assessment index: Potential Ecological Risk (PER).

The Potential Ecological Risk (PER) was developed by Hakanson (1980) to assess the degree of contamination by pollutants in sediments, although it is widely used for soil analysis (Islam et al. 2015; Yang et al. 2015; Zhou et al. 2016). PER was calculated using equations 3, 4, and 5,

(Eq.3) $$R_i = \sum E_i$$

where E_i is the value of the single ecological risk index for PHE *i*, and is defined as:

(Eq.4) $$E_i = T_i \times F_i$$

(Eq.5) $$F_i = C_i / B_i$$

Table 1. Geoaccumulation, Enrichment Factor and Potential Ecological Risk

I_{geo} class	I_{geo} values	Contamination level
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} \leq 1$	Uncontaminated/moderately contaminated
2	$1 < I_{geo} \leq 2$	Moderately contaminated
3	$2 < I_{geo} \leq 3$	Moderately/heavily contaminated
4	$3 < I_{geo} \leq 4$	Heavily contaminated
5	$4 < I_{geo} \leq 5$	Heavily/extremely contaminated
6	$I_{geo} \geq 5$	Extremely contaminated
	EF values	**Contamination level**
	EF < 2	Clean-light pollution
	2 ≤ EF < 5	Moderate pollution
	5 ≤ EF < 20	Significant pollution
	20 ≤ EF < 40	Strong pollution
	EF ≥ 40	Extreme pollution
	PER values	**Contamination level**
	RI < 150	Clean-light pollution
	150 ≤ RI < 300	Moderate pollution
	300 ≤ RI < 600	Significant pollution
	RI ≥ 600	Extreme pollution

T_i is the toxic-response factor for the given PHE, which mainly reflects the PHE toxicity level and the degree of environment sensitivity to PHE pollution; and T_i values for As, Cd, Cu, Ni, Pb, Sb, Zn are 10, 30, 5, 5, 5, 40 and 1, respectively. F_i value is the ratio of each metal pollutant calculated between the sample concentration and background value (Hakanson 1980; Yang et al. 2015; Zhou et al. 2016).

Classification of the potential ecological risk of toxic metals is shown in **Table 1**.

2.6. Statistical analysis

The data obtained in the analytical determinations were treated with the statistical program IBM-SPSS Statistics 22 (SPSS, Inc., Chicago, IL). The results obtained in all the determinations were the average values with a standard deviation and were expressed on a dry material basis. Different analyses of variance (ANOVAs) were carried out, together with homogeneity of variance tests. In the case of homogeneity of variance, the minimum significant distance test among soil properties was carried out as a post hoc test, or otherwise Dunnett's T3 test.

3. Results

3.1. Soil characteristics

The shooting range soils have an extremely, or very strongly, acid pH, sandy loam texture, very low Kjeldahl nitrogen content (< 0.60 g kg^{-1}), medium to high organic matter (2.7-8.4%) content and low cation exchange capacity (< 4.2 $cmol_{(+)}$ kg^{-1}). These soils differ from the control soil which is strongly acid (5.3), has a silt loam texture, medium nitrogen (2.97 g kg^{-1}) and organic matter (5.62%) contents, and a slightly higher cation exchange capacity than that of the previous soils (5.09 $cmol_{(+)}$ kg^{-1}). This can be explained by the distance of the control soil compared to the shooting range soils (**Table 2**). The differences in soil texture between the shooting range soils and the control soil (**Table 1**) can be explained by the addition of sand in the shooting range to avoid waterlogging.

Furthermore, the soils contain high levels of Fe (8.33-35.86 g kg^{-1}) and Al (2.23-9.92 g kg^{-1}) oxides. However, the content of Mn oxides is slightly lower (0.01 to 0.13 g kg^{-1}), with a value in some soils below the detection limit (S4, S5, S9, S10).

The geology of the slate and sandstone quartzite, and the existence of an ericaceous shrub layer in the areas most distant to the berm affect the soil characteristics, favoring acidity, diminishing the clay content (< 11%) and slightly increasing the organic matter content, as described by Forteza et al. (1982) for soil profiles in studied region (NW of Castilla y León).

