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Can Isotopes Be Used as Lead Tracers in Shooting-Range Soils?

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Abstract: Lead isotopes have been widely used to assess the sources of Pb in the soil environment since lead isotopes ratios have a specific signature that allows us to use them as environmental tracers. However, some lead sources are difficult to be identified. This article contains the lead isotope data from soils and shot pellets collected in an abandoned shooting range (NW Spain). Twelve soil and three-shot pellet samples were randomly collected and analyzed using MC-ICP-MS. The isotope ratios are shown, and analyses proved that Pb originated predominantly from the used shot pellets. Contaminated soils exhibited an isotopic composition ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$) close to some shot pellets from different manufacturers. These results offer new, valuable data for other researchers working on lead contamination research and the identification sources of Pb for adjacent areas to shooting-range facilities and for wildlife ecotoxicology. Still, the use of several ammunitions derived from different sources, such as recycled Pb, showed that it is hard to identify the lead source and these kinds of facilities.

Keywords: civilian shooting; isotope ratio analysis; lead stable isotopes; lead ammunition; shot pellets; recycled lead; soil contamination; source identification

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1. Introduction

Due to natural and anthropogenic causes, lead is a widely distributed element in all ecosystems, including the most remote ones. Lead has four stable isotopes (^{208}Pb, ^{206}Pb, ^{207}Pb and ^{204}Pb) whose ratios depend on the U/Th ratio, geological and environmental conditions, etc. Whereas ^{204}Pb is not radiogenic and does not change significantly over time, the first three forms are radiogenic and come from the decomposition of ^{238}U, ^{235}U and ^{232}Th, respectively [1–4]. In this sense, the isotopic ratio of Pb, released both from natural or anthropogenic sources, is maintained during physical and physicochemical processes. As a result, lead isotope ratios are frequently used in environmental studies as environmental tracers to identify potential lead sources [1–6]. Determinations by MC-ICP-MS (multiple-collector inductively coupled plasma mass spectrometry) allow us the measurement of very low concentrations in different environmental samples, being also a perfect and helpful tool for the analysis of isotopes of different elements with accuracies of up to ±0.001% [1,2,4,7–11].

Military and civilian shooting activities are a significant source of lead contamination to the environment, including soil biota, e.g., [5,12–15], and different works have been carried out with lead isotopes to assess their use as potential tracers of contamination by lead for wild fauna or humans near polluted areas by lead, such as mining soils, civilian/military shooting fields and hunting areas [1,5,16–22]. However, the knowledge and use of lead isotopes for soils from civilian and military shooting areas is still not well studied and requires attention [5,8,12,17,21–23] since lead isotopes signatures can be very different, due to different ammunition origins, and sometimes, the isotope identification can be overlapped with topsoil signatures [5]. More data are needed to improve databases about soil contamination by lead ammunition and their potential risk for plants and wildlife fauna.

This study reported lead isotopic data from an abandoned trap shooting range facility in NW Spain, with lead concentrations ranging from 80 to 720 mg kg^{-1} as pseudototal amounts and significant contents of bioavailable lead due to the acidic soil pH [23]. Additionally, higher levels of polycyclic aromatic hydrocarbons (PAHs) were found as a result of the usage of clay pigeons for shooting activities [14], and lead contamination was seen throughout the soil profile at various soil depths [24]. Here, we showed the lead isotope ratios ($^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$) from 3 shot pellets and 12 soil samples from various locations in the shooting range facility. Lead isotope ratios from soils and shots pellets were measured by MC-ICP-MS. They were compared with isotopic data from previously published ammunition debris (shot pellets, civilian and/or military bullets).

