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**Assessment of iron-based and calcium-phosphate nanomaterials for immobilisation of  
Potentially Toxic Elements in soils from a shooting range berm**

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## **Abstract**

Shooting range facilities in military areas have been indicated as a hotspot of land degradation with high contents of Potentially Toxic Elements (PTEs). Currently, based on the new nanomaterials with specific characteristics, nanoremediation technologies are used to immobilise and to reduce the availability of PTEs in field and laboratory conditions. In this study, the effects of nano-hydroxyapatite and/or hematite on PTEs immobilisation (As, Cd, Cu, Pb, Sb and Zn) in military shooting range soils were assessed through the measure of available and leachable forms with three single-extractions: calcium chloride (0.01M CaCl<sub>2</sub>), low molecular weight organic acids (10mM LMWOAs) and toxicity characteristic leaching procedure (TCLP). A sequential chemical extraction was used to determine the distribution of the PTEs in the different geochemical phases of the soils before and after the nanomaterial treatments. Results showed that the availability of PTEs decreased, especially for Pb (40-95%) and Zn (50-99%) after nanomaterial treatments. When both nanomaterial (hydroxyapatite + hematite) were combined, the immobilisation rate improved. However, when each nanomaterial was added individually to the soils, some elements, such as, Cu or Sb, showed a slight increment of their mobilisation. The sequential chemical extraction showed that the highest percentage of PTEs were mainly in the residual fraction before and after adding nanomaterials, being even higher in soils after the nanomaterial treatments. Likewise, the mobile fractions decreased after the treatment with nanomaterials. Our findings suggest that nanoremediation techniques improve the soil conditions, but they should be used carefully to avoid mobilisation of non-target PTEs or unexpected potentially impacts for soil biota.

**Keywords:** metal, nanomaterials, availability, immobilisation, nanoremediation, military impact.

## **Abbreviations:**

**CPNs:** hydroxyapatite nanomaterials; **FeNs:** Fe<sub>2</sub>O<sub>3</sub> nanomaterials; **LMWOAs:** Low Molecular Weight Organic Acids; **NMs:** Nanomaterials; **PTEs:** Potentially Toxic Elements; **TCLP:** Toxicity Characteristic Leaching Procedure.

## 1. Introduction

Civilian and military shooting ranges are hotspots of soil contamination and land degradation, mainly by accumulation of potentially toxic elements (PTEs) (primarily by Cu, Pb, Sb and Zn), as a consequence of degradation of the ammunition used in manoeuvre training activities (Althoff et al., 2007; Fayiga and Saha, 2016; Sanderson et al., 2018). According to Panagos et al. (2013), there are more than 85,000 contaminated sites by military activities and war-affected zones in the European Union, which generates an important environmental concern and a high risk for the ecosystem, including soils, water bodies, crops, grazing animals and food webs (Rodríguez-Seijo et al., 2016~~aa,b~~, ~~2017~~; ~~Rodríguez-Seijo et al., 2016b~~; ~~Rodríguez-Seijo et al., 2017~~; Sanderson et al., 2018, 2012a; Tandy et al., 2017).

In the last years, several techniques have been applied to reduce soil contamination, such as phytoremediation, excavation and transport to landfill sites, soil washing or chemical immobilisation (Liu and Zhao, 2007; Rajapaksha et al., 2015; Xu et al., 2016; Yoo et al., 2016). Some these techniques are focused into a reduction of available contents since these forms can transfer to the food web and involve toxic effects in microorganisms, plants and animals (e.g. Rodríguez-Seijo et al., 2017; Tandy et al., 2017). More, specifically, the chemical immobilisation is an affordable and inexpensive technique, which can involve the application of soil amendments to adsorb, reduce, complex or co-precipitate PTEs (Arenas-Lago et al., 2016; Ogawa et al., 2015; Okkenhaug et al., 2016; Sanderson et al., 2018; Souza et al. 2020).

In this sense, application of nanomaterials (NMs) for soil remediation at soils from shooting ranges have showed shown outstanding results, due to NMs have advantageous characteristics such as their high reactivity, stability, small particle size or large specific surface area, which may favour the retention of PTEs (Arenas-Lago et al., 2019, 2016; Lago-Vila et al., 2019; Liu and Lal, 2012; Liu and Zhao, 2013; Ogawa et al., 2015; Rajapaksha et al., 2015; Ray and Shipley, 2015). Explicitly, iron metal-based and phosphate-based NMs are the most used NMs in remediation activities, due to their low-cost, their environmental-friendly behaviour and their scavenger capacity of PTEs (As, Cd, Cr, Cu, Pb, Zn) (Liu and Lal, 2012; Ogawa et al., 2015; Sanderson et al., 2018; Soares et al., 2018; Xu et al., 2016).

In previous studies with soils from trap shooting range and small-arms firing range areas (Arenas-Lago et al., 2016; Lago-Vila et al., 2019), hydroxyapatite (HPNs) and tricalcium phosphate nanoparticles (CPNs) were able to form stable associations with Pb (trap shooting range) and with Pb, Cu and Zn (small-arms firing range), and to decrease their available contents in both facilities. In these previous studies, after phosphate nanoparticles application, the results indicated that the P-fraction released seemed

not to involve a risk to groundwater. Likewise, several different studies have suggested that iron nanoparticles (FeNs) may reduce the available contents of As, Pb and/or Sb for shooting ranges, mining and/or industrial soils and, minimising the environmental impacts after their application (Arenas-Lago et al., 2019; Galdames et al., 2017; Mar Gil-Díaz et al., 2014a; Sanderson et al., 2018). However, information about the effectiveness of immobilization treatments in military fields remains scarce, as well as the effects of the combined application of different types of nanomaterials to avoid possible remobilization of contaminants.

The main objective of study is to assess the effectiveness of CPNs and FeNs for the immobilisation of As, Cd, Cu, Pb, Sb and Zn, in a backstop from a military shooting range (NW Spain), characterised previously by Rodríguez-Seijo et al. (2016<sup>ba</sup>). The specific objectives include: i) to determine the changes of the “operationally defined” extractable metal content of soils using different extractants (CaCl<sub>2</sub> and LMWOAs) and ii) to assess the leachability of these PTEs after the extraction with a toxicity characteristic leaching procedure (TCLP), analysing the effectiveness of NMs to reduce the available contents of PTEs. Finally, Tessier sequential extraction was used to assess the distribution of PTEs among the different geochemical phases in the shooting range soils, before and after adding the nanomaterials, as well as the influence of these nanomaterial in the distribution of PTEs in the soils.

## **2. Material and Methods**

### **2.1. Material**

#### *2.1.1. Study area and soil sampling*

This study was performed in the military shooting range and training centre of “El Teleno” (León, Spain - 42° 20' 28" N, 6° 16' 15" W). This facility (6100 ha) is divided into three sections: i) an artillery projectile fall area, ii) an artillery settlement and observatories area and iii) a manoeuvres area.

The manoeuvres area is a shooting range (300 m x 90 m) for lightweight and portable arms with a backstop berm of about 5-7 m high and firing positions 100, 200 and 300 m away, with no vegetation cover in more than 50 % of the surface area and some ericaceous plants in the rest of the area. More information about the facility was previously published (Rodríguez-Seijo et al. 2016b).

Soil samples were collected in the manoeuvres area from three zones of the backstop berm at different heights (upper - S1, middle - S2 and lower - S3 zone), previously characterised by Rodríguez-Seijo et al. (2016b).

#### *2.1.2. Nanomaterials (NMs)*

Two kinds of NMs were applied to the soil samples to investigate the PTEs extractability changes: i) tricalcium phosphate (CPNs) [MKN-030-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>; 99% pure; 30 nm size] supplied by mKnano (M K Impex, Corp., Ontario Canada), and ii) Iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>) (FeNs) [NO-0055-SG-0500 Iron(III) oxide, 98% pure, 20–40 nm, 40–60 m<sup>2</sup> g<sup>-1</sup>, spherical] supplied by IOLITEC (Ionic liquids Technologies GmbH, Germany). Both NMs were previously characterised by Arenas-Lago et al. (2019, 2016) and Lago-Vila et al. (2019). Physicochemical properties of the NMs are shown in Table S1 (Supplementary data).