Table 2. Soil general characteristics

Sample	Unit	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	Control soil
Distance	meters	0	0	0	10	50	100	150	200	250	300	± 5000
pH $_{H_2O}$		4.13 *f*	4.22 *ef*	4.52 *d*	4.03 *f*	4.62 *cd*	4.65 *cd*	4.34 *e*	4.55 *cd*	4.80 *bc*	4.84 *b*	5.37 *a*
pH $_{KCl}$		3.91 *f*	4.02 *e*	4.20 *b*	3.62 *c*	3.73 *g*	3.73 *g*	3.68 *h*	4.05 *de*	4.15 *c*	4.06 *d*	4.38 *a*
OM	%	3.22 *fg*	6.13 *d*	3.49 *f*	6.51 *c*	7.09 *b*	3.06 *g*	6.73 *c*	2.38 *c*	2.70 *h*	8.41 *a*	5.62 *e*
N	g kg^{-1}	0.60 *bc*	0.63 *b*	0.51 *cd*	0.47 *de*	0.19 *f*	0.41 *e*	0.10 *f*	0.17 *f*	0.20 *f*	0.44 *de*	2.97 *a*
Soil texture												
Sand	%	62.13 *c*	67.28 *b*	69.66 *b*	61.1 *c*	69.71 *b*	68.69 *b*	74.61 *a*	67.42 *b*	75.94 *a*	69.91 *b*	28.69 *d*
Silt		29.32 *b*	24.58 *c*	22.59 *c*	32.54 *b*	24.42 *c*	21.54 *cd*	16.66 *de*	22.68 *c*	16.48 *de*	24.28 *c*	62.55 *a*
Clay		8.79 *ab*	8.38 *b*	7.99 *b*	6.60 *cd*	6.11 *d*	10.01 *a*	8.98 *ab*	10.14 *a*	7.83 *bc*	6.05 *d*	9.00 *ab*
USDA Classification		SL	SL	SL	SL	SL	SL	SL	SL	SL	SL	SIL
Exchangeable cation content and effective cation exchange capacity												
Al^{3+}	cmol$_{(+)}$ kg^{-1}	2.49 *abc*	1.89 *abc*	2.17 *abcd*	2.50 *abc*	2.31 *abc*	1.61 *cde*	2.34 *abc*	1.32 *de*	2.56 *ab*	2.87 *a*	0.88 *e*
Ca^{2+}		1.22 *b*	0.88 *bc*	1.39 *b*	0.44 *cd*	u.l.	u.l.	u.l.	0.44 *cd*	u.l.	0.14 d	2.64 *a*
K^{+}		0.24 *ab*	0.18 *ab*	0.29 *a*	0.13 *b*	0.06 *b*	0.16 *b*	0.07 *b*	0.25 *ab*	0.06 *b*	0.12 *b*	0.12 *b*
Mg^{2+}		0.21 *c*	0.12 *cde*	0.17 *cd*	0.10 *def*	0.02 *f*	0.06 *ef*	0.03 *ef*	0.36 *b*	0.02 *f*	0.07 *def*	1.21 *a*
Na^{+}		0.04 *bcd*	0.03 *cd*	0.02 *d*	0.03 *cd*	0.05 *bc*	0.04 *bcd*	0.04 *bcd*	0.04 *bcd*	0.09 *b*	0.02 *d*	0.24 *a*
ECEC		4.20 *ab*	3.10 *bcd*	4.03 *abc*	3.20 *bcd*	2.44 *cd*	2.05 *d*	2.48 *cd*	2.41 *d*	2.73 *bcd*	3.22 *bcd*	5.09 *a*
Oxides content												
AlOx	g kg^{-1}	6.90 *c*	7.08 *c*	6.45 *d*	6.51 *d*	6.44 *d*	5.79 *e*	6.44 *d*	8.24 *b*	8.28 *b*	9.93 *a*	2.23 *f*
FeOx		18.00 *de*	19.36 *c*	17.67 *e*	12.73 g	14.26 *f*	18.93 *cd*	23.01 *b*	35.86 *a*	18.99 *cd*	24.13 *b*	8.32 h
MnOx		0.01 *e*	0.01 *e*	0.01 *e*	u.l.	u.l.	0.04 *d*	0.09 *b*	0.07 *c*	u.l.	u.l.	0.13 *a*

Average values (n = 9). In each row, values followed by different italic letters differ significantly ($p < 0.05$). Distance Distance from Berm, *OM* Organic matter, *SL* Sandy Loam, *SIL* Silt Loam, *ECEC* Effective cation exchange capacity, *AlOx* aluminium oxides, *FeOx* iron oxides, *MnOx* manganese oxides, *ul* values below the detection limit.