2. Experimental Design, Materials, and Methods

Sample Locations and Lead Content in Soils and Shoot Pellets, and Their Measurements of Lead Isotopes by MC-ICP-MS

The studied soils in this work were previously characterized, and their results were published in different works [14,23,24]. For this work, we have used the same soil samples previously analyzed (0–15 cm depth), with different degrees of contamination and distance from the firing point, while the lead contents were analyzed using X-ray fluorescence (XRF) [23,24]. The stable lead isotopes in the analyzed soils (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) were determined in all the samples according to the methodology indicated by [3,4,25]. Lead stable isotope ratio measurements were performed with MC-ICP-MS (Thermo-Finnigan Neptune) at CACTI-UVigo (Universidade de Vigo, Vigo, Spain), and the lead contents in blank samples were less than 0.1 ppb (detected signal was lower than 0.002 V). Detailed conditions about isotope analysis were previously reported [4], and all samples were analyzed in duplicate. The MC-ICP-MS and instrumental parameters for isotope ratio analysis and the Pb stable isotope ratios in reference material SRM 981 (NIST) are indicated in the Supplementary Material (Tables S1 and S2).

Regarding the shoot pellets, they were randomly selected from all ammunition debris collected from the studied soils and during the soil sieving for physicochemical analysis. Due to the shooting range facility being abandoned in 1999, we cannot assess the manufacturer of these shoots' pellets. In this sense, shoot pellets showed different degrees of weathering, such as irregular surfaces, slightly brown crust, and lower weight than expected [24]. Samples were digested according to the methodologies indicated by different authors [5,18,26], and isotope ratios were carried out using the same methods as for soil samples. After that, soil samples and shot pellets were compared with isotopic data from probable sources [27–32]: leaded petrol, burned coal, natural background, waste incinerators, industrial sources and other ammunition types (bullets, shot pellets, etc.).

3. Results and Discussion

We found that stable isotope ratios for studied soils ranged between 1.123 and 1.1709 for $^{206}Pb/^{207}Pb$ and between 2.084 and 2.134 for $^{208}Pb/^{206}Pb$ (Table 1). These values were very similar to values indicated by [5] for lead isotopes from hunting areas in Spain and within the range stated by [12] for agricultural soils contaminated by civilian shooting activities in the Czech Republic. However, these values were lower than those reported by [22] for military soils in South Korea, with $^{206}Pb/^{207}Pb$ ratios ranging from 1.171 to 1.199, and for sediments near hunting areas (1.17–1.18, Table 1) [33]. When comparing these values with different natural or anthropogenic lead sources, these data suggest that lead ammunition is the primary source of lead in these soils (Figure 1). Although some samples can have a similar isotope ratio to industrial sources (Figure 1), the study zone is in a small town (around 20,000 inhabitants) without significant lead-related industries.

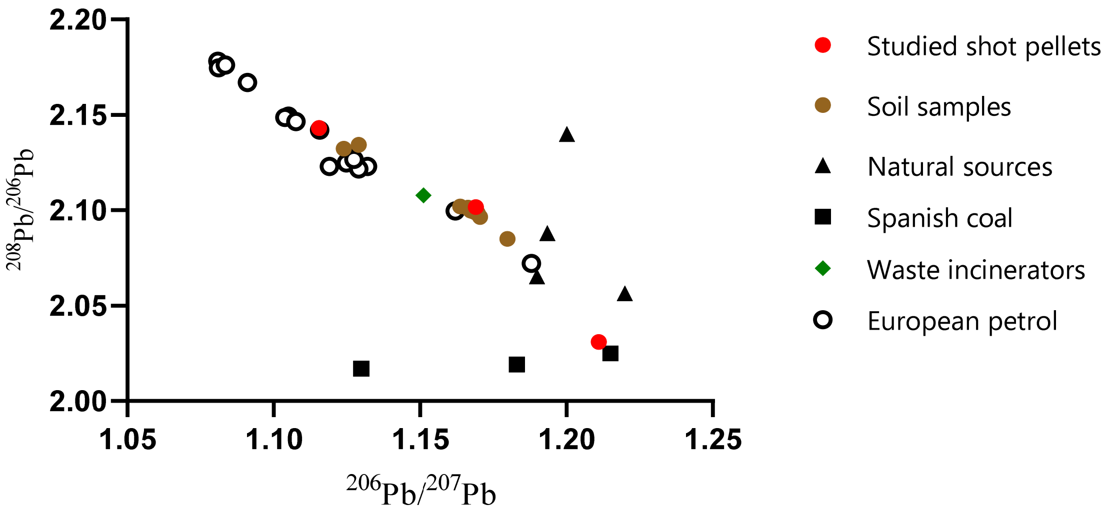

Figure 1. Scatter plot for $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ of lead isotope ratios for different environmental components in the vicinity of the study area. Data from [27–32].

