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LEAD IN FISHING TACKLE AND AMMUNITION (PART 3)

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1. INTRODUCTION

1.1 Background

The European Chemicals Agency (ECHA) is seeking scientific evidence for the case made by the Fédération Internationale de Tir aux Armes Sportives de Chasse (FITASC, 2020) that the use of steel gunshot on shooting ranges (as an alternative to lead shot) will mobilise lead and other heavy metals, thereby potentially increasing the availability of lead for uptake and toxicity to terrestrial and aquatic organisms. The case by FITASC was made in response to a public consultation by ECHA on the use of lead and steel shot. ECHA invited Ramboll under the Framework Contract FWC-355 to review the statement (below) made by FITASC by reviewing published information on the fate of lead and steel shot in soils. This claim will be assessed for its scientific and technical robustness with specific attention given to:

1) The statement made by FITASC in its response to ECHA's public consultation is as follows:

   "shooting steel shot on soils containing lead shot will acidify the soil at the site, accelerate lead corrosion and promote metal transport that will facilitate the migration of lead, antimony and other heavy metals from the contaminated site and deposit them in solution further downstream. Because they are more mobile, heavy metals will also migrate more easily to the water table. Furthermore, commercial steel shot generates manganese and nickel as additional undesirable pollutants. The presence of manganese in particular is known to amplify the toxic effects of existing lead pollution."

2) The key parts of FITASC's submission to ECHA include the sections 'behaviour of steel shot on the ground' (page 28); 'sporting steel shot over sporting lead shot: major environmental hazards' (page 30); and 'conclusions: lead, steel and soil' (page 75).

1.2 Project Aim

Ramboll reviewed published literature on the fate of lead and steel shot at shooting ranges to determine whether the statement made by FITASC is scientifically defensible. The statement was assessed for its scientific and technical robustness with specific attention given to the following questions posed by ECHA in its request to Ramboll:

1) Is there available field evidence that steel shot acidifies soil and accelerates lead corrosion at shooting ranges?
2) Review the theoretical evidence that could support or refute the claims, specifically in relation to understanding of the fate and behaviour of metals (including Fe, Pb, Ni, As and Mn) in soils under different physico-chemical conditions, with particular emphasis on how speciation affects fate and behaviour in the environment; and
3) What is the relative expected contribution of iron from steel shot (under reasonably foreseeable conditions of use) to soil acidification from all relevant sources that may contribute to acidify soil (including rain, microorganisms, metabolism, etc)?

The report is structured to highlight the specific claims provided in the FITASC report. The section 2, the behaviour of steel shot in surface soil is considered relative to a typical steel shot composition, as well as how differences in composition may affect environmental fate and toxicity. In section 3 the existing environmental condition of shooting ranges is outlined, and evidence provided for anticipated changes to lead contaminated soil chemistry in the event of the replacement of lead shot with steel equivalents following regulatory restriction. Brief context has been provided, where relevant, and the assessment of the evidence provided by FITASC

(Appendix 1) is supplemented by both theoretical modelled metal speciation behaviour, as well as specific field evidence (in regions with longstanding lead bans) and peer-reviewed scientific literature on the topic.

2. BEHAVIOUR OF STEEL SHOT IN SOILS

This section of the report addresses the statements made on page 28 of the FITASC report (FITASC, 2020), as follows:

- In air, steel corrodes faster than lead;
- Steel corrosion products can migrate through soils, which may have a localised impact on water quality; and
- The environmental toxicity of steel shot is driven not by iron itself, but by metal coatings (such as copper and zinc) added by shot manufacturers to prevent corrosion.

2.1 Typical steel shot composition

For the purposes of this report, a typical steel shot composition is presented in Table 1. The steel shot may be typically low in carbon content (<0.1%), but also contain manganese (<0.5%) and lesser amounts of phosphorous and sulphur. If steel shot comprises scrap metal, then shot may contain metals such as copper, nickel, chromium and molybdenum in lesser amounts (Mann et al, 1994). While it is accepted that like lead, the ultimate composition of steel shot may vary depending on the quality of the metal stock, the composition discussed within this report is assumed to be the typical worst case, using the highest composition of elements reported in the literature and by stakeholders. In addition, some steel shot is coated to reduce corrosion, either with oils (Mann et al, 1994) or other metals Fäth et al (2018). As anti-corrosion coatings can vary widely by manufacturer this report considers the typical composition to be that of uncoated shot (Table 1) and presents the implications of coatings separately in section 2.3.

Table 1 Typical composition of steel shot (provided by ECHA)

Element	**Composition (% w/w)**	
	Lower	**Upper**
Fe	98	99
C	0.85	1.2
Mn	0.6	1.2
Si	0.4	1.2
S	0	0.05
P	0	0.05

2.2 Steel shot in surface soil

The FITASC report (2020) states that the corrosion rate of steel shot will be faster than lead shot, stating that iron can be “*five times to thirty times higher than that of lead.*” The lower figure is taken from an unreferenced “fact sheet” and could not be verified, and the higher figure is taken from a presentation by the International Shooting Sport Federation (ISSF), which references 10-year atmospheric corrosion studies in an urban environment (Uhlig and Revie, 1989), which may not be environmentally relevant to shooting ranges as it does not consider natural water and soil process which can be highly variable. While lead, on average, corrodes more slowly than does steel, in poorly aerated soils or soils high in organic acids, the corrosion rate may be four to six times higher than average rates (Uhlig and Revie, 2008). According to Uhlig and Revie (2008) the factors that control corrosivity of a given soil are porosity (aeration), electrical conductivity, dissolved salts, including depolarisers or inhibitors, moisture and pH. Unlike in air, the manufacturing process or composition of steel has little effect on corrosion rates in natural waters and soils. A possible exception to this may be in acidic environments, when steel containing manganese and small amounts of sulphur, exhibits decreased acid corrosion.