3.2. Total and extractable PHEs content

Table 3 shows the total content of the PHEs analyzed, the most common in the ammunitions used. The highest concentrations correspond to Pb (13.83-4451.57 mg kg^{-1}), followed by Sb (1.80-96.10 mg kg^{-1}), Cu (4.50-88.52 mg kg^{-1}), As (13.24-62.47 mg kg^{-1}), Zn (13.32-46.19 mg kg^{-1}), Ni (11.53-46.30 mg kg^{-1}) and Cd (0.30-1.00 mg kg^{-1}). Significant differences between the berm soils (S1-S3) and shooting range soils (S4-S10) were observed. In the berm, differences between the samples from the top (S1), middle (S2) and bottom (S3) sectors were also found. The highest PHEs contents corresponded to the soil from the bottom sector.

Table 3. Soil PHEs content (mg kg^{-1})

Sample codes	Distance	As	Cd	Cu	Ni	Pb	Sb	Zn
S1	0	55.29 *a*	0.95 *a*	26.78 *c*	19.40 *cd*	507.73 *c*	21.40 *c*	39.10 *c*
S2	0	42.48 *b*	1.00 *a*	63.15 *b*	17.00 *de*	3247.92 *b*	67.54 *b*	46. 19 *b*
S3	0	62.47 *a*	1.00 *a*	88.52 *a*	46.30 *a*	4451.57 *a*	96.10 *a*	31. 68 *d*
S4	10	28.30 *c*	0.53 *b*	7.80 *efg*	15.90 *def*	43.00 *d*	7.01 *cd*	20.70 *ef*
S5	50	27.72 *cd*	0.59 *b*	5.60 *fg*	17.21 *de*	22.57 *f*	8.61 *cd*	18.02 *efgh*
S6	100	13.24 *e*	0.43 *c*	12.31 *def*	17.72 *cde*	13.83 *f*	6.04 *cd*	23.31 *e*
S7	150	37.31 *bc*	0.40 *c*	14.80 *de*	12.89 *ef*	18.46 *f*	4.40 *d*	13.32 *h*
S8	200	13.80 *e*	0.58 *b*	27.98 *c*	23.12 *c*	22.80 *f*	5.55 *cd*	19. 18 *efg*
S9	250	14.20 *e*	0.30 *c*	4.50 *g*	11.53 *f*	39.01 *e*	1.80 *d*	13.82 *gh*
S10	300	41.06 *b*	0.60 *b*	9.66 *defg*	14.60 *def*	13.80 *f*	5.42 *cd*	16.11 *fgh*
Control soil	± 5000	17.56 *de*	0.30 *c*	15.91 *d*	28.98 *b*	15.36 *f*	2.47 *d*	63.02 *a*
European topsoil values	9.88	0.284	17.30	37.30	32.60	1.04	68.10	
GRL Canada industrial criteria	12	22	91	50	600	40	3600	
Dutch target values	29	0.8	36	35	85	3	140	
Dutch intervention values	55	12	190	210	530	15	720	

Average values (n=9). In each column, values followed by different italic letters differ significantly ($p < 0.05$). *Distance* Distance from Berm (m), European topsoil values (FOREGS 2005), *GRL* Generic reference levels established for Canada (Industrial criteria) [CCME 2007; Laporte-Saumure et al. 2011] and Dutch target and intervention values (VROM 2000).

The differential distribution between the berm soils and shooting range soils is due to the shot dynamics, with the highest residue found in the berm. In addition, the fact that there are differences between the different berm sectors are due to ammunition sliding from the top to the bottom, where it accumulates and weathers over time (Sanderson et al. 2012b; Rodríguez-Seijo et al. 2016a).