However, the range of isotope ratios for collected shot pellets differed with $^{206}Pb/^{207}Pb$ ratios of 1.1155, 1.1691 and 1.211, while $^{208}Pb/^{206}Pb$ ratios were 2.1431, 2.1016 and 2.0309, respectively (Table 2). Interestingly, the one-shot pellet showed for the $^{206}Pb/^{207}Pb$ ratio a value of 1.1691, and 2.1016 for $^{208}Pb/^{206}Pb$, a value very similar to the different soil samples, suggesting that it was primarily used in this installation (Figure 2b). This higher variability is expected in shooting ranges because shooting pellets can have different origins and manufacturers with Pb from various lead ores, as reviewed by [14,24,34–36] for lead ammunition, even with the use of recycled lead for shoot pellets, such as 'home-made' ammunition that could mask lead origin specificity [34–38]. As indicated by [36,38], remanufacturing or reloading cartridges involves reusing previously fired cases and reloading these with the other components, including primers and propellants. As highlighted by [34], when various lead sources are recycled from a different product (e.g., mix of recycled batteries and other uses), the distinctive isotopic ratio may become progressively less characteristic, and therefore, the source determination can be more complex [19,34,36,37]. When the shot pellets ratio was compared with other shot pellet manufacturers (Table 2, Figure 2), it suggested a potential European origin for the potentially most used pellet, with similar ratios as indicated by different authors for European manufacturers [5,39,40]. Additionally, it was interesting to see that one-shot pellets have a lead isotope rate very similar to American lead pellets, suggesting the use of American manufacturers (Figure 2a,b). However, this shooting range was abandoned several years ago, and we cannot know which ammunitions were mainly used to compare and verify our results.

Table 1. According to the literature, lead stable isotopes ratios from different shooting range soils and soil sediments near shooting and hunting areas. Measurement precision is indicated according to the different studies—average values.