2.2.1 Transformation of steel shot in soil

The main component of steel shot is iron (Fe >98%). Transformation of steel shot is described below. For reference, this is a similar process to the one for lead described by FITASC in its report (although FITASC then departed from this explanation when describing steel shot, *cf.* page 77 of the FITASC report (2020):

1) At the soil surface, the steel shot reacts with oxygen (atmospheric or dissolved in water) and becomes covered with iron oxide coating. The chemical stability of metallic iron and the low solubility of its oxides means that there is negligible impact on the environment when exposed to air. However in surface soil, shot is in greater contact with humidity, rainwater and soil particles, therefore, the iron oxide coating may dissolve into soil solution depending on the timescale and environmental conditions (pH, moisture, ionic concentration and composition of the soil solution, etc);
2) Under the effects of environmental factors such as the acidity of acid rain and soil porewater, and reactions with carbon dioxide and humic acids, the oxide coating begins to dissolve with ionic iron species released into the soil;
3) The surface of the shot is again "encapsulated" by a coating of iron compounds (hydroxide, carbonate, sulphate); and
4) The “encapsulated condition” persists only if the iron oxide coating is in chemical equilibrium with the surrounding environmental conditions. However, natural or anthropogenic factors (acidity, carbon dioxide content or humic acid concentration) promote the dissolution of iron oxides: the gangue dissolves again, releasing more ionic iron into the soil, which may adsorb onto soil particles or leach to waters (depending on soil type and conditions), and create the conditions for further oxidation of the metallic iron.

In this report, the corrosion differences of the oxide coatings of lead or steel shot are not investigated. However, it may be stated that in general, iron is lower than lead in the galvanic series where the corrosion of steel shot (of poor quality) could in theory be higher than that of lead shot. For the same reason, iron is not expected to enhance galvanic corrosion. In contrast to the FITASC report, Ramboll considers that the oxidation of metals on the shot surfaces is attributable to oxygen dissolved in water, not atmospheric oxygen; with particular reference to soils, such oxidation would be primarily attributable to moisture and resultant dissolved oxygen.

2.2.2 Fate and behaviour of metals under different physico-chemical conditions in soil

2.2.2.1 Speciation

Speciation is known to affect the environmental fate of metals. In the aquatic environment, the speciation of iron, lead, nickel, arsenic, manganese and antimony by thermodynamic modelling (Takeno et al, 2005) is generally understood as Eh-pH diagrams (Figure 1). From the diagrams it can be observed that in oxic conditions iron (Fe) is precipitated, whereas lead (Pb) and nickel (Ni) exist as cationic species. Manganese (Mn) exists as cationic Mn^{2+} but precipitates at high pH. Arsenic (As) is prevalent as oxyanionic species and antimony (Sb) as oxide species.

It is noteworthy, that the diagrams represent speciation of only one element in a water solution. Speciation in soils, however, is not as simple. The ionic and elemental compositions can be rather complex and is further influenced by soil sorption/precipitation reactions. Particularly the soil chemistry of antimony is rather poorly understood. Also, not all illustrated redox and pH conditions in the diagrams are found in soils.

The range for pH in soil is generally considered to be approximately 4 to 9. In extreme conditions, i.e. in acidic sulphate soils, the pH can be very low (pH <3) or in sodic soils it can be very high (pH >10) (Husson, 2013).

In soils, the redox range (Eh) can vary from -300 to +900 mV. Depending on redox conditions, soils can be classified as follows:

- aerated soils +400 mV (or 300 mV);
- moderately reduced 100-400 mV (or 300 mV);
- reduced 100 to -100 mV; and
- highly reduced soils -100 to -300 mV.

At firing ranges the conditions in surface soil are considered oxic (without waterlogged conditions) where iron (potentially dissolved from steel) is expected to accumulate in surface soils. Although lead is reported to be more mobile in reduced soil conditions (Antić-Mladenović, 2017), these conditions are not expected at firing ranges and the speciation chemistry of lead and iron under reduced condition is not considered in detail in this report. It is noted that wetlands were excluded from the scope of this study as wetlands were considered by ECHA in a previous report to the European Commission.