In the case of Spain, each Regional Government has the power to define guideline values for regulatory purposes and to set the criteria that declare a soil as contaminated (Romero-Freire et al. 2015). However, military areas are not subject to the application of Reference Levels in Spanish Legislation (BOE 2005) and the Regional Government (Junta de Castilla y León), has not proposed

General Reference Levels (GRL) based on literature data and according to the use of the soil: agriculture, natural and/or industrial use.

Therefore, to evaluate the total PHE content and soil contamination in this study, the GRLs of different reference guides were used. These are commonly used in the evaluation of shooting ranges (e.g. Laporte-Saumure et al. 2011), as well as the industrial levels of Canada (CCME 2007) and target and intervention levels of the Netherlands (VROM 2000).

It was observed that: 1) the levels of the berm soils (S1-S3) exceeded the trigger values indicated by the Canadian and Dutch guidelines for Pb (600 mg kg^{-1}; 530 mg kg^{-1}, respectively) and Sb (40 mg kg^{-1}, 15 mg kg^{-1}, respectively); 2) the levels of all soils exceeded the Canadian GRL (12 mg kg^{-1}), S1 and S3 also exceeded the Dutch intervention levels (55 mg kg^{-1}); and 3) the Cd, Cu, Ni and Zn levels were lower than the GRL of both guides, even though they did exceed the Dutch target values.

It was observed that hazardous concentrations of PHEs were confined to berm soils, as a result of spent ammunition and weathering in the soil. However, in contrast to other shooting ranges, low contents of Pb and Cu were observed in the other soils meters away from the berm (Rodríguez-Seijo et al. 2016a). The environmental impact strategies carried out by the Spanish Ministry of Defence involve the collection of all cartridges and ammunition residues deposited in the firing positions of the shooting range, which a priori may explain the absence of high levels of Pb and Cu away from the berm (S5-S10).

Table 4 shows the contents of PHEs extracted with $CaCl_2$ and DTPA. The proportion of extracted metal with both reagents, compared with the total content, follows the sequence Pb > Cu > Zn > Cd > Ni > Sb > As. The extracted Pb and Cu contents are high, with extraction efficiencies above 10% (**Figure 2**). Extracted Zn levels are also high, although the largest proportion was observed only in the berm soils (**Figure 2**). The extracted As, Cd, Ni and Sb contents are low (< 10% of the total content) (**Figure 3**).