Sample	Soil Use	Depth (cm)	Pb mg kg^{-1}	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{208}Pb/^{206}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	Country	Reference
Soils											
Contaminated Soil	Civilian shooting range	0–15	82.71	18.3	15.634	38.362	2.096	1.17	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	195.5	18.287	15.634	38.377	2.098	1.169	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	160.9	17.479	15.552	37.272	2.132	1.123	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	259.61	18.236	15.625	38.297	2.099	1.167	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	187.46	18.258	15.634	38.336	2.099	1.167	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	277.38	18.224	15.626	38.294	2.101	1.166	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	222.82	18.267	15.628	38.345	2.098	1.168	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	378.17	18.23	15.629	38.307	2.101	1.166	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	366.16	18.231	15.627	38.299	2.1	1.166	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	724.85	18.174	15.617	38.204	2.102	1.163	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	402.08	18.268	15.633	38.369	2.1	1.168	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–15	442.78	17.59	15.56	37.52	2.134	1.129	-	Spain	This study
Control soil	Civilian shooting range	0–15	82.36	18.463	15.65	38.494	2.084	1.179	-	Spain	This study
Contaminated Soil	Civilian shooting range	0–5	-	-	-	-	-	1.166	-	Czech Republic	[12]
Contaminated Soil	Civilian shooting range	5–15	-	-	-	-	-	1.154	-	Czech Republic	[12]
Contaminated Soil	Civilian shooting range	15–30	-	-	-	-	-	1.165	-	Czech Republic	[12]
Contaminated Soil	Civilian shooting range	30–x	-	-	-	-	-	1.187	-	Czech Republic	[12]
Control soil	Civilian shooting range	0–5	-	-	-	-	-	1.181	-	Czech Republic	[12]
Control soil	Civilian shooting range	5–15	-	-	-	-	-	1.181	-	Czech Republic	[12]
Control soil	Civilian shooting range	15–30	-	-	-	-	-	1.178	-	Czech Republic	[12]
Control soil	Civilian shooting range	30–x	-	-	-	-	-	1.188	-	Czech Republic	[12]
Contaminated Soil	Shooting range	0–25	1432	-	-	-	-	1.133	2.407	Netherlands	[21]
Contaminated Soil	Shooting range	0–25	2362	-	-	-	-	1.133	2.407	Netherlands	[21]
Contaminated Soil	Shooting range	0–25	1432	-	-	-	-	1.133	2.407	Netherlands	[21]
Contaminated Soil	Shooting range	0–25	2362	-	-	-	-	1.133	2.407	Netherlands	[21]
Contaminated Soil	Hunting area	0–5	-	-	-	-	2.096	1.171	-	Spain	[5]
Contaminated Soil	Hunting area	0–5	-	-	-	-	2.094	1.162	-	Spain	[5]
Contaminated Soil	Hunting area	0–5	-	-	-	-	2.107	1.158	-	Spain	[5]
Contaminated Soil	Hunting area	0–5	-	-	-	-	2.108	1.153	-	Spain	[5]
Contaminated Soil	Hunting area	0–5	-	-	-	-	2.114	1.154	-	Spain	[5]
Contaminated Soil	Hunting area	0–5	-	-	-	-	2.11	1.154	-	Spain	[5]
Contaminated Soil	Hunting area	0–5	-	-	-	-	2.106	1.152	-	Spain	[5]
Contaminated Soil	Military shooting range	0	28,040	18.53	15.69	38.77	-	1.18	2.47	South Korea	[22]
Contaminated Soil	Military shooting range	5–15	24,043	18.26	15.45	38.21	-	1.18	2.47	South Korea	[22]
Contaminated Soil	Military shooting range	15–30	19,763	18.5	15.65	38.96	-	1.18	2.49	South Korea	[22]
Contaminated Soil	Military shooting range	0	5127	18.46	15.53	38.09	-	1.19	2.45	South Korea	[22]
Contaminated Soil	Military shooting range	5–15	4147	18.63	15.53	38.22	-	1.2	2.46	South Korea	[22]
Contaminated Soil	Military shooting range	15–30	185	18.62	15.77	39.08	-	1.18	2.48	South Korea	[22]
Contaminated Soil	Military shooting range	0	11,137	18.6	15.88	38.9	-	1.17	2.45	South Korea	[22]

Table 1. *Cont.*

Sample	Soil Use	Depth (cm)	Pb mg kg^{-1}	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Country	Reference
Contaminated Soil	Military shooting range	5–15	5297	15.14	15.11	35.98	-	1	2.38	South Korea	[22]
Contaminated Soil	Military shooting range	15–30	4293	16.67	16.56	39.62	-	1.01	2.39	South Korea	[22]
Control soil	Military shooting range	0	14	18.82	16.1	40.7	-	1.17	2.53	South Korea	[22]
Control soil	Military shooting range	5–15	21	18.21	15.55	38.73	-	1.17	2.49	South Korea	[22]
Control soil	Military shooting range	15–30	33	18.55	15.95	40.03	-	1.16	2.51	South Korea	[22]
Sediments											
Contaminated sediment	Hunting area	-	25.86				2.0843	1.1830	2.4693	Spain	[33]
Contaminated sediment	Hunting area	-	31.17				2.0875	1.1803	2.4649	Spain	[33]
Contaminated sediment	Hunting area	-	12.56				2.0907	1.1768	2.4630	Spain	[33]

"-" not indicated.

Table 2. The average lead isotopic signature of the studied shot pellets and shot pellets from different brands.