## 2.2. Methods

### 2.1.1. Soil characterisation

Soil characteristics were determined in a previous study (Rodríguez-Seijo et al., 2016b) (Table S2, supplementary data). Soils were analysed for pH (1/2.5, w/v), organic matter content (Walkley and Black, 1934), Kjeldahl-N (organic plus ammonium-N) (Bremner and Mulvaney, 1982), effective cation exchange capacity (ECEC) and exchangeable cations (Al<sup>3+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>) (Hendershot and Duquette, 1986), particle size distribution (Gee and Or, 2002) and the Fe, Mn and Al oxides using dithionite– citrate method (Sheldrick and McKeague, 1975). Pseudototal PTEs contents were extracted from 0.2 g of soil by acid digestion (*aqua regia* procedure) with a mixture of HNO<sub>3</sub> and HCl (1:3 v/v) in a microwave oven (Ethos 1; Milestone) (experimental conditions: 9 bar, 190 °C and 45 min) (Rodríguez-Seijo et al., 2016b). All analysis were performed by ICP-OES (Perkin Elmer Optima 4300DV) at CACTI (University of Vigo, Spain). Limit of Quantitation for studied elements were 0.05 (As), 0.005 (Cd), 0.1 (Cu), 0.02 (Pb), 0.04 (Sb) and 0.005 (Zn) mg kg<sup>-1</sup>. Calibration curves were constructed using pellets of certified soil and sediment reference materials (San Joaquin 2709a, Montana I Soil 2710a and Montana II Soil 2711a). Satisfactory precision (reproducibility) and accuracy (percent of recovery) within ± 15 % were obtained.

### 2.2.2. Batch experiments

Four treatments were prepared by applying CPNs and FeNs to the studied soils: i) a single application of CPNs mixed at 5 % w/w with soil, ii) a single application of FeNs mixed at 5 % w/w with soil, iii) a combined application of both NMs at 5 % w/w with soil (2.5 % of each NMs), and iv) a control treatment (without NMs).

For this, based on batch experiments, soil treatments with NMs were performed following the methodology indicated Liu and Lal (2012) and Liu and Zhao (2013) and used previously by Arenas-Lago et al. (2016). In brief, different suspensions were prepared for each nanoparticle in ultrapure water (UPW) (5g NMs/L) by ultrasonic treatment for 1 h. Sodium citrate (5 mM) was added to the suspensions as a stabiliser. The final pH of the suspension was 7.2. Then, 10 grams of each studied soil was treated with 100 mL of the suspension of NMs in polypropylene bottles. Each mixture was shaken during 24 h. Finally, they were kept in darkness for ageing at room temperature for ten days and 2 h of shaking per day. Subsequently, the mixtures were dried at 30°C and homogenised in a Fritsch rotary sample divider Laborette 27, obtaining three similar soil samples of each mixture (soil + CPNs; soil + FeNs and; soil + CPNs + FeNs) and also soil samples without NMs.

### *2.2.3. Soil extraction assessing to decrease the available and leached PTE contents.*

The effects of soil treatments on PTEs availability and leachability were evaluated using CaCl<sub>2</sub>, low molecular weight organic acids (LMWOAs) and TCLP extraction.

The “operationally defined” extractable content of PTEs was determined in both, untreated and treated soil samples after the extraction with i) 0.01 M CaCl<sub>2</sub> (acidified) solution (1:10 w/v soil to extractant ratio, 2 h shaking) (Houba et al., 2000), and ii) 10 mM LMWOAs solution (acetic, lactic, citric, malic, and formic acids with a molar relation ratio of 4:2:1:1:1) (Feng et al., 2005) (1:10 w/v soil to extractant ratio, 16 h shaking). Both extractions are widely used to assess the available PTEs contents in soils and the PTEs contents under rhizosphere soil simulated conditions, respectively (Feng et al., 2005; Menzies et al., 2007). The difference between the PTEs concentrations detected in non-treated and treated extracts were used to estimate the metal contents retained by NMs (Arenas-Lago et al., 2019, 2016).

Batch toxicity leaching experiments using TCLP were conducted following the USEPA Method 1311 (USEPA, 1992) with minor modifications. Briefly, extraction fluid number 2 (0.1 M glacial acetic, pH 2.87 ± 0.05) was used as extraction fluid, in a liquid to the stable ratio of 1:20 (2 g of untreated or treated soil, 40 mL of TCLP extraction solution) in 100 mL high-density polyethylene bottles. Then, the mixture was shaken (18h, 22 ± 2 °C, 120 rpm) and centrifuged (4000 rpm, 15 min). The supernatant was passed through a 0.45 µm polycarbonate filter.

For comparison, the same TCLP tests were also carried out with the untreated soils. All tests were in triplicate. The As, Cd, Cu, Pb, Sb and Zn element leachability (%) in soil samples was calculated with the following equation (Eq. 1) (Dermatas et al. 2006; Xu et al. 2016):



$$\text{TCLP (\%)} = \frac{(C_{\text{TCLP}}, \text{mg L}^{-1}) (0.02 \text{ L})}{(Q, \text{mg g}^{-1}) (2 \text{ g})} \times 100 \% \quad (\text{equation 1})$$

where  $C_{\text{TCLP}}$  is the concentration of each element in the TCLP extract and  $Q$  is the content of each element in the soil sample before the TCLP treatment (untreated soils) (Liu and Zhao, 2007). The TCLP leached concentrations were compared with the regulatory guidelines: As (5 mg L<sup>-1</sup>), Cd (1 mg L<sup>-1</sup>), Pb (5 mg L<sup>-1</sup>) and Sb (1 mg L<sup>-1</sup>) (Not reported threshold values for Cu and Zn were found) (Cao and Dermatas, 2008; Laporte-Saumure et al., 2011; USEPA, 1992).

All extractions were acidified using 1% HNO<sub>3</sub> as recommend by Liu and Zhao (2007) to avoid microbial growth. Finally, PTEs concentrations were determined by ICP-OES.

#### 2.2.4. pH assessing in soils treated with NMs

Soils treated with NMs were assessed for pH variations after adding CPNs and/or FeNs following the same methodology mentioned above in *section 2.2.1.* for soils pH analysis.

#### 2.2.5. Sequential chemical extraction

Tessier sequential extraction (Tessier et al., 1979) has been recommended by several authors to assess the metal associations in shooting ranges soils (Van Vleek et al. 2011; Kwon et al. 2013; Islam et al. 2016; Kelebemang et al. 2017; Sanderson et al. 2018), and to verify the effectiveness of amendments on the reduction of metal availability for contaminated soils with As and Sb (e.g. Gil-Díaz et al. 2014b, 2017).

The Tessier sequential chemical extraction procedure consists of five operationally called *fractions*: i) Water-soluble and exchangeable: The soil is extracted with 1 M MgCl<sub>2</sub>, pH 7.0 at room temperature and continuous agitation for 1 h. ii) Bound to carbonates: The residue from (i) is leached with 1 M NaOAc (pH 5.0 adjusted with acetic acid). iii) Bound to Fe-Mn oxides: The residue from (ii) is extracted with 0.04 M NH<sub>2</sub>OH-HCl in 25% (v/v) HOAc (96 ± 3 °C) with occasional agitation to dissolved the free iron oxides. iv) Bound to organic matter: The residue from (iii) is treated with 0.02 M HNO<sub>3</sub> and 30 % H<sub>2</sub>O<sub>2</sub> (ratio 3:5) at pH 2 adjusted with HNO<sub>3</sub> (85 ± 2 °C) with occasional agitation for 2 h. The necessary 30 % H<sub>2</sub>O<sub>2</sub> is added later to be sure organic matter is removed. After cooling, 3.2 M NH<sub>4</sub>OAc in 20% (v/v) HNO<sub>3</sub> is added to prevent adsorption of PTEs onto the oxidised soils. v) The residual fraction, which is evaluated by the difference between the pseudototal concentrations determined before and the sum of the four previous fractions. Between each extraction, the extractant was separated by centrifugation (4400g for 30 min), the supernatant was removed with a syringe and the suspension was passed through the 0.45

µm filter and analysed to determine the PTEs concentration by ICP-OES. Finally, the residue was washed with Milli Q water, after centrifugation of 30 min and this second supernatant was discarded.