Table 4. PHEs $CaCl_2$ and DTPA extractable metal contents

Soil	**As**	**Cd**	**Cu**	**Ni**	**Pb**	**Sb**	**Zn**
				$CaCl_2$-Extractable			
S1	0.61 *bc*	0.06 *a*	10.53 c	0.62 *b*	350.44 *c*	0.67 *c*	5.09 *b*
S2	0.92 *a*	0.06 *a*	41.3 *b*	0.56 *bc*	1752.87 *b*	4.63 *b*	12.15 *a*
S3	0.47 *c*	0.06 *a*	66.18 *a*	0.53 *bc*	2694.80 *a*	6.94 *a*	12.15 *a*
S4	0.28 *d*	0.02 *b*	2.53 *d*	0.49 *cd*	34.86 *d*	0.05 *g*	1.55 *c*
S5	u.l.	0.01 *cd*	0.75 *de*	0.31 *ef*	13.07 *e*	0.18 *e*	0.46 *d*
S6	0.19 *de*	u.l.	1.35 *de*	0.39 *de*	4.70 *e*	0.01 *d*	0.59 *d*
S7	0.25 *d*	0.01 *cd*	0.95 *de*	0.14 *g*	7.26 *e*	u.l.	0.42 *d*
S8	0.76 *ab*	u.l.	1.52 *de*	0.24 *fg*	9.36 *e*	0.01 *d*	0.56 *d*
S9	0.04 *e*	u.l.	0.06 *e*	0.02 *h*	2.04 *f*	0.01 *d*	0.34 *d*
S10	0.28 *d*	0.01 *cd*	1.41 *de*	0.16 *g*	6.06 *e*	0.03 *d*	1.01 *c*
Control soil	0.08 *e*	0.02 *bc*	2.8 *d*	1.94 *a*	4.24 *e*	0.09 *e*	0.44 *d*
Soil	**As**	**Cd**	**Cu**	**Ni**	**Pb**	**Sb**	**Zn**
				DTPA-Extractable			
S1	0.03 *bc*	0.03 ab	9.42 *c*	0.34 *b*	61.74 *c*	0.28 *b*	3.42 *b*
S2	0.08 *b*	0.03 *a*	25.85 *b*	0.34 *b*	416.23 *b*	1.75 *a*	8.02 *a*
S3	0.03 *bc*	0.03 *a*	42.46 *a*	0.34 *b*	1039.66 *a*	1.68 *a*	7.94 *a*
S4	0.03 *bc*	0.01 *c*	2.03 *d*	0.31 *b*	21.80 *d*	u.l.	1.23 *c*
S5	0.09 *b*	u.l.	0.35 *e*	0.08 *d*	8.02 *e*	u.l.	0.23 *d*
S6	u.l.	u.l.	0.61 *e*	0.34 *b*	3.04 *g*	u.l.	0.41 *d*
S7	0.06 *bc*	u.l.	0.41 *e*	0.08 *d*	3.04 *g*	u.l.	0.14 *d*
S8	0.16 *a*	u.l.	0.66 *e*	0.23 *c*	4.98 *f*	u.l.	0.30 *d*
S9	0.04 *bc*	u.l.	0.12 *e*	0.07 d	0.97 *i*	u.l.	0.20 *d*
S10	0.07 *bc*	u.l.	0.90 *e*	0.21 *c*	1.69 *h*	u.l.	0.52 *cd*
Control soil	0.01 *c*	0.02 *b*	2.00 *d*	1.79 *a*	3.00 *g*	0.02 *c*	0.24 *d*

Average values (n = 9). In each column, values followed by different italic letters differ significantly ($p < 0.05$). ul values below the detection limit.