Manufacturer	Ammunition Type	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{207}Pb/^{208}Pb$	Country of Origin (Manufacturer)	Country of Study	Reference
-	Shotgun pellet	1.2110	2.0309	38.5550	18.9844	15.5330	-	-	Spain	This study
-	Shotgun pellet	1.1691	2.1016	38.4110	18.2779	15.6769	-	-	Spain	This study
-	Shotgun pellet	1.1155	2.1431	37.1570	17.3480	15.6347	-	-	Spain	This study
Remington	Shotgun pellet	1.2276	-	-	-	-	-	USA	USA	[41]
Winchester	Shotgun pellet	1.2290	-	-	-	-	-	USA	USA	[41]
Remington	Shotgun pellet	1.2308	-	-	-	-	-	USA	USA	[41]
-	Shotgun pellet	1.2297	2.0009	-	19.3050	-	-	-	USA	[41]
-	Shotgun pellet	1.2230	2.0110	-	19.1900	-	-	-	Canada	[19]
-	Shotgun pellet	1.1560	-	-	-	-	-	-	Czech Republic	[12]
-	Shotgun pellet	1.2300	-	-	-	-	-	USA	Argentina	[42]
-	Shotgun pellet	1.2239	-	-	-	-	-	Argentina	Argentina	[42]
-	Shotgun pellet	1.1668	-	-	-	-	-	-	Argentina	[42]
Browning CAL12	Shotgun pellet	1.1529	2.0991	-	-	-	0.4132	-	Spain	[5]
Eley	Shotgun pellet	1.1550	2.1190	-	-	-	-	UK	UK	[39]
Eley	Shotgun pellet	1.1520	2.0980	-	-	-	-	UK	UK	[39]
Eley	Shotgun pellet	1.1530	2.1200	-	-	-	-	UK	UK	[39]
Eley	Shotgun pellet	1.1470	2.1300	-	-	-	-	UK	UK	[39]
Gamebore	Shotgun pellet	1.1320	2.1340	-	-	-	-	UK	UK	[39]
Gamebore	Shotgun pellet	1.1410	2.1150	-	-	-	-	UK	UK	[39]
Gamebore	Shotgun pellet	1.1420	2.1270	-	-	-	-	UK	UK	[39]
Gamebore	Shotgun pellet	1.1390	2.1160	-	-	-	-	UK	UK	[39]
Gamebore	Shotgun pellet	1.1410	2.1140	-	-	-	-	UK	UK	[39]
Gamebore	Shotgun pellet	1.1380	2.1270	-	-	-	-	UK	UK	[39]

