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Lead and PAHs contamination of an old shooting range: A case study with a holistic approach

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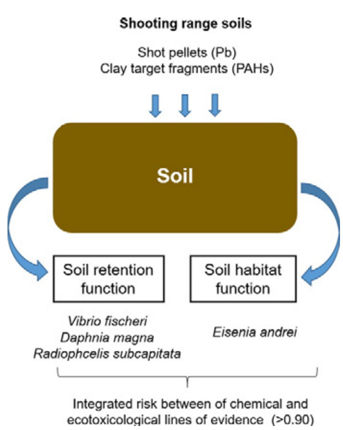
HIGHLIGHTS

- Toxicity of multi-contaminated soils from a shooting range was determined.
- Soils do not show toxicity effects to aquatic organisms.
- Earthworm toxicity was related with Pb and PAH levels in soil.
- Uptake by direct ingestion is the main toxicity pathway for terrestrial organisms.
- The risk assessment of studied soils were high or unacceptable at Tier 2.

GRAPHICAL ABSTRACT



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ABSTRACT

Soil pollution at firing ranges is an issue of growing importance, due to the accumulation in soils of contaminants derived from ammunition and clay targets. The concentration of Pb and PAHs was determined in five soils of an abandoned shooting range in Galicia (northwest Spain), and an ecotoxicological characterization was performed in order to obtain an assessment of risks. Therefore, the retention capacity of soils was assessed using test organisms of different trophic levels, and the role of soils as habitat for soil invertebrates was assessed by reproduction tests and bioaccumulation assays with earthworms. The sum of 15 PAHs ranged between 38 and 360 mg kg^{-1}, which exceed, together with Pb (160–720 mg kg^{-1}), the Galician generic reference value for urban and sporting field soils. Bioaccumulation in *E. andrei* showed contents up to 104,000 μg Pb kg^{-1}_{dw}, and up to 645 μg PAHs kg^{-1}_{fw}. High contents of Pb and PAHs in soil samples and in *Eisenia andrei* whole body, caused a reduction in the number of juveniles produced, whereas, *Vibrio fischeri*, *Raphidocelis subcapitata* and *Daphnia magna* displayed a slight toxic response to the soil elutriates tested. Therefore, the function of these soils to retain contaminants seemed not compromised, probably due to the high organic matter content and pH values, which are weakly acidic. The habitat function was affected, indicating that soil solution is not the only route of exposure to contaminants to *E. andrei*. The integration of chemical and ecotoxicological lines of evidence give rise to high risks values,

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restricting the use of these areas, and pointing for risks to surrounding ecosystems due to possible trophic transferences. The calculation of risks using the chemical and ecotoxicological data, required by Spanish legislation, could be a good approach to communicate with those responsible and/or involved in the management of contaminated sites.

1. Introduction

Lead is the main material used for ammunition production, due to its high specific gravity, workability, and ease to melt. With some differences depending on their use, ammunitions (bullets, pellets, etc.) are mainly composed of Pb (90–99 wt%). It was estimated that >100,000 shooting ranges exist all over the world, where up to 72,600 tons of Pb from ammunition are scattered on soils each year (Xifra Olivé, 2006; Perroy et al., 2014). Skeet shooting modalities use shotguns and cartridges loaded with Pb pellets (95–100% weight), that are scattered over the surface of the shooting range (Perroy et al., 2014), especially in the intermediate zones were Pb concentrations can reach up to 630,700 mg kg^{-1} (Craig et al., 2002; Duggan and Dhawan, 2007; Kajander and Parri, 2014).

In addition to pellets, mobile clay targets can also pose an environmental risk. Each clay target weight about 100–110 g and they can spread into fragments of different sizes (<5 cm). Until 2004, targets were composed of coal tar pitch or petroleum (30–32 wt%), clay or limestone (67–70 wt%), and fluorescent paint. The first, which was used as a binder, it is rich in carcinogenic substances, such as polycyclic aromatic hydrocarbons (PAHs) (3000 to 40,000 mg PAHs kg clay $targets^{-1}$) (Peddicord and Lakind, 2000; Lobb, 2006).

The environmental impacts of ammunitions on soil and biota were ignored for many decades, under the assumption that Pb from ammunition remained inert in the metallic form (Vantelon et al., 2005). However, once they are deposited on soil, usually fragmented, Pb and other metals are slowly oxidized to more mobile forms (e.g. Pb^{2+} or Pb^{4+}), that can be absorbed by roots or readily adsorbed to organic matter, clays or Fe and Mn oxides (Vantelon et al., 2005; Bennett et al., 2007). Due to all the reasons above and to the high probability of Pb and other elements entering the food web, national authorities from different countries are giving more attention to shooting ranges (Quy, 2010; Luo et al., 2014a; Sanderson et al., 2014).