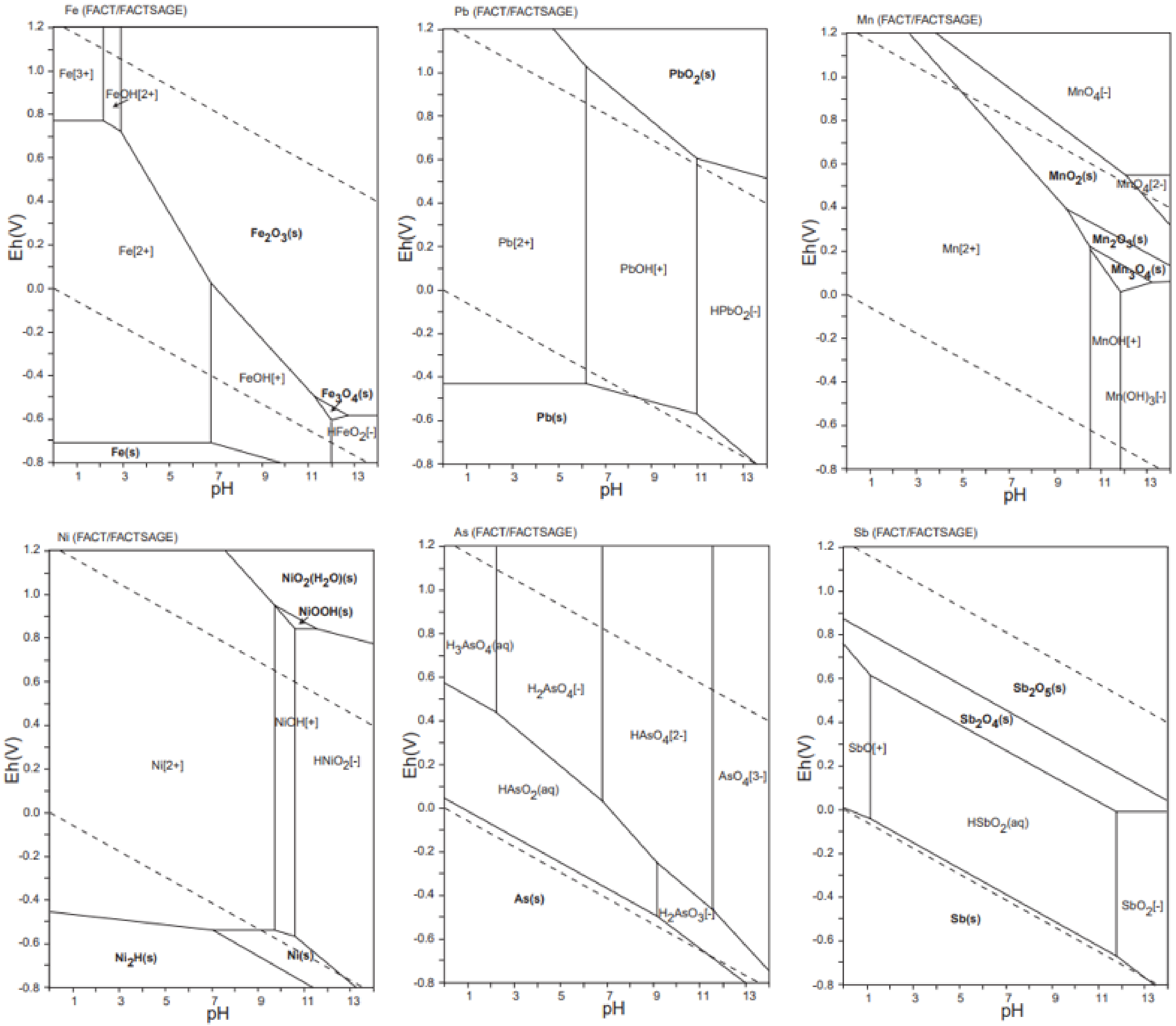


Figure 1. Eh-pH speciation diagrams of Fe, Pb, Mn, Ni, As and Sb (Takeno, 2005. FACTSAGE database)

2.2.2.2 Environmental fate

The prevalent species of iron, lead, manganese, nickel and arsenic, and their leaching risk from soil to groundwater or surrounding watercourses is presented in Table 2. The leaching risk was assessed depending on the species sorption tendency to soil. The sorption behaviour of metal species relies on the basics of soil chemistry (e.g. Bohn et al, 2005), speciation modelling (Takeno, 2005) and literature references for soil (Lindsay and Schwab, 1982). Basically, all elements exist as species that are retained by most soils. Therefore, leaching risk is not estimated to be high for any of the species excluding Fe^{3+}. For Fe^{3+} leaching risk is high because the environmental conditions where this species is found are extremely acidic, promoting dissolution of all metals in soil.

In typical soil conditions, iron is considered poorly soluble due to the formation of (hydr)oxide precipitates. The soil iron (hydr)oxides act as an important adsorbent for metal-OH^+ cations and oxyanionic species. Soluble species mainly exist in rather reduced conditions, as soluble organic species or in highly acidic conditions not typical in most soils.

In acidic conditions, the environmental fate of dissolved Pb^{2+}, $Ni^{2+}$and Mn^{2+} depend on their sorption onto soil cation exchange sites and, in particular for lead, on their retention to organic complexes. In non-acidic conditions the mobility of lead is further reduced because of the adsorption of $Pb(OH)^+$ species onto soil iron or aluminium (hydr)oxide surfaces. Also, precipitation of manganese occurs at higher pH. Nickel is more soluble than lead as it does not form hydroxide species, and has a lower tendency to be retained by organic matter.

Arsenic in soils exist as oxyanionic arsenate species. Oxyanionic species are adsorbed onto soil iron- and aluminium (hydr)oxides surfaces by ligand exchange mechanism. The sorption tendency of these oxyanionic species tend to increase with lower soil pH – the opposite to iron, lead, nickel and manganese.