Table 2. *Cont.*

Manufacturer	Ammunition Type	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{207}Pb/^{208}Pb$	Country of Origin (Manufacturer)	Country of Study	Reference
Hull	Shotgun pellet	1.1560	2.1060	-	-	-	-	UK	UK	[39]
Hull	Shotgun pellet	1.1580	2.1110	-	-	-	-	UK	UK	[39]
Hull	Shotgun pellet	1.1540	2.1000	-	-	-	-	UK	UK	[39]
Lyalvale Express	Shotgun pellet	1.1520	2.1250	-	-	-	-	UK	UK	[39]
Lyalvale Express	Shotgun pellet	1.1590	2.1140	-	-	-	-	UK	UK	[39]
Lyalvale Express	Shotgun pellet	1.1530	2.1170	-	-	-	-	UK	UK	[39]
Lyalvale Express	Shotgun pellet	1.1500	2.1260	-	-	-	-	UK	UK	[39]
R.C. (Italy)	Shotgun pellet	1.1450	2.1230	-	-	-	-	Italy	UK	[39]
-	Shotgun pellet	1.1800	-	-	-	-	-			[43]
-	Shotgun pellet	1.1765	2.0700	-	-	-	-	-	Japan	[44]
-	Shotgun pellet	1.1494	2.1400	-	-	-	-	-	Japan	[45]
-	Shotgun pellet	1.1510	2.1290	-	18.1610		0.4083		Poland	[46]
-	Shotgun pellet	1.1699	2.0885	-	-	-	0.4093		Spain	[33]
-	Shotgun pellet (hunting use)	1.1548	2.1073	-	-	-	-	-	Ecuador	[17]
-	Shotgun pellet (hunting use)	1.1548	2.1010	-	-	-	-	-	Ecuador	[17]
-	Shotgun pellet (hunting use)	1.1551	2.0966	-	-	-	-	-	Ecuador	[17]
-	Shotgun pellet (hunting use)	1.1622	2.0960	-	-	-	-	-	Ecuador	[17]
-	Shotgun pellet (hunting use)	1.1652	2.0962	-	-	-	-	-	Ecuador	[17]
Humasson	Shotgun Pellets	1.2200	-	-	-	-	-	Canada	Canada	[46]
Challenger	Shotgun Pellets	1.1600	-	-	-	-	-	Canada	Canada	[46]
CIL "Canuck"	Shotgun Pellets	1.0800	-	-	-	-	-	Canada	Canada	[46]
Remington	Shotgun Pellets	1.2300	-	-	-	-	-	USA	Canada	[46]
Winchester	Shotgun Pellets	1.1500	-	-	-	-	-	USA	Canada	[46]
Kent USA	Shotgun Pellets	1.1000	-	-	-	-	-	USA	Canada	[46]
Federal	Shotgun Pellets	1.2300	-	-	-	-	-	USA	Canada	[46]
Eley	Shotgun Pellets	1.0800	-	-	-	-	-	UK	Canada	[46]
Vee	Shotgun Pellets	1.1500	-	-	-	-	-	Spain	Canada	[46]
Sellier & Bellot	Shotgun Pellets	1.1700	-	-	-	-	-	Czech Republic	Canada	[46]
Douillerie	Shotgun Pellets	1.1600	-	-	-	-	-	France	Canada	[46]
PD Olympie	Shotgun Pellets	1.1600	-	-	-	-	-	Poland	Canada	[46]
Mondial	Shotgun Pellets	1.1700	-	-	-	-	-	Hungary	Canada	[46]

"-" not indicated.