### 2.3. Data analyses

All extractions and treatments were performed in triplicate unless stated otherwise. All extraction reagents were of analytical grade. Statistical analysis was done with SPSS 21. Different analyses of variance (ANOVA) were carried out to test for significant differences among tested soils, after testing for normal data distribution and the homogeneity of variances. When significant differences were found, Dunnett's T3 test was performed to found significant differences among tested soils. A level of significance of 0.05 was chosen for rejecting the null hypothesis.

## 3. Results and Discussion

### 3.1. Soil characteristics and pseudototal, available and leaching contents of PTEs.

Studied soils are sandy loam according to USDA classification, with an acidic pH (4.13-4.52) and a low effective cation exchange capacity (ECEC) ( $< 4.20 \text{ cmol}_{(+)}\text{kg}^{-1}$ ) (Table S2) (Rodríguez-Seijo et al. 2016b). Soils show medium-high contents of organic matter (3.22-6.13 %), with low levels of Kjeldahl nitrogen (0.51-0.63 g kg<sup>-1</sup>), high levels of Fe oxides (17.67-19.36 g kg<sup>-1</sup>) and Al oxides (6.09-7.08 g kg<sup>-1</sup>), but low for Mn oxides (0.01 g kg<sup>-1</sup>). Although the soil samples have high pseudototal contents of PTEs (Table 1), military areas are not subject to the application of reference levels according to Spanish Legislation (BOE, 2005; Rodríguez-Seijo et al., 2016ba). However, according to Canadian guidelines (CCME, 2007) for industrial areas and shooting range soils/military areas (Laporte-Saumure et al., 2011), the pseudototal contents of Pb and Sb are over the referred guidelines (Table 1). This can be a serious transfer issue of PTEs to adjacent ecosystem compartments. High contents of Pb are mainly due to the fact that lead-antimony ammunition is widely used for military uses, and it is the primary source of both elements in these soils. Likewise, the high content of Cu in S3, located at the bottom of the berm, is also a consequence of using Cu-coated ammunition (Evangelou et al., 2012; Rodríguez-Seijo et al., 2016ba).

The available (CaCl<sub>2</sub>), rhizospheric (LMWOAs) and leachable contents (TCLP extraction) of PTEs in soils untreated are shown in Table 1. Extractions with CaCl<sub>2</sub> show a high proportion of available contents respect to the pseudototal contents, especially for Cu (up to 75%) and followed by Pb (< 64%), Zn (< 38 %), Sb (< 7 %), Cd (< 6 %) and As (< 2 %). The available contents extracted with LMWOAs are much lower than those extracted with CaCl<sub>2</sub>, except for Sb, being this element the PTE most available after rhizospheric extraction (up to 22%) and followed by Zn (< 21%), Cu (< 12%), Pb (< 8%), Cd and As

(<1%). Regarding the leachable contents through TCLP test and according to the leachability ratio, Pb showed the highest potential to be leached (25-55 %), followed by Cu (7-40 %), Zn (10-34 %), Sb (6-11 %), Cd (3-5 %) and As (< 1%). Despite these values, Pb contents were over the regulatory limits for all samples (5 mg L<sup>-1</sup>), while for other elements the limits were not overpassed. Thus, Pb is the main element in these soils that supposes a potential risk for surrounding environments (Table 1) (Laporte-Saumure et al., 2011; USEPA, 1992). Several authors have found similar results for shooting range soils (Cao and Dermatas, 2008; Dermatas et al., 2006; Sanderson et al., 2015), with high available contents of Pb, Cu and Zn, where usually, the Pb was easily leached to the surrounding environments. In general, these high available contents of PTEs are related to ammunition weathering due to adverse environmental conditions such as acidic soil pH or water erosion (Naidu et al., 2008; Rodríguez-Seijo et al., 2016<sup>a,b</sup>; Sanderson et al., 2012a, 2012b).

Our results show that As and Sb tend to be less mobile than Cu and Pb at these acidic soil pH values. Different studies have indicated that As and Sb ions have a strong affinity for Al and Fe oxides, which may explain their limited availability and mobility in the studied soils (Kabata-Pendias, 2010; Pierart et al., 2015; Sanderson et al., 2012b; Wilson et al., 2010). However, Sb showed a high availability (up to 22% of the pseudototal content) when it was extracted with LMWOAs. This result may be explained due to effective extraction of some LMWOAs, such as citrate and malate, which favour the Sb mobility through inhibition of the Fe oxide crystallisation (Komárek et al., 2013; Ptak and McBride, 2015).

**Table 1.** Pseudototal, available and leaching contents of potentially toxic elements (PTEs) from studied soils before different treatments.

Element	Pseudototal content (mg kg <sup>-1</sup> )						GRL industrial soils
	S1	S2		S3			
As	<b>55.3</b> ± 8.5 <i>ab</i>	<b>42.5</b> ± 2.4 <i>b</i>		<b>62.5</b> ± 5.4 <i>a</i>		12	
Cd	0.95 ± 0.10 <i>a</i>	1.00 ± 0.71 <i>a</i>		1.00 ± 0.33 <i>a</i>		22	
Cu	26.8 ± 4.2 <i>c</i>	63.2 ± 4.49 <i>b</i>		88.5 ± 9.77 <i>a</i>		91	
Pb	507 ± 51 <i>c</i>	<b>3248</b> ± 62 <i>b</i>		<b>4452</b> ± 940 <i>a</i>		600	
Sb	21.4 ± 2.3 <i>c</i>	<b>67.5</b> ± 13.3 <i>b</i>		<b>96</b> ± 28.12 <i>a</i>		40	
Zn	39.1 ± 0.79 <i>b</i>	46.2 ± 1.31 <i>a</i>		31.7 ± 3.59 <i>c</i>		360	
Element	CaCl <sub>2</sub> extracted (mg kg <sup>-1</sup> )						
	S1	Extraction efficiency (%)	S2	Extraction efficiency (%)	S3	Extraction efficiency (%)	
As	0.92 ± 0.03 <i>a</i>	1.66	0.92 ± 0.09 <i>a</i>	2.16	0.57 ± 0.01 <i>b</i>	0.91	
Cd	0.06 ± 0.01 <i>a</i>	6.32	0.06 ± 0.01 <i>a</i>	6.00	0.06 ± 0.01 <i>a</i>	6.00	
Cu	10.5 ± 0.5 <i>c</i>	39.29	41.3 ± 2.53 <i>b</i>	65.35	66.2 ± 3.06 <i>a</i>	74.80	
Pb	350 ± 11 <i>c</i>	69.03	1752 ± 152 <i>b</i>	53.94	2694 ± 160 <i>a</i>	60.51	
Sb	0.67 ± 0.20 <i>c</i>	3.13	4.61 ± 0.30 <i>b</i>	6.83	6.93 ± 0.30 <i>a</i>	7.22	
Zn	5.09 ± 0.11 <i>b</i>	13.02	12.1 ± 1.1 <i>a</i>	26.19	12.1 ± 0.6 <i>a</i>	38.17	
Element	LMWOAs extracted (mg kg <sup>-1</sup> )						
	S1	Extraction efficiency (%)	S2	Extraction efficiency (%)	S3	Extraction efficiency (%)	
As	<DL	0.00	<DL	0.00	0.40 ± 0.15	0.01	
Cd	<DL	0.00	<DL	0.00	0.01 ± 0.00	0.01	
Cu	1.10 ± 0.4 <i>c</i>	0.04	4.06 ± 0.34 <i>b</i>	0.06	10.8 ± 0.9 <i>a</i>	0.12	
Pb	21.8 ± 4.1 <i>c</i>	0.04	149 ± 5 <i>b</i>	0.05	360 ± 8 <i>a</i>	0.08	
Sb	3.14 ± 0.1 <i>c</i>	0.15	13.3 ± 1.0 <i>b</i>	0.20	21.2 ± 0.1 <i>a</i>	0.22	
Zn	1.13 ± 0.3 <i>c</i>	0.03	7.28 ± 0.2 <i>a</i>	0.16	6.72 ± 0.02 <i>b</i>	0.21	
Element	TCLP leachable contents (mg L <sup>-1</sup> )						
	S1	Leachability ratio (%)	S2	Leachability ratio (%)	S3	Leachability ratio (%)	TCLP maximum
As	0.02 ± 0.01 <i>b</i>	0.45	0.18 ± 0.09 <i>a</i>	2.8	0.03 ± 0.05 <i>b</i>	1.98	5
Cd	0.04 ± 0.00 <i>a</i>	4.21	0.05 ± 0.00 <i>a</i>	5	0.04 ± 0.00 <i>a</i>	5	1
Cu	0.13 ± 0.10 <i>c</i>	0.42	0.68 ± 0.11 <i>b</i>	0.31	1.98 ± 0.50 <i>a</i>	0.29	-
Pb	<b>8.07</b> ± 3.90 <i>c</i>	25.51	<b>39.7</b> ± 3.8 <i>b</i>	23.46	<b>117</b> ± 37 <i>a</i>	55.11	5
Sb	0.16 ± 0.02 <i>b</i>	11.96	0.29 ± 0.11 <i>a</i>	8.13	0.37 ± 0.09 <i>a</i>	6.53	-
Zn	0.25 ± 0.03 <i>b</i>	10.05	0.55 ± 0.02 <i>a</i>	21	0.61 ± 0.12 <i>a</i>	34.28	-