The sorption of metal species to soil depend on soil conditions. However, the soil conditions influence not only the sorption properties, but also speciation itself. Based on the principles of soil chemistry (e.g. Bohn et al, 2005) soil properties are known to have following effects:

- *Soil minerals*: In general, the electrostatic sorption capacity (i.e. cationic exchange capacity, CEC) is higher in clay soils with fine mineral texture and lower in coarse mineral soil. The sorption capacity for metal hydroxide cations and oxyanionic species increases with higher soil iron/aluminium (hydr)oxide content.

- *Organic matter*: soils rich in organic matter have a high sorption capacity towards cationic heavy metals species (high CEC, complex or chelate formation). On the other hand, the formation of soluble organic metal species enables the solubility of metals that would otherwise exist as precipitates.

- *pH*: soil pH dictates the chemical speciation of metals and their sorption tendency. In general, the solubility of metals usually increases in acidic conditions and decreases at higher pH (because at higher pH many metals tend to precipitate). However, it is noteworthy that, in *highly* alkaline soil conditions, some metals tend to dissolve or hydrolyse into anionic species (e.g. nickel, lead, manganese) that are poorly retained by soil. Adsorption to soil organic matter increases with increasing pH.

- *Redox:* soil redox conditions dictate the speciation of redox-sensitive metals and semimetals. Soil redox condition can also impact the soil sorption capacity. In reducing conditions Fe(III) can be reduced to Fe(II). The ferrous iron Fe(II) has a lower tendency to form precipitates (absorbent for metals like lead).

Table 2. Leaching risk of Fe, Pb, Mn, Ni and As species from soil to water bodies. Leaching risk was estimated according to sorption tendency in respect to soil condition where species are found. Note that the toxicity of metals species is not assessed, only their mobility.

Element	Prevalent species	Soil conditions	Main sorption mechanisms	Leaching risk[1] (low / moderate / high)
Iron	Fe^{3+}	oxic, extremely acid pH<2	electrostatic sorption or complex/chelate formation. In practice these acidic conditions cause dissolution of most metals in soil	high (in extremely acidic conditions)
	Fe^{2+}	reduced, slightly acidic	electrostatic sorption or complex/chelate formation	moderate/low (high in acidic conditions)
	$Fe(OH)_2^+$	oxic acidic, moderately reducing non-acidic	Precipitation onto soil particles (as metal-OH^+ species)	low
	$Fe(OH)_3$	oxic and moderately reducing non-acidic	Precipitation as iron hydroxide	low
Lead	Pb^{2+}	acidic or slightly acidic	electrostatic sorption or complex/chelate formation	Moderate (high in extremely acid conditions)
	$Pb(OH)^+$	non-acid	Precipitation onto soil particles (as metal-OH^+ species)	low
Manganese	Mn^{2+}	reducing, moderately reducing, acid oxic	electrostatic sorption	moderate (high in extremely acid conditions)
	$Mn(IV)O_2$	oxic, non-acidic	Precipitation	low
Nickel	Ni^{2+}	reducing, moderately reducing, oxic,	electrostatic sorption or complex/chelate formation	moderate (high in extremely acid conditions)

		acidic, non-acidic		
Arsenic	$HAsO_4^{2-}$	acidic or slightly acidic	sorption by ligand exchange	moderate
	$H_2AsO_2^-$	non-acid	sorption by ligand exchange	moderate

Footnotes

[1]low= forms precipitates in all soil types

moderate=retained by cation exchange or complex/chelate formation (sorption depends highly on soil clay and organic matter content)

high=poorly retained in the prevailing conditions

2.3 Comparative aquatic toxicity of steel shot

Although not explicitly described in this report, the conceptual model under consideration is the fate and potential leaching of lead or iron (and associated metals) to the aquatic environment (either as groundwater or surface water bodies). As such, evidence provided by Fäth et al (2018) describes lead-free shot alternatives may pose an unanticipated risk to aquatic ecosystems. Although the test system focused on a simple aqueous exposure without consideration to abiotic environmental factors (e.g. pH, water chemistry, soil type), the authors found unanticipated leaching of non-target metals from steel shot, which was attributed to coatings (zinc) or alloys (manganese). In the case of steel shot containing manganese, concentrations found in the test system were approximately 300 times less than the reported 48-hour EC_{50} for *Daphnia magna* and induced no significant difference (relative to controls) in toxicity over the 22 day exposure period tested. While this study indicates that minor elements from lead-free shot may leach out into the aquatic environment, in the case of steel, toxic effects are driven by manufacturing of shot with coatings such as zinc, rather than intrinsic properties of steel shot themselves. Future regulatory consideration may need to be given to the manufacturing and coating of steel shot, although this is beyond the scope of this report.

A study with *Daphnia magna* found that the dissolved form of metals typically associated with lead and steel shot (primary metals, plus alloys and coating components) determined the following order of aquatic toxicity, based on a 48-hour EC_{50} (Khangarot and Ray, 1989):

$$Cu > Zn > Pb > Cr > As > Ni > Fe > Mn > Sn > W > Sb$$

Compared to lead (48h EC_{50} = 17 µmol/L), iron was found to be around 7 to 8 times less toxic (48h EC_{50} = 129 µmol/L) on a dissolved metal basis in an aquatic test system. In addition, manganese (a common alloy in steel shot; Table 1) was found to be around 8 to 9 times less toxic than lead, and similarly toxic as iron (48h EC_{50} = 151 µmol/L).