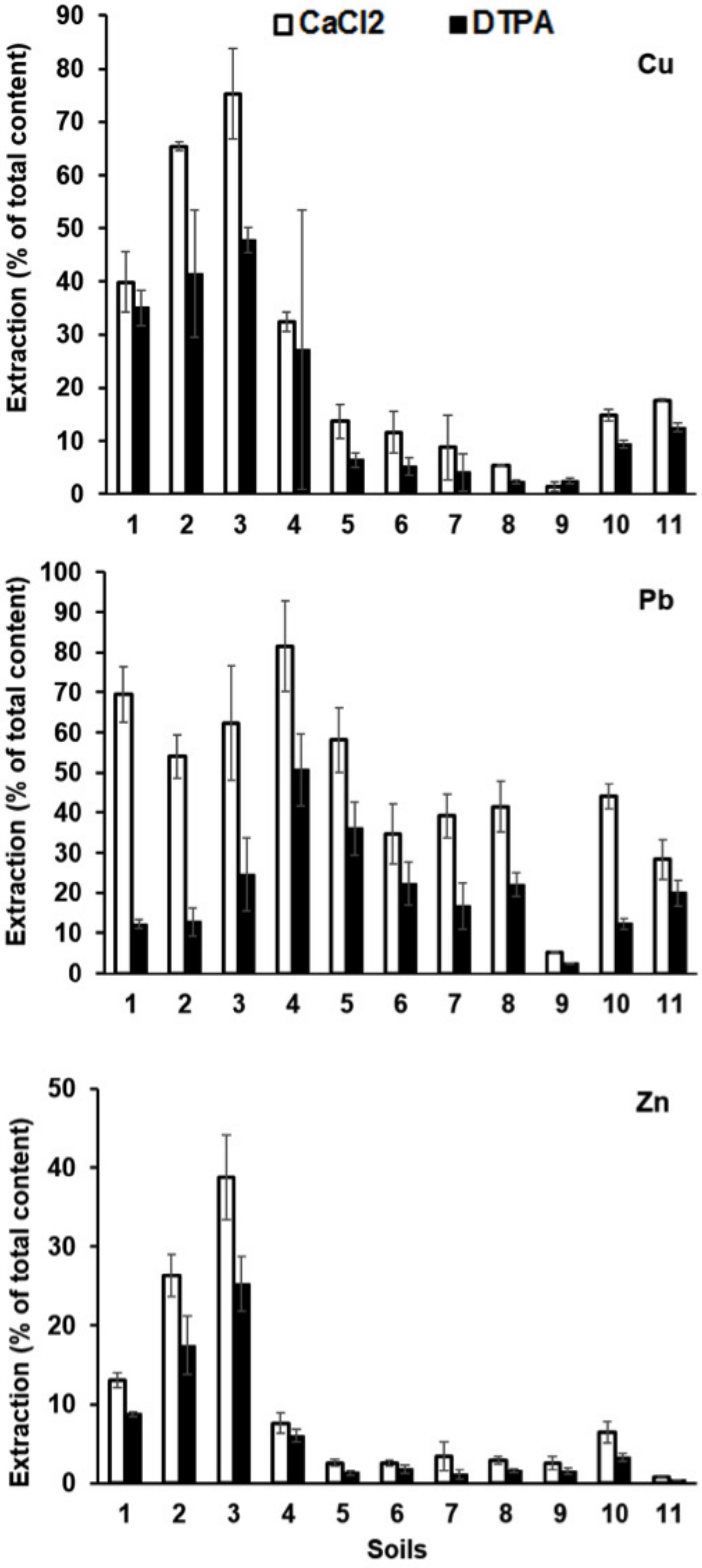

Figure 2. Extraction efficiency (relative to the total content) for each soil and extraction method for Cu, Pb and Zn. Hanging bars are the standard deviation.