<DL Below the detection level. Mean values (n ≥ 3) followed by different letters are significantly different from others (*p* < 0.05). Results were partially published in Rodríguez-Seijo et al. (2016b).

GRL. Generic reference levels for Cu, Pb, Sb and Zn at industrial soils and shooting ranges according to Canadian Guidelines (CCME 2007; Laporte-Saumure et al. 2011) (Values in bold are over GRL).

TCLP maximum. The maximum concentration of contaminants for toxicity characteristic leaching procedure according to the reference guidelines (USEPA 1992; Laporte-Saumure et al. 2011) (Values in bold are over maximum concentration values for each element).

### *3.2. Impact of NMs treatments on soil pH*

The influence of NMs treatments on soil pH was assessed after adding the NMs to the soils (Fig. 1). A substantial increase of pH from very strong acidic to slightly acid values was observed after 10 days for all soils and treatments, being the pH values lower when FeNPs and CPNs were added together than after adding FeNs or CPNs individually (Fig. 1). In any case, the decrease in pH during the first 24 h may be associated with reaching the chemical balance between soils and nanoparticles after 10 days of measuring. Despite the low solubility of CPNs and FeNs, the dissolution of a small proportion of nanoparticles is a process already observed by other authors (He et al., 2008; Montalvo et al., 2015; Wang et al., 2016). This process may influence the release of acid ions from the soil exchange complex, such as  $H^+$  and  $Al^{3+}$ , which favour acidification of soils. At the same time, the undissolved nanoparticles may adsorb these cations -and the available PTEs-favouring the increase of the soil pH (Fig. 1). These results are according to those found for hydroxyapatite (Boisson et al., 1999) and iron NMs (Gil-Díaz et al., 2017, 2018) treatments in acidic soils contaminated with metals. Moreover, an increment of soil pH usually favours the immobilisation of some metal cations, such as Pb ions, through processes of ion exchange and surface complexation. However, these pH values may also favour the mobilisation of metalloids, such as Sb and As (Gil-Díaz et al., 2017, 2018; Palansooriya et al., 2020).

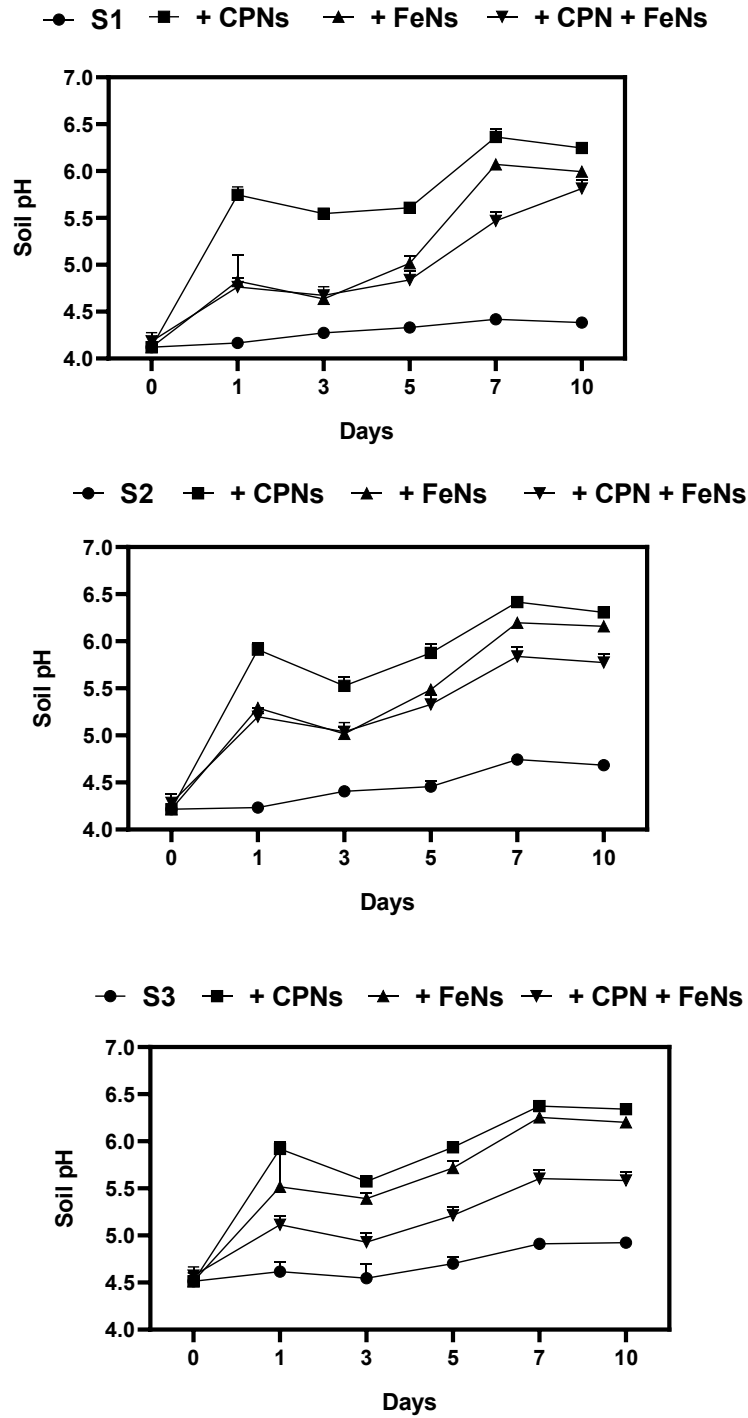


Fig. 1. Changes of pH in the contaminated shooting range soils amended with iron nanomaterials (+FeNs), hydroxyapatite (+CPNs) and both nanoparticle (FeNs + CPNs). Average values ( $n = 3$ ). Error bars represent the standard deviation of three replicates.