3. HAZARD PREDICTIONS OF INCREASING USE OF STEEL SHOT

This section of the report addresses the claims made on page 30 of the FITASC report (FITASC, 2020), which may be summarised as follows:

- In the presence of steel, the pollution risk of lead increases;
- Shooting steel shot on soils containing lead shot will acidify the soil at the site, accelerate lead corrosion and promote metal transport; and
- Any change in ammunition manufacturing materials is very likely to have a major negative impact on soil chemistry.

3.1 Current baselines

Due to the historical use of lead shot, shooting ranges currently represent a highly localised, but contaminated soil environment. Section 3 investigates the current baselines in the “worst case” ranges, then considers both the theoretical and field evidence of the potential for steel shot to increase metal contamination, in particular, the potential for increased lead hazard (availability) in soils and water bodies. Finally, in contrast to the FITASC report, Ramboll considers the literature describing the use of ferrous remediation strategies, including how replacement of lead shot with steel may present future remediation opportunities.

3.1.1 Brief overview of shooting ranges, geographical distribution and existing tonnages

There are currently around 4000 permanent clay shooting ranges distributed across 30 countries Europe (Table 3). According to industry stakeholder declarations provided by ECHA, the estimated total lead shot used annually at these ranges amounts to approximately 35,000 tons per year (some ranges may use >40 tons per year, others may use <1 ton per year).

Table 3. Clay target shooting range distribution throughout Europe

Countries	Number of clay target shooting ranges	Contribution to total range number (%)
Czech Rep	550	13.80
UK	428	10.74
France	400	10.04
Sweden*	400	10.04
Finland	380	9.53
Norway*	351	8.81
Italy	350	8.78
Hungary	200	5.02
Spain	200	5.02
Germany	150	3.76
Slovakia	120	3.01
Russia	79	1.98
Austria	63	1.58

Portugal	56	1.40
Estonia	38	0.95
Ireland	35	0.88
Greece	26	0.65
Switzerland	24	0.60
Netherlands*	23	0.58
Denmark*	20	0.50
Iceland	20	0.50
Lithuania	18	0.45
Belgium	13	0.33
Cyprus	9	0.23
Slovenia	9	0.23
Latvia	6	0.15
Malta	6	0.15
Poland	5	0.13
Romania	4	0.10
Belarus	3	0.08
Total	3986	100

Footnote: *ECHA has already consulted 4 MS (Denmark, The Netherland, Sweden and Norway) where alternatives to lead shot are used in shotgun ranges. They had no information on this or had not investigated this issue in detail in the ranges where steel shot is used.

3.1.2 Existing estimates of lead in soil

Primary constituents of lead shot are lead and antimony (Mann et al, 1994). The amount of antimony can vary from 0.5% to 6.5% depending on size and desired hardness of the pellet. Arsenic (approximately 0.1% to 0.2%) may be added to the alloy to facilitate sphere formation, tin (approximately 0.1%) may also be an intentional inclusion in the pellet alloy. Further stakeholder engagement conducted by ECHA found metal concentrations across two grades of lead shot, which is shown in Table 4.

Table 4. Typical composition of different grades of lead shot (provided by ECHA)

		Composition (% w/w)	
Shot type	**Element**	**Lower**	**Upper**
Lead shot, high grade	Pb	99.9	99.9
	Sb, Sn, Cu, Al, Zn, Fe, Cr, Se, Mg, Mn, Na, Ba, Sr, In, Ga, Te, Ag, Bi, Au, Ca, Pt	0	0.2
	Ni, Co, Tl	0	0.1
	As, Cd, Hg	0	0.025
Lead shot, general grade	Pb	95	95
	Sb, Sn	0	15
	S, O, Cu, Al, Zn, Fe, Cr, Mg, Mn, Na, Ba, Sr, In, Ga, Te, Ca, Si, K	0	10
	Se	0	5

	Bi	0	2
	Co, Ni	0	1
	Pt, Ag, Au	0	0.25
	As	0	0.2
	Tl	0	0.1
	Cd, Hg	0	0.025

Reported lead concentration in shooting range soils vary depending on the amount of yearly shooting, years of operation of shooting ranges, as well as the grades of lead shot used at the range (Table 4). Due to the irregular distribution of shot at shooting ranges, different sampling strategies can cause a high variability in reported concentrations of lead and other metals (Craig et al, 2002). In field study conducted at shooting ranges in Finland (Tolvanen et al, 2017) the lead concentration in peatland and sandy-moraine was 17,000 mg/kg and 19,000 mg/kg respectively. In the case of antimony, concentrations were 45 mg/kg in peatland and 790 mg/kg in sandy moraine samples. In a comprehensive review of 35 years of shooting range studies, Dinake et al (2019) found that worst case lead concentrations in European shooting range soils can vary between 10,000 mg/kg and 100,000 mg/kg. Given the estimated concentrations of other metals found in lead shot (Table 4), it is clear that high levels of soil contamination (from both lead and other associated metals) can be expected at currently operating shooting ranges.