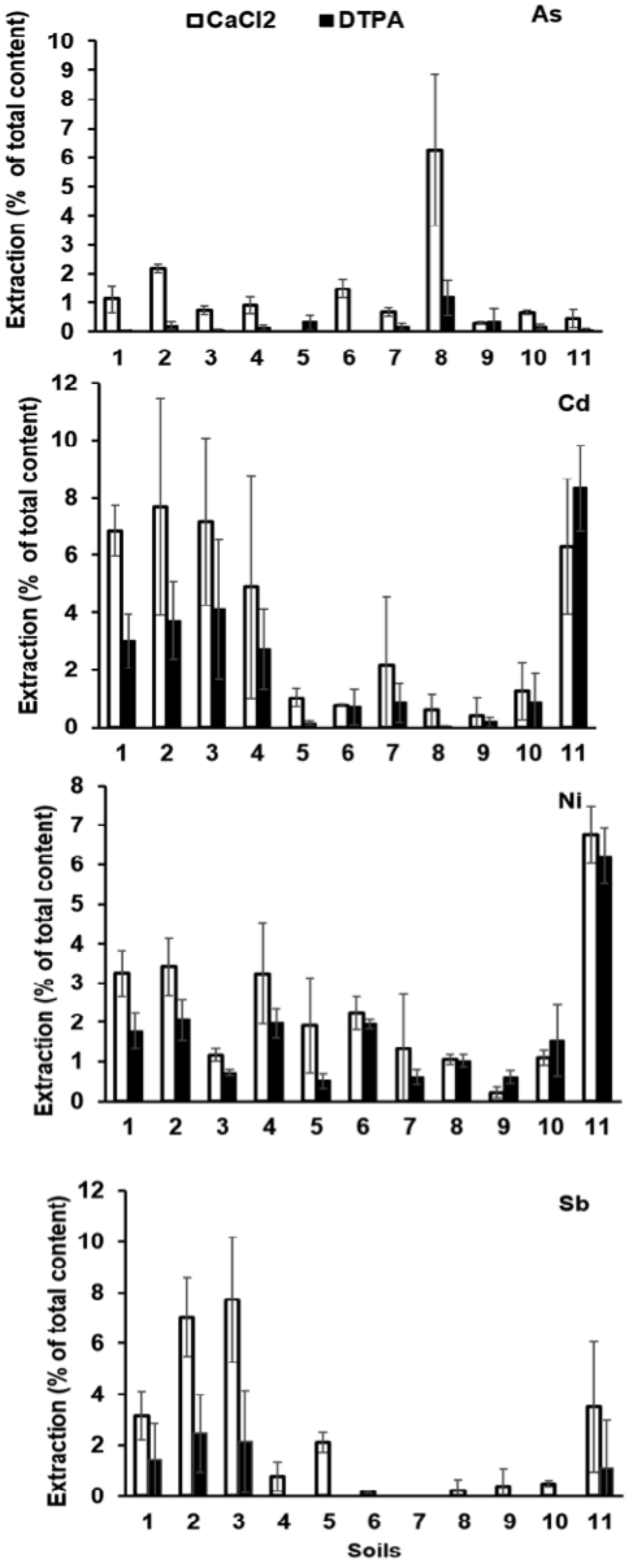

Figure 3. Extraction efficiency (relative to the total content) for each soil and extraction method for As, Cd, Ni and Sb. Hanging bars are the standard deviation.

The ammunition fragmentation, the high acidity of the soil and the existence of rainfall, concentrated in the winter months in the area, may favor a rapid transformation of Pb and Cu from ammunition to mobile species (Pb to Pb^{2+}, Cu to Cu^{2+}), which explains their high availability in the studied soils (Chen et al. 2002; Naidu et al. 2008; Sanderson et al. 2012a, 2012b; Rodríguez-Seijo et al. 2016b). However, As, Cd, Ni and Sb are less mobile than Cu and Pb at acidic pH and their ions also have a strong affinity for Al and Fe oxides, which explains their limited availability and mobility in the studied soils (Pierce and Moore 1982; Cao et al. 2003; de la Fuente et al. 2010; Kabata-Pendias 2010; Wilson et al. 2010; Sanderson et al. 2012b; Alloway 2013; Pierart et al. 2015).

3.3. Contamination level and risk assessment

As in the case of total and available content, the study of pollution indices shows that contamination by PHEs is mainly restricted to berm soils (S1, S2, S3) and to the closest one (S4) (**Table 5**).

It can be observed that Pb and Sb are the elements that show enhanced geoaccumulation, with “extremely contaminated" levels (I*geo* ≥ 5) in berm soils, while As, Cd and Cu have accumulated, although to a lesser extent (moderately contaminated). Arsenic and Sb present moderate accumulation in all other soils, although the inexistence of a pattern similar to that of Pb seems to indicate a natural origin due to slates that form part of the geology of the area (Alloway 2013). Nickel and Zn show no signs of accumulation in any of the soils.

Table 5. I*geo* and EF values of studied PHEs

Soil	Potentially harmful elements						
	As	**Cd**	**Cu**	**Ni**	**Pb**	**Sb**	**Zn**
I*geo*							
S1	1.90	1.16	0.05	-1.53	3.38	3.74	-1.38
S2	1.52	1.21	1.28	-1.72	6.05	5.44	-1.14
S3	2.08	1.19	1.77	-0.27	6.51	5.99	-1.69
S4	0.79	0.32	1.96	-1.82	-0.16	2.14	-2.30
S5	0.90	0.46	-2.21	-1.70	-1.12	2.51	-2.50
S6	-0.16	0.01	-1.07	-1.66	-1.82	1.92	-2.13
S7	1.33	-0.28	-1.05	-2.11	-1.41	1.38	-2.94
S8	-0.10	0.45	0.11	-1.28	-1.10	1.83	-2.41
S9	-0.06	-0.68	-2.52	-2.28	-0.33	0.21	-2.88
S10	1.47	0.38	-1.43	-1.94	-1.76	1.80	-2.67
Control soil	0.24	-0.66	-0.71	-0.90	-1.67	0.66	-0.69
EF							
S1	3.53	2.11	0.98	0.33	9.81	12.64	0.36
S2	2.80	2.26	2.38	0.30	64.91	42.31	0.44
S3	6.54	3.54	5.29	1.28	141.29	98.61	0.48
S4	2.90	2.09	6.50	0.48	1.50	7.37	0.34
S5	2.74	2.02	0.30	0.45	0.68	8.33	0.26
S6	0.86	0.98	0.46	0.31	0.27	3.65	0.22
S7	4.17	1.37	0.80	0.39	0.63	4.31	0.22
S8	0.49	0.72	0.57	0.22	0.25	1.88	0.10
S9	1.50	0.97	0.27	0.32	1.24	1.80	0.21
S10	2.43	1.14	0.27	0.23	0.26	3.05	0.14
Control soil	1.01	0.54	0.52	0.46	0.27	1.34	0.53