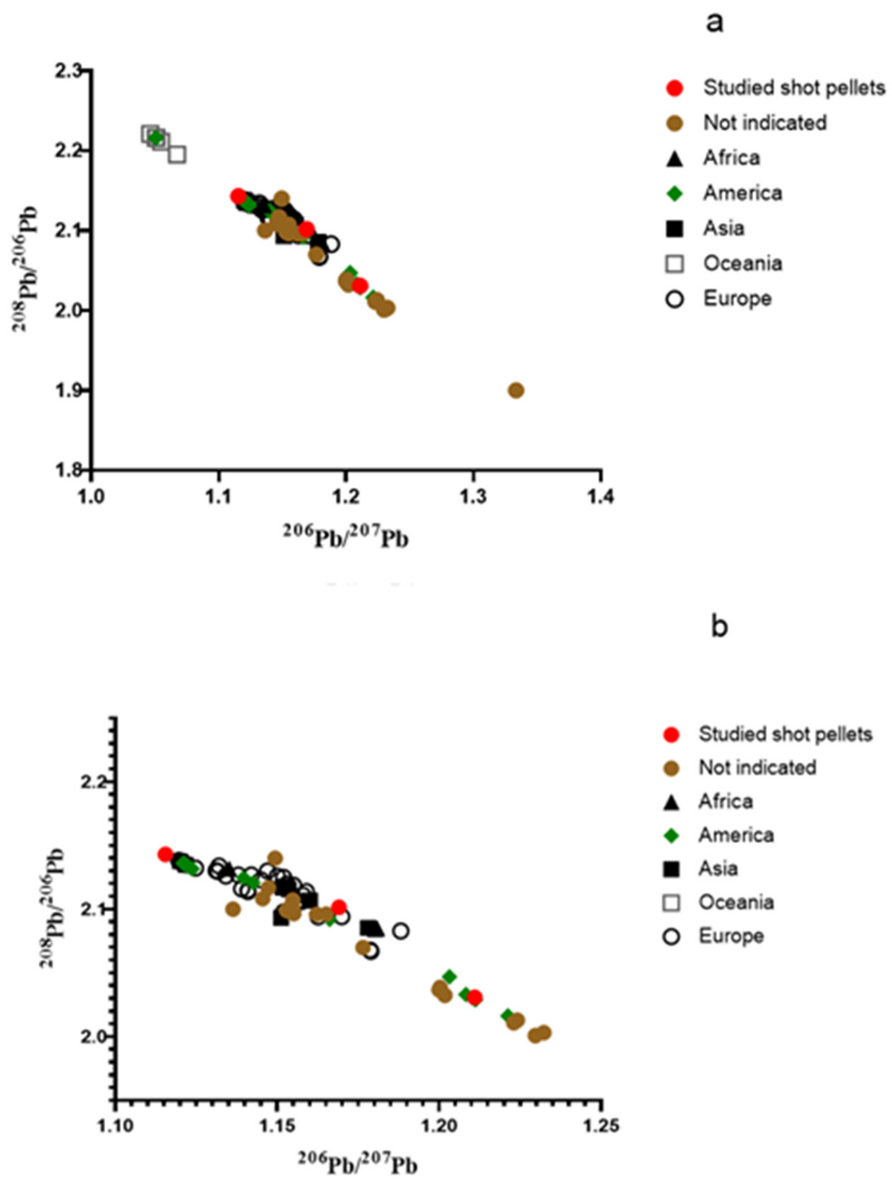

Figure 2. (**a**) Scatter plot for ^{208}Pb/^{206}Pb versus $^{206\text{Pb}}$/^{207}Pb of lead isotope ratios for different shot pellet and ammunition manufacturers and studied soils. "Not indicated" means that authors have not reported a probable origin of shot pellet manufacturer/brand. (**b**) Detail of the crowded central region. Data compiled from [5,16–22,26,33,34,39,41–45].

Research Implications of the Present Data

Lead isotope ratios have been widely used to differentiate sources of environmental lead in several environmental matrices due to lead released to the environment (e.g., exhausted from gasoline, and industrial sources) maintaining a characteristic signature and usually does not change during the manufacturing processes [1–6,9–12,21,37]. However, our results showed the difficulties of using isotopic signatures from lead ammunition as tracers of lead in shooting or hunting areas and their potential use in wildlife studies due to the different use of different ammunition sources from different world regions or different origins from previous uses [34–38,47]. This fact is that the manufacture of lead ammunition (e.g., bullets or shotgun pellets) can have various sources, such as mining, recycling and mixing scrap metal, car batteries, etc. Additionally, some shooting ranges can recover some spent ammunition that can be recycled, remanufactured and reused for shotgun cartridges [34,36–38,47,48]. During the fusion processes, the purification and addition of other additives, such as Sb, are aggregation phenomena that make the projectiles from the same box and manufacturer have different ratios and compositions, making it impossible to relate to the brand/batch manufacture. In this sense, Gulson et al. [9] also remarked that comparison with published literature could be difficult since several papers only show data from major isotope $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios, or sometimes only $^{207}Pb/^{206}Pb$ ratios, a problem that we found in our study since several papers only published one isotope ratio, as highlighted in Table 2. Finally, there are some possible issues in the interpretation of soil contamination arising from the lead due to the use of primers (e.g., Pb styphnate, $C_6HN_3O_8Pb$ or lead peroxide PbO_2) that ignite in the firearm barrel to provide the propulsion to the projectile, and they should also be considered [48].

4. Conclusions

Studies about lead source identification with lead ammunition in wildlife fauna or flora should be cautioned. However, we need more data on lead isotopes and soils contaminated by shooting/hunting activities to generate a robust database with lead shooting pellets or lead ratios from shooting ranges. In the cases where lead isotopes are measured, all isotopic ratios should be measured and published, not only one ratio (e.g., $^{207}Pb/^{206}Pb$) (Table 2). The data we offer here could be helpful for researchers involved in forensic sciences or lead tracers, such as the toxicological effects of lead in wildlife fauna.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app12178803/s1, Table S1: Operating parameter settings of the Thermo-Finnigan Neptune MC-ICP-MS and instrumental parameters for isotope ratio analysis, Table S2: Pb stable isotope ratios in reference material SRM 981 (NIST).

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