3.1.3 Existing major environmental hazards of lead in shooting ranges

Years of daily shooting have caused lead shot to accumulate on soil surface. As the surface layer capacity is reached, lead will start to migrate towards the lower soil layers. The dynamic process of lead migration through these soil layers is driven soil properties as stated in section 2.2.2.2. Some example soil types are considered below (Tarvainen et al, 2011).

If the shooting range is situated in peatland, soluble lead will be somewhat retained within the peat, but a proportion of lead will exist in mobile soluble form, driven by the low pH (<4-5) found in such soils. Soluble mobile lead species can migrate through the peat into surface water bodies and can remain for decades or hundreds of years depending on the amount of lead and environmental conditions. A wetland environment downstream from these shooting areas may act as sink (receptor) or pathway for lead. It is noted that wetlands are excluded from this project scope.

If the shooting ground is situated in sandy soils, the humus layer may retain lead for decades if the soil surface remains undisturbed. However, as described previously, when the capacity of the surface layer is filled, the surplus lead will migrate into lower layers of soil. The ability for lead to reach the groundwater in these soils is driven by factors such as pH, organic matter, cation exchange capacity (CEC) and oxide content that can vary considerably (Tarvainen et al, 2011). Lead may affect the groundwater quality and potentially limit future uses as a drinking water resource, for example.

3.2 Anticipated impact of steel shot overlying lead shot

Theoretical modelling of predicted impacts from the addition of steel shot to lead shot-contaminated soils is presented in this section, in addition to a discussion of the potential for iron to increase soil acidification, and the outcome of a review of field studies of the environmental fate of steel and lead shot.

3.2.1 Modelled speciation

The ionic speciation of soluble metals was assessed by Ramboll using a simple VisualMinteq model in hypothetical “worst case” conditions at pH 4 and 7. Calculations and justification of the parameters are presented in Appendix 2. Input data were drawn from published literature. For lead, soil concentrations were represented by data collected from studies on shooting ranges conducted over 35 years (Dinake et al, 2019), which were used to predict a comparable concentration of replacement steel shot over a similar time period:

- Highest soil contamination by Pb 100 000 mg/kg (Dinake et al, 2019)
- Estimated steel deposits in soil 68,293 mg/kg, with total concentrations of:
    - Fe (98.8 % w/w) 67,473 mg/kg (ECHA, upper limit value in shot)
    - Mn (1.2 %w/w) 820 mg/kg (ECHA, upper limit value in shot)
    - Ni (1.2 %w/w) 820 mg/kg (hypothetical value)
- Soil background values:
    - Fe 100,000
    - Mn 2,000 mg/kg
- Estimation of the maximum solution concentration based on Kd-values
    - Pb 50 mg/l
    - Fe 34 mg/l
    - Mn 1.6 mg/l
    - Ni 1.5 mg/l
- DOC (dissolved organic carbon) 0 (no organic matter) and 50 mg/l (high organic matter content).

Results and conclusions of the speciation modelling

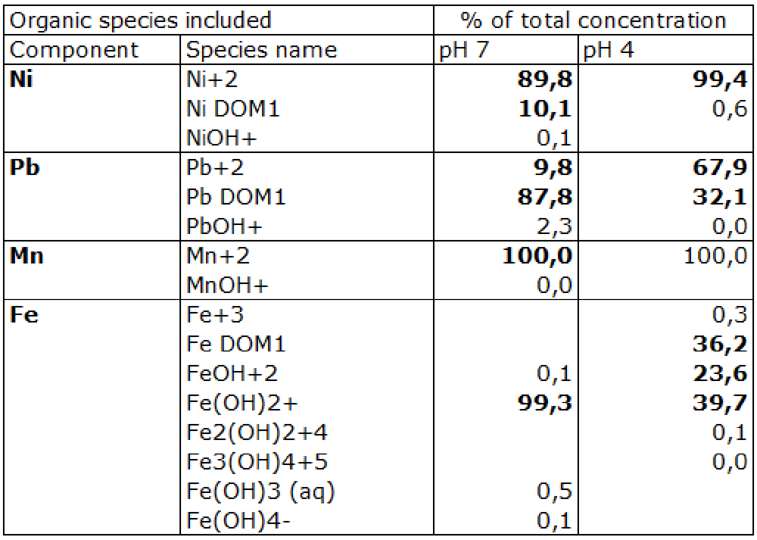
Distribution of chemical species in the VisualMinteq model are demonstrated in Table 5 and Table 6. In summary, the metals that potentially dissolve from steel shots are not considered to enhance the mobility of lead. Instead, according to the speciation modelling, iron is likely to reduce the mobility of lead when iron exists as species that are easily precipitated into soil. The iron (hydr)oxides precipitates are known to have a high affinity towards lead sorption (e.g. Gustafsson et al, 2011), particularly at non-acidic conditions.

In acidic conditions (pH 4) with the presence of organic matter, a proportion of the iron exist as organic species. This indicates that iron and lead species could compete for the same organic sorption sites in acidic soils, which could potentially increase mobility of dissolved lead. However, even in acidic conditions, with high amounts of organic matter, most of the iron exists as inorganic species that have a high sorption capacity towards lead. So, as an overall impact, the iron from steel shot would still be expected to reduce the mobility of lead. Also, the affinity of lead to organic complex formation is greater than that of iron. Therefore, the amount soluble iron should be very high in respect to lead.