When applying the Enrichment Factor (EF) (**Table 5**), the influence of the parent material can be differentiated more clearly than with Igeo as the background values of the analyzed element and a reference element are considered as a correction factor, Fe in this case (Acevedo-Figueroa et al. 2006).

It is noted that Pb is the element with the highest enrichment, followed by Sb, Cu, As and Cd. Nickel and Zn show no enrichment in the analyzed soils. The highest enrichment, with values of "extreme pollution" for Pb and Sb, was located in the berm due to the constant supply of ammunition to the soil, which is fragmented and exposed to air and water, suffering a strong weathering. In the case of Cu, As and Cd, values of "significant" and "moderate enrichment" were observed, both in the berm soils and the closest one.

In order to analyze the joint influence of different PHEs, the ecological risk (**Figure 4**) was evaluated. It was confirmed that the berm soils (S1-S3) have very high contents, considered as "extreme pollution" (RI: 1047-4693). In all other soils, "significant or moderate pollution" (RI < 300) was observed, reconfirming the influence of the ammunition residue in the berm as the main source of contamination, which is confined to that area.

3.4. Implications for environmental management

This pollution assessment has implications for the management of such facilities: the berms soils should not be used for any other purpose and represent a potential risk to groundwater. For this reason, impact mitigation measures should be carried out, such as increasing screening berms for the removal of ammunition residues, in addition to the correction of the strong soil acidity by liming and/or addition of organic amendments, in order to reduce the mobility of two of the main pollutants, Pb and Cu (USEPA 2005; Laporte-Saumure et al. 2011; Rajapaksha et al. 2015).

4. Conclusions

The main contaminant of the analyzed soil is Pb (up 4451.57 mg kg^{-1}), followed by other co-contaminants, such as Sb (up 96.10 mg kg^{-1}) or Cu (up 88.52 mg kg^{-1}). In general, soils have low available content of different PHEs, with the exception of Pb and Cu whose available content, exceeds 10% of the total content. All of this is favored by the ammunition fragmentation in the berm, the strong acidity, and the organic matter content, which contribute to increasing the Pb and Cu availability.

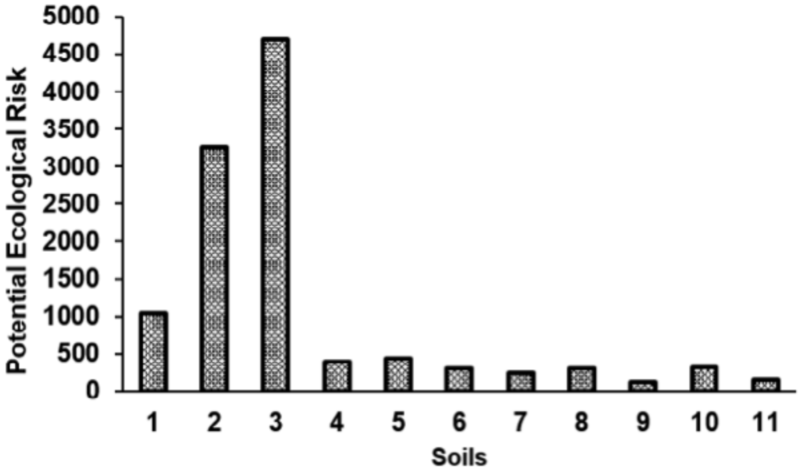

Figure 4. Potential ecological risk (PER) of the different soil samples studied.

The environmental strategy implemented in firing positions, with the collection of cartridges, seems to give good results seen in the absence of high contents of PHEs in range soils, although actions should be increased in the berm soils.

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