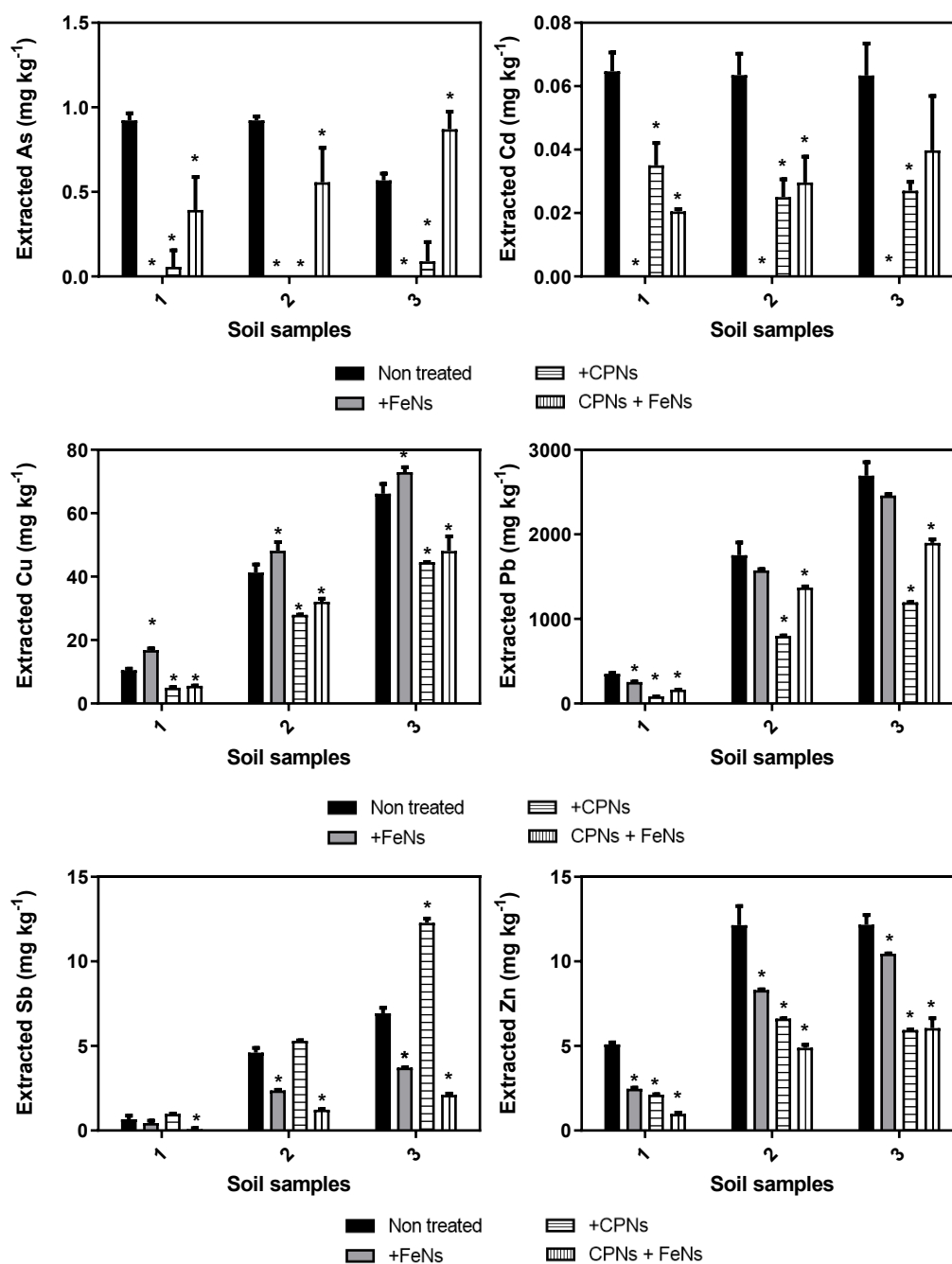
### *3.3. Available and leaching contents of PTEs in soils after treatment with NMs.*

Most of the NMs -and their mix- applied to the studied soils favoured, after the different extraction (CaCl<sub>2</sub>, LMWOAs, and TCLP), the decrease of the available and leaching PTEs contents in the shooting range soils (Figs. 2, 3 and 4, respectively).

In general, after treatment with CPNs, FeNs and their mixture, the CaCl<sub>2</sub>-extractable contents of PTEs were significantly lower than those in control soils. The results indicate that CPNs were the most effective NMs for immobilization of Cu (32-52% reduction), Pb (54-76%) and Zn (50-80%). Conversely, the mix of CPNs + FeNs was the most efficient for Sb retention (69-88%), while FeNs treatment was the greatest for As and Cd immobilization ( $\approx 100\%$ ) (Fig. 2). Besides, CPNs and the mix of NMs (CPNs + FeNs) were also appropriate to reduce the Cd available concentrations. However, the results also show that NMs could increase the mobility of As (soil 3 for combined treatment), Cu (all samples for FeNs treatment) and Sb (all samples for CPNs treatment) (Fig. 2). Also, the LMWOAs-extractable contents of PTEs generally decreased after applying each NMs or their mix to the soils. The CPNs were the most effective NMs for immobilization of Pb (67-87%) and Zn ( $\approx 100\%$ ); FeNs for Cu (19-54%), and CPNs + FeNs for As ( $\approx 100\%$ ) and Sb (47-84%). However, the Cu and Sb available concentrations did not decrease after adding CPNs and CPNs + FeNs, respectively (Fig. 3).