In the speciation model, practically all nickel and manganese existed as cationic species (Ni^{2+} and Mn^{2+}). In theory, dissolved Mn^{2+} or Ni^{2+} from steel could increase the soil solutions EC (conductivity). And with higher EC (resulting from metals lower in the galvanic series than lead) corrosion of lead shot could be enhanced. However, the literature relating to field soils and experimental studies does not provide evidence that this occurs at shooting ranges or that the amount potentially released from steel shot would have any significance at firing ranges. A summary of the speciation model results is provided below:

- No soluble species with the combination of Pb and Fe/Mn/Ni were detected with or without organic matter
    - metals from steel do not increase the Pb solubility by forming highly soluble multimetal Pb species
- At pH 7 the predominant soluble species is $Fe(OH)^{2+}$, which precipitates as (hydr)oxide in soil
- At pH 4 the predominant soluble species are $Fe(OH)^{2+}$ (24 %) and $Fe(OH)^{2+}$ (40 %) or organic species (36 %) Fe DOM1
    - inorganic species precipitate as (hydr)oxide in soil
    - organic species may remain soluble
- At pH 7 soluble Pb exists mainly as organic species (88 %) of (PbDOM1) and Pb^{2+} (10 %)
    - Pb has a high affinity towards retention by organic matter
    - organic species may remain soluble
- At pH 4 soluble Pb exists mainly as inorganic Pb^{2+} (68 %) or as soluble organic species (32 %) (PbDOM1)
- At pH 4 and 7 soluble Mn exists as inorganic species only; no soluble organic species.

Table 5. Distribution of soluble species (VisualMinteg model) in a hypothetical scenario of Pb contaminated soil with high soluble organic matter content amended with high amount of steel shots



Organic species included		% of total concentration	
Component	Species name	pH 7	pH 4
Ni	Ni+2	**89,8**	**99,4**
	Ni DOM1	**10,1**	0,6
	NiOH+	0,1	
Pb	Pb+2	**9,8**	**67,9**
	Pb DOM1	**87,8**	**32,1**
	PbOH+	2,3	0,0
Mn	Mn+2	**100,0**	100,0
	MnOH+	0,0	
Fe	Fe+3		0,3
	Fe DOM1		**36,2**
	FeOH+2	0,1	**23,6**
	Fe(OH)2+	**99,3**	**39,7**
	Fe2(OH)2+4		0,1
	Fe3(OH)4+5		0,0
	Fe(OH)3 (aq)	0,5	
	Fe(OH)4-	0,1	

Table 6. Distribution of soluble species (VisualMinteg model) in a hypothetical scenario of Pb contaminated soil with no organic matter content amended with high amount of steel shots

No organic species		% of total concentration	
Component	Species name	pH 7	pH 4
Ni	Ni+2	**99,9**	**100,0**
	NiOH+	0,1	
Pb	Pb+2	**81,1**	**100,0**
	PbOH+	**18,6**	0,0
	Pb(OH)2 (aq)	0,1	
	Pb2OH+3	0,1	
	Pb3(OH)4+2	0,1	
	Pb4(OH)4+4	0,0	
Mn	Mn+2	**100,0**	**100,0**
	MnOH+	0,0	
Fe	Fe+3		0,5
	FeOH+2	0,1	**37,4**
	Fe(OH)2+	**99,3**	**61,7**
	Fe2(OH)2+4		0,3
	Fe3(OH)4+5		0,1
	Fe(OH)3 (aq)	0,5	
	Fe(OH)4-	0,1	

3.2.2 Acidification mechanisms in soil

Soil acidity is known to promote steel corrosion. However, to our knowledge, there is no indication that steel itself would promote soil acidification. In steel shot, iron exists in the metallic form. With respect to time scale, a proportion of iron oxidation in steel shot is expected.

In reduced soil conditions Fe^0 is oxidised to Fe^{2+}. In surface soil, where shots are deposited, the redox conditions are usually oxic: Fe^0 oxidises into ferric iron, Fe^{3+}. In steel, metallic iron exists in its elemental oxidation state (Fe^0). Because of corrosion the Fe in steel shots oxidises to form hydroxides through a series of reactions:

1. $4\ Fe^0 + 2\ O_2 + 8\ H^+ \rightarrow 4\ Fe^{2+} + 4\ H_2O$
2. $4\ Fe^{2+} + 8\ OH^- \rightarrow 4\ Fe(OH)_2$ in *reduced* conditions
3. $4\ Fe^{2+} + 4\ H^+ + O_2 \rightarrow 4\ Fe^{3+} + 2\ H_2O$
4. $4\ Fe^{3+} + 12\ OH^- \rightarrow 4\ Fe(OH)_3$

Overall reaction: $Fe^0 + 3\ O_2 + 6\ H_2O \rightarrow 4\ Fe(OH)_3$

According to these step-wise reactions:
- oxidation of Fe increases pH (reactions 1 and 3: consumption of acidifying H^+ in the reactions); and
- hydrolysis of Fe^{2+}or Fe^{3+} lowers pH (reactions 2 and 4: consumption of alkaline OH^- in the reactions)

The actual overall acidifying/alkalising impact depends on the degree of Fe hydrolysis:
  - no effect with hydrolysis of Fe^{2+} to $Fe(OH)_2$ or Fe^{3+} to $Fe(OH)_3$.
  - with lower degree of hydrolysis pH expected to *increase*: $Fe^0 + 3\ O_2 + 6\ H_2O \rightarrow 4\ Fe(OH)_2^+ + 4\ OH^-$

The degree of oxidation and hydrolysis depend on soil conditions, such as pH, redox state, temperature, and moisture content; however, based on the step-wise reactions of iron oxidation and hydrolysis, iron is not expected to have acidifying effects. Thus, the mobility of Pb is not expected to be enhanced due to the corrosion of Fe in steel shoots.