Although the effects of the pellets in birds have been widely documented over the past 30 years (Mateo et al., 2014; Pain et al., 2015), only in the last few years studies focusing lead toxicity on soil organisms have increased: i) microarthropods (Migliorini et al., 2004; Luo et al., 2014b; Selonen et al., 2014); ii) enchytraeids (Rantalainen et al., 2006; Luo et al., 2014c); and/or iii) earthworms (Ming et al., 2012; Luo et al., 2014a; Sanderson et al., 2014). Meanwhile, the toxicity of soils contaminated with PAHs from clay targets, has been considered low for aquatic organisms (Baer et al., 1995) and birds (Gonzalez, 2003). In both cases, the reduced potential for causing toxic effects was related to the low availability of PAHs in soil.

In Spain, over 770 shooting ranges are active, with >50,000 users. In the case of skeet shooting, Guitart and Mateo (2006) explained that about 60 million cartridges are used, representing a contribution to the soil of about 2000 mg Pb $year^{-1}$. In a previous work of our research group (Rodríguez-Seijo et al., 2016), an abandoned shooting range in northwest Spain was studied, and it was found that Pb content exceeded the Spanish Generic Reference Level (GRL) (100 mg kg^{-1}) in 11 out of 12 studied soils (DOG, 2009). Moreover, even soils far away from the firing position exceeded the limits established by the USEPA (400 mg kg^{-1}) (USEPA, 2001).

Due to the high levels of contamination, these soils are apparently compromised for other uses, and due to the high number of shooting ranges throughout the world, and particularly in Spain, a deeper analysis of the risks they pose to surrounding ecosystems and corresponding services is required. This will allow setting priorities for future interventions targeting remediation for the use that better fits each site in particular, as indicated by Spanish legislation (BOE, 2005). Moreover, despite of some papers which have tested the ecotoxicity of shooting ranges soils on soil organisms (e.g. Migliorini et al., 2004; Luo et al., 2014a, 2014b, 2014c; Sanderson et al., 2014; Selonen et al., 2014), very few have performed a risk assessment evaluation considering the chemical and the ecotoxicological lines of evidence, following a tiered approach.

The previous study performed in the abandoned shooting range was now extended with the following objectives: i) to analyze, in soils with higher contents of Pb and abundance of clay target fragments (five soils in total), the content in PAHs; ii) to assess the capacity of these soils to retain contaminants, by determining toxicity of elutriates to bioindicator species of different trophic levels, *Vibrio fischeri* Beijerinck, *Daphnia magna* Strauss, *Raphidocelis subcapitata* (Korshikov) Nygaard et al. and the bioaccumulation of Pb and PAHs in *Eisenia andrei* Bouché and finally, iii) to study the impacts of contaminants in the habitat function of these soils with reproduction tests with *E. andrei*.

In order to demonstrate how these requirements can be integrated to provide a preliminary, but quantitative, evaluation of risks for supporting decision, chemical and ecotoxicological information will be integrated for the calculation of risks of soils samples from the abandoned shooting range under evaluation. This will be performed according to the methodology described by Jensen and Mesman (2006), for the environmental risk assessment of contaminated sites.

2. Material and methods

2.1. Study area and soil characterization

Soil samples were collected from an abandoned shooting range located in Monforte de Lemos, (Galicia, NW Spain) at a depth of 0–15 cm. Five out of twelve soils previously characterized by Rodríguez-Seijo et al. (2016) were selected, based on Pb contents and remains of clay targets (>2 mm). Details of the study area and physicochemical characterization of soils (stoniness, soil pH, total Kjeldahl-N, organic matter content, effective cation exchange capacity and available phosphorus) were previously described by Rodríguez-Seijo et al. (2016).

The particle-size analysis was carried out according to the method described by Gee and Bauder (1986). The clay and silt fractions were determined by the pipette method, and the sand fraction was separated trough sieving. The pellets and clay targets fragments (>2 mm) were identified, collected, and examined in detail, revealing different degrees of weathering and irregular surfaces. Pellets have white or slightly brown crust, and a lower weight than expected for the aforementioned calibers (average weight loss 10 ± 5.3%) (Rodríguez-Seijo et al., 2016). The resume of soil characteristics, pellets and clay target fragments are summarized in Table 1.

An artificial soil, with 5% organic matter and pH 6.5, was used as control in ecotoxicological assays, according to the OECD guidelines Test No. 222 for testing of chemicals (OECD, 2004a). Water holding capacity (WHC) of soils was determined according the methodology described on the standard protocol ISO 17512-1 (ISO, 2008). Thus, for this purpose soil samples were placed in plastic flasks and immersed in water for 3 h. After this period, samples were drained for 2 h, by rejecting the excess of water with absorbent paper. The WHC was determined by weighing each replica before and after drying at 105 °C, until weight stabilization