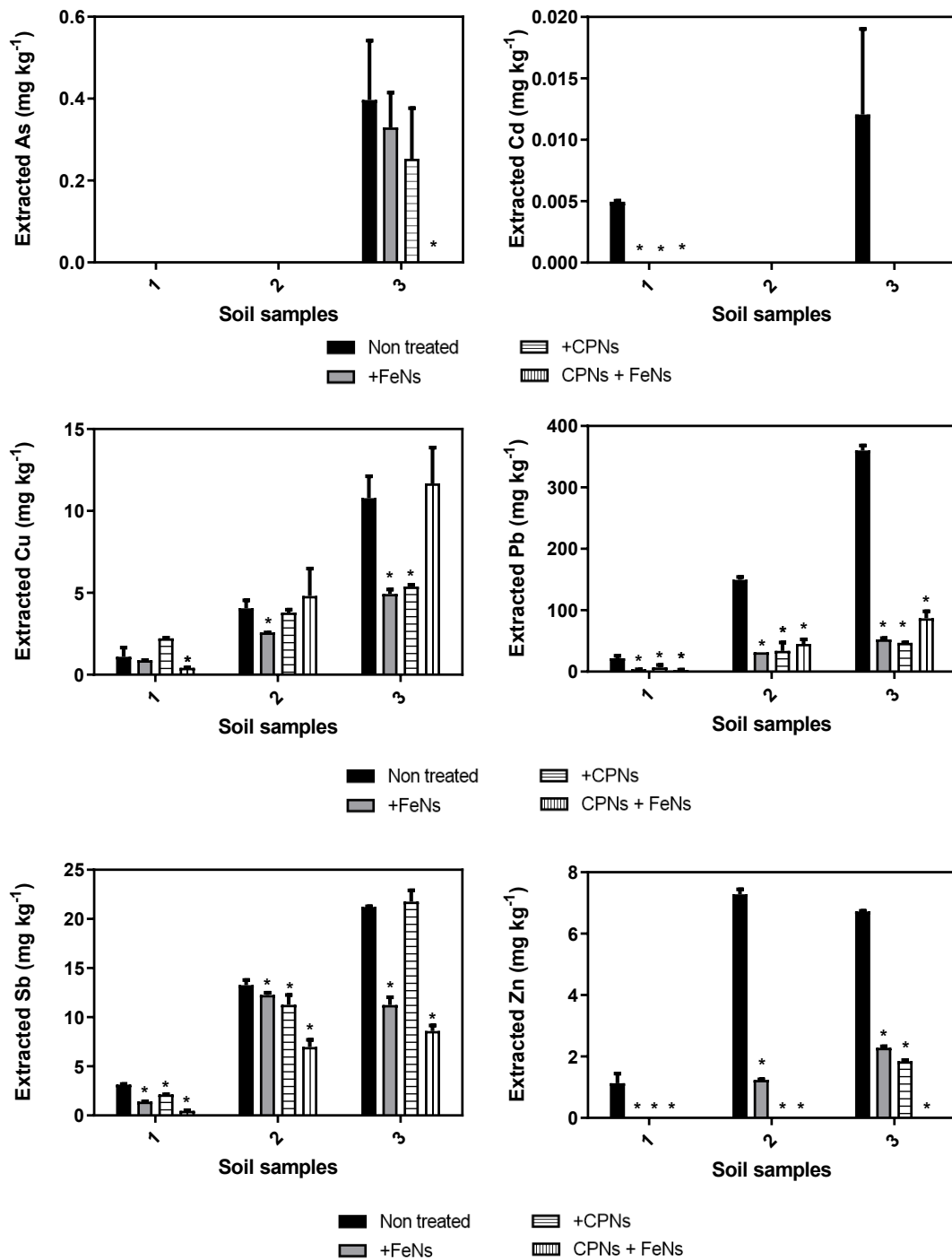
Therefore, these NMs, using LMWOAs as extractant, were not effective for these PTEs in the shooting range soils. Similar results were found by Arenas-Lago (2016), who indicated that Cu, Pb and Zn in shooting sports range soils decrease around 95%, 70% and 20 %, respectively after CPNs treatment using CaCl<sub>2</sub> as extractant. This study also indicated that CPNs were very efficient to reduce the Pb (80%), and Zn (95%) contents using LMWOAs as extractant. However, there is still controversy about the use of these extractants (or others) as representative of the available fraction of PTEs. The disparity in the extractable contents by CaCl<sub>2</sub> and LMWOAs suggests that the release of PTEs may come from different soil pools and therefore, to have different efficiency in assessing the availability of PTEs in soils (Arenas-Lago et al., 2016; Soriano-Disla et al., 2010; Wang et al., 2003). Some authors have indicated that the CaCl<sub>2</sub>-extractable contents of PTEs may represent the exchangeable soil fraction (Feng et al., 2005; Geebelen et al., 2003). Besides, the exchangeable soil fraction is related with the PTEs weakly linked to exchangeable positions of different soil components, such as organic matter, Fe and Mn oxides and clay compounds, among others (Arenas-Lago et al., 2014; Fonseca et al., 2011; Gasparatos et al., 2015).

Nevertheless, LMOWA represents the availability PTEs fraction in the soil linked to the element contents more likely to be uptake by plant species (Feng et al., 2005).



**Fig. 2.** Potentially toxic elements determined by CaCl<sub>2</sub> extraction solution (mg kg<sup>-1</sup>). Non-treated soil (Nt), treated with calcium phosphate (+ CPNs), iron nanomaterials (+ FeNs) and combined treatment (CPNs + FeNs). Mean values (n=3). Error bars represent the standard deviation of the mean value. Asterisks indicate a significant difference between non-treated (control) and treated samples (p < 0.05).





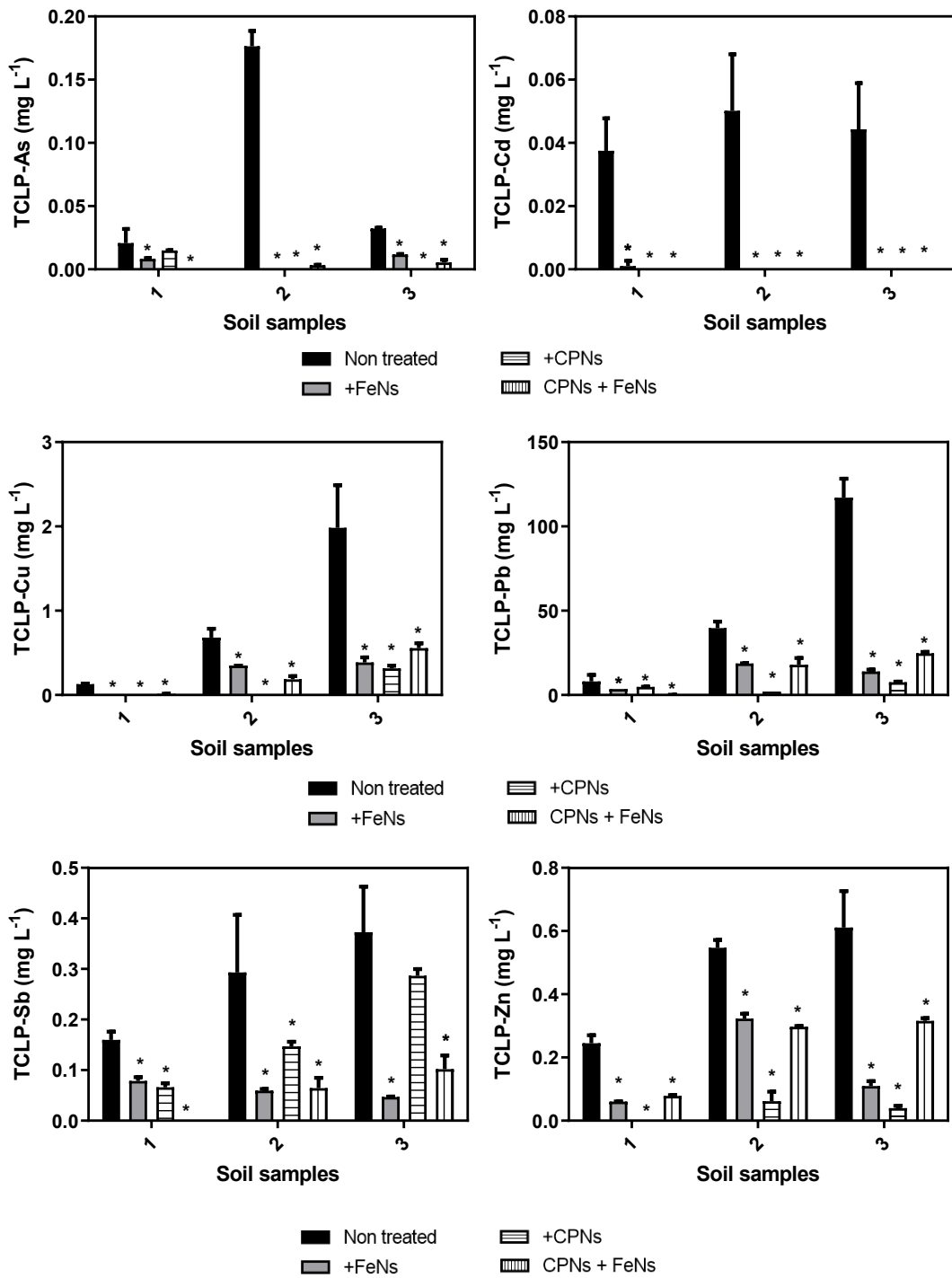
**Fig. 3.** Potentially toxic elements determined by LMWOAs extraction solution (mg kg<sup>-1</sup>). Non-treated soil (Nt), treated with calcium phosphate (+ CPNs), iron nanomaterials (+ FeNs) and combined treatment (CPNs + FeNs). Mean values (n=3). Error bars represent the standard deviation of the mean value. Asterisks indicate a significant difference between non-treated (control) and treated samples (p < 0.05).

Also, several studies have indicated nanosized metal oxides, and specifically, iron nanoparticles, have a high metal adsorption capacity, and they are widely used in water treatment, mainly to adsorb and reduce the content of metals (Ali, 2012; Hua et al., 2012). In line with the mentioned above, the use of NMs based on iron for soil remediation is currently a rising research line, where several studies have already indicated that different kind of iron nanoparticles such as, nano-zero valent iron, iron sulphates, iron Fe-Mn binary oxides, among others, are highly efficient to retain metals or other PTEs in contaminated soils (An and Zhao, 2012; Di Palma et al., 2015; Lefevre et al., 2015; Liu and Lal, 2012; Zheng et al., 2017). Moreover, Wang et al. (2015a) have researched the effects of both phosphate and Fe-oxide nanoparticles on water and soil remediation. They studied the interaction between hydroxyapatite nanoparticles and goethite nanoparticles finding that the capacity of hydroxyapatite nanoparticles as a nanofertiliser and soil remediator is controlled by the interactions with the iron oxide nanoparticles and the natural organic contents depending on the pH.

In this regard, a few studies have investigated the combined application of both hydroxyapatite and hematite nanomaterials. For example, Cui et al. (2020) indicated that hematite together hydroxyapatite decreased soil redox potential and increased pore water pH. Besides, their combination may decrease phosphate release from hydroxyapatite, increase soil pH and promote the reduction of available metals in soil solution, increasing the metal immobilization. In this line with our study, Wang et al. (2015b) reported that using column experiments to study the cotransport and retention of hydroxyapatite nanoparticles, the mobility of both were substantially lower during cotransport than their individual transport due to hetero-aggregation of hydroxyapatite-hematite complexes, which could explain the type of interactions that may exist between hydroxyapatite and hematite nanoparticles in our study.

The TLCP extraction has been widely successfully used by several authors to assess the soil contamination in shooting ranges berms, toxicity characteristics of soils and to assess the metal leachability of the untreated and treated shooting range soils (Ahmad et al., 2016; Laporte-Saumure et al., 2011), also using nanoremediation practices (Liu and Zhao, 2013; Xu et al., 2016). Our results show that using the TCLP-test showed all PTEs concentrations were reduced after adding CPNs, FeNs, and CPNs + FeNs (Fig. 4), being CPNs treatment more efficient for Cu (84-100% reduction), Pb (40-95%) and Zn (88-100%); while the CPNs + FeNs treatment was the greatest for As (82-100%) and FeNs was for Sb immobilization (72-100%). For Cd, all treatments were effective due to concentrations were below the detection level, and metal mobilisation was not detected. As it was mentioned above, the Pb exceeded the

regulatory limit for untreated soils (Table S2). However, after adding CPNs, the available contents of Pb were below the regulatory limits for S1 and S2, and near to limits for S3 (Fig. 4). These results suggest TCLP-test together with the NMs application are efficient to reduce the leachable contents of PTEs in the studied soils.



**Fig. 4.** Potentially toxic elements determined by TCLP extraction solution (mg L<sup>-1</sup>). Non-treated soil (Nt), treated with calcium phosphate (+ CPNs), iron nanomaterials (+ FeNs) and combined treatment (CPNs + FeNs). Mean values (n=3). Error bars represent the standard deviation of the mean value. Asterisks indicate a significant difference between non-treated (control) and treated samples (p < 0.05).

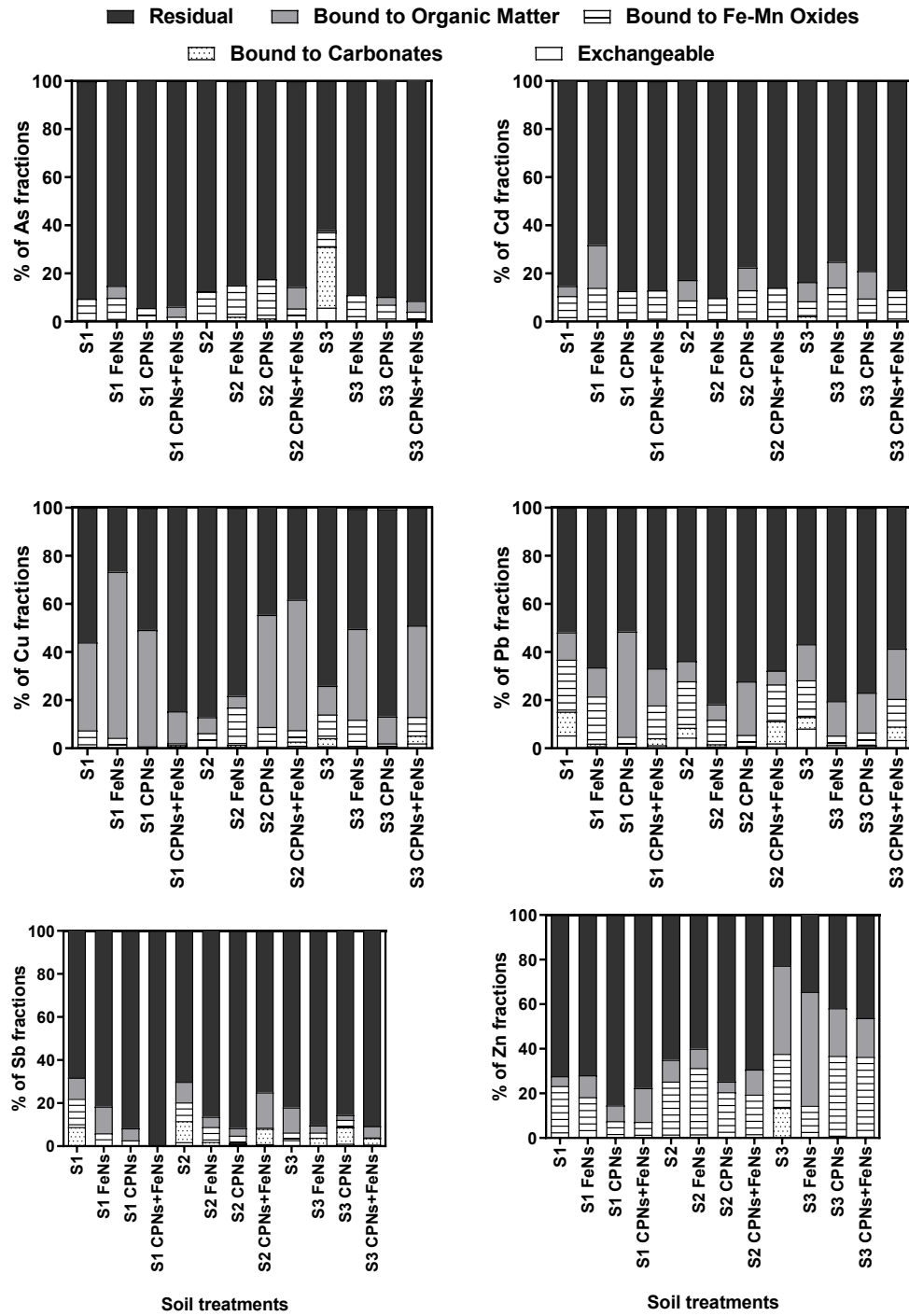
### *3.4. Tessier sequential chemical extraction: Potentially toxic elements fractionation in soils non-treated and treated with NMs.*

The Tessier sequential chemical extraction was performed to assess the distribution of PTEs among the different geochemical phases in the shooting range soils before and after adding the different NMs. Figure 5 shows the proportion of PTEs associated with each fraction, respectively, in the different soils treated and untreated with the NMs. The findings indicated that the greatest percentage of PTEs in untreated soils were mainly in the residual fraction (As:  $\approx 90\%$  -  $60\%$ ; Cd:  $> 80\%$ ; Cu:  $\approx 90\%$  -  $50\%$ ; Pb:  $\approx 70\%$  -  $50\%$  Sb:  $\approx 80\%$  -  $60\%$  Zn:  $\approx 75\%$  -  $20\%$ ). However, the fractions of PTEs environmentally relevant and thus, with the highest mobility (exchangeable fraction and carbonate-bound) were much lower. The mobility factor (sum of exchangeable fraction and carbonate-bound with respect to the sum of all fractions) showed that the percentage of mobile fractions represents: 0.35 to 30% to the total content of As, 0-2% for Cd; 0.6-4.2% for Cu, 8.5-15.2% for Pb, 1.4-11.5% for Sb and 0-13.6% for Zn. The potentially available fractions (PTEs associated with organic matter and oxides) (Sanderson et al., 2018) were lower than the residual fraction but greater than the most mobile fractions. In a previous study, Rodríguez-Seijo et al. (2016b) determined by means of Geoaccumulation index (Igeo) and the Enrichment Factor (EF) that PTEs, such as Pb and Sb, showed very high values for these parameters in S1, S2 and S3. However, other PTEs, such as As, Cd and Cu showed mean values or even low, as Ni and Zn. These results together with the findings obtained with the sequential chemical extraction may explain the different origin of PTEs in the soils. On one hand, the Pb and Sb residual fraction have their majority origin in the accumulation of fragments and particles of ammunition ( $< 2$  mm) that are in continuous degradation realising Pb and Sb to the most labile soil fractions, as a consequence of the climatic and soil conditions. On the other hand, the high percentage of the other PTE residual fractions are related with a natural origin and the geology of the studied area, which consists mostly of orthoquartzite, sandstones and black slate (Rodríguez-Seijo et al. 2016b).

After adding the different NMs amendments, the proportion of PTEs associated to the residual fraction, organic matter and oxides increased, and therefore, there was a reduction of the most mobile fractions (exchangeable fraction and carbonate-bound): below than 0.5% (with CPNs) and 2% (with FeNs) for As;  $< 1.11\%$  (with CPNs) and  $< 1\%$  (with FeNs) for Cu;  $< 1.5\%$  (with CPNs) and  $< 2\%$  (with FeNs) for Pb;  $< 2.8\%$  (with CPNs) and  $< 6.5\%$  (with FeNs) for Sb, and undetectable level for Cd and Zn

after application of each NMs. Similar results for combined treatment were observed, although it was not effective for Cd (soil 1), Cu and Sb.

Sequential chemical extractions have been previously used to assess the behaviour PTEs, such as Pb and Sb, on shooting ranges soils, and the effectiveness of soil amendments to reduce metal availability (Fayiga and Saha, 2017; Okkenhaug et al., 2016; Sanderson et al., 2018; Yan et al., 2016). As our results show, ours NMs amendments can favour the immobilisation of the different PTEs in less available forms, as indicated by different authors with the addition of CPNs (Liu and Zhao, 2013; Ogawa et al., 2015; Zhang et al., 2010), FeNs (Liu and Zhao, 2007; Ogawa et al., 2015; Xu et al., 2016) and iron-based sorbents (Okkenhaug et al., 2016). Besides, the fixation and retention of PTEs in shooting range soils and mining soils using CPNs and/or FeNs were verified in previous studies by TEM (Transmission Electron Microscopy) and TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) (Arenas-Lago et al., 2019).



**Fig. 5.** Percentage of PTEs determined after the Tessier sequential chemical extraction for each fraction in the shooting range soils. Non-treated soil (S1, S2 and S3), treated with calcium phosphate (+ CPNs), iron nanomaterials (+ FeNs) and combined treatment (CPNs + FeNs).

### 3.5. Considerations to avoid metal mobilization and environmental impacts.

Despite the high efficacy of phosphates to stabilise PTEs, their high mobility in the subsoil may cause a hazardous environmental issues (e.g., eutrophication of stream and groundwaters at higher doses) (Park et al. 2011; Liu and Lal, 2012). In this study, we observed that extractable phosphorous contents were below than 5%, 4% and 1% after the TCLP, LMWOAs and CaCl<sub>2</sub> extractions, respectively. Therefore, CPNs treatment does not show an eutrophication risk by phosphorus and released P content could play a role as nano-fertiliser for further restoration measures (Arenas-Lago et al., 2016; Liu and Lal, 2012; Soliman et al., 2016; Taşkın et al., 2018). According to previous results, Arenas-Lago et al. (2016) found that P extractable contents from treated samples were less than 12% and 1% after LMWOAs and CaCl<sub>2</sub> extractions, respectively. Furthermore, Lago-Vila et al. (2019) also indicated that Pb availability in firing and skeet shooting ranges was reduced after hydroxyapatite treatment, which favour the germination and growth of different species, such as *Sinapis alba* L., *Lactuca sativa* L. and *Festuca ovina* L. assessed with biotest assays. Also, Jin et al. (2016) and Ding et al. (2017) found that extractable PTEs were reduced after applying nano-hydroxyapatite at the same concentration that present study to contaminated soils with Pb. Besides, these authors showed that the ryegrass (*Lolium perenne* L.) grows better after NMs application.

For iron-based NMs, Liu et al. (2016) found that these NMs may act as macronutrients when they are applied in low concentrations (Liu et al., 2016). Also, some authors showed that iron-based NMs can be used to reduce plant oxidative stress and to improve the plant growth under adverse conditions, such as soils with high contents of PTEs (Siddiqi and Husen, 2017; Soares et al., 2018). However, Gómez-Sagasti et al. (2019) reported that nanoscale zero-valent iron particles could harm the microbial organisms from sandy-loam soils and mobilisation problems with some elements such as Cu, Cd and Sb in treated soils.

According to our results, combined treatment (CPNs+FeNs) is a good option for retaining metal mixtures, such as Pb and Sb in shooting range soils, since these NMs can retain Pb without mobilising Sb (Griggs et al., 2011; Ogawa et al., 2016, 2014, 2015). In this sense, Kameda et al. (2017) and Tandy et al. (2017) found that simultaneous application of FeSO<sub>4</sub> and several amendments of CaCO<sub>3</sub> and ViroSoil™ (a red mud composed by iron and aluminium oxides, and calcium and magnesium minerals) were the best option for immobilisation of Pb and As/Sb. In line with the above, several studies reported that the only use of phosphates can favour the retention of a certain metal but mobilise other elements such as Sb (Cao et al., 2013; Fayiga and Saha, 2017; Griggs et al., 2011; Liu and Zhao, 2013), which can be related with



the increment of the soil pH after CPNs treatment. Besides, when phosphates are added at high concentrations, for example, stabilising Pb (mainly  $Pb^{+2}$ ), Sb can be released because of competition of phosphates and the anionic form [Sb(V)] (the most common Sb species in shooting range soils) for the same sorption sites, mainly on iron (Fe) (hydr)oxides (Griggs et al., 2011; Okkenhaug et al., 2013; Scheinost et al., 2006; Tandy et al., 2017; Vithanage et al., 2017).

#### **4. Conclusions**

Our results showed that the studied NMs can be suitable for PTEs immobilisation in shooting ranges, mainly for Pb, the most significant PTE in civilian and military shooting range.

The application of NMs should be carried out with caution in multi-contaminated soils to avoid immobilisation and mobilisation of antagonist PTEs, as indicated for some elements, such as Pb/Zn and As/Sb. In this sense, before application of NMs, it is necessary to assess the soil pH, the possible release of NMs over time and the kind of ammunition used in the studied areas. In any case, combined treatments of NMs could be the best option to avoid metal mobilisation in multi-contaminated soils by different PTEs. Furthermore, more studies are needed with low concentrations of NMs (< 1%), and with plant growth experiences to verify whether the reduction of available contents are also reflected in a reduction of metal accumulation from soil to plants, less oxidative stress response, or their impact on microbial activities.

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