In the FITASC report (2020) the claim that iron released from steel shot contributes to acidification of soils is based on a single consultancy report (not peer reviewed) by Hurley (2004). The author performed a leaching test with carbonated water (pH 6-6.5) and two shot types: steel and lead shots. The pH of the solution with both steel and lead shots was initially reported to increase, followed by a decrease. Low pH was linked to soluble iron. However, only the impact of hydrolysis was considered, not the oxidation reactions of iron.

The changes in pH in Hurley (2004) do not contradict the theoretical chemistry of the series of reactions for iron, as stated above. The overall endpoint of the reactions depends on the starting oxidation state of the iron, and should be used to determine the likely hazard of steel (iron) and lead shot in soils. The oxidation of iron in steel can initially increase pH, but this increase is subsequently lowered by the hydrolysis reactions of Fe^{2+} or Fe^{3+}. The final pH in water solution was reported to be 5.1 (0.2 to0.7 units lower than initial pH). According to the chemical reactions of iron the reduction in pH does not originate from the overall reactions of Fe^0. However, if the iron in the steel shots used in the tests reported by FITASC had oxidised prior to the test, the acidifying impact in the aqueous solution may be possible, however at shooting ranges shots are fired before corrosion takes place. As for comparison to the reported acidic solution pH 5.1 by Hurley (2004), the pH of dissolved water in equilibrium with atmospheric CO_2 is 5.65. In soil, similar changes in the pH are not expected to occur because of soil buffering capacity. The buffering capacities vary in different soils, but this is not investigated in the Hurley (2004) report as to "*avoid possible complex interactions from clays and biomass sorption and soil-based electrolytes which would obscure the primary corrosion process.*"

In the same FITASC report, it was contended that lead corrosion was considered elevated because of the presence of steel shot. The corrosion rate of metals can be higher in solutions with increased salt concentrations. In water solution, the Fe species dissolved from steel shot may have increased the solution's electric conductivity (EC). However, in most soil types, iron is poorly soluble and therefore EC is not expected to increase.

In summary, the claims made by FITASC (2020) regarding iron driven soil acidification and subsequent mobilisation of lead are underpinned by a single study in water (Hurley, 2004), in which conditions in the soil compartment were not explicitly considered. Given the pH buffering capacity of soils and their ability to precipitate metal ions, Ramboll considers the specific claim of acidification made by FITASC (2020) to be unreliable.

In the broader context of natural soil acidification (such as microbial acidification in peatlands or the influence of acid rain), iron driven acidification is of relatively low significance. The overall impact from oxidation and hydrolysis reactions of Fe^0, the main component of steel shot, is not considered acidifying. In order to observe acid production from steel shot, the iron deposited into soil should initially exist as oxidised species (Fe^{2+} or Fe^{3+}). According to Mann et al (1994) steel shots are oiled to prevent rusting and the initial oxidation of Fe is not expected to occur. In theory, acid production is possible if part of the iron in steel shot is oxidised before being fired to shooting range (due to the hydrolysis of Fe^{2+} or Fe^{3+}). The significance of this acid formation compared to natural biological processes or acid rain in soil is not possible to reliably estimate within the information available in this project. In any case, the potential acid formation from hypothetical steel shot iron hydroxide coatings is not expected to significantly influence soil pH (because of soil buffering reactions) even if the proportion of oxidised Fe in steel shots could be determined.

3.2.3 Field evidence of steel and lead shot behaviour in soils

Shooting ranges with peat and sandy soils in Finland were studied by Tolvanen et al (2017). The ranges selected were both used for shooting for decades. In the peat land range, the shooting was started in 1976 and in the sandy soil range the shooting was started in 1968. The selected ranges have been influenced by long-term lead load.

In the study (Tolvanen et al, 2017) where steel shot (Saga®:n Eurotrap steel) were added to lead-contaminated peatland soil (pH 4) (Figure 2) and sandy moraine soil (pH 6) (Figure 3), no scientific evidence was found to support the fact that adding steel shot to lead soils would increase the lead solubility. In this study, control conditions were defined as lead contaminated shooting range soils without the addition of steel shot (referred as “No steel shots” in the graphs below).

Leach tests were made in liquid–solid ratio 10 (L/S10 ratio), mimicking 12 environmental freezing and melting cycles over a one-month period (23.1.2017 to 20.2.2017). Before the test cycles were carried out with the lead shooting range soils and steel shot, test samples (i.e. shot) were oxidised for 10 weeks. The amount of steel shot added to testing systems was considered equivalent to a small shooting range after approximately 20 years of shooting with steel shot. The 12 cycles are considered representative of 10 years in a northern European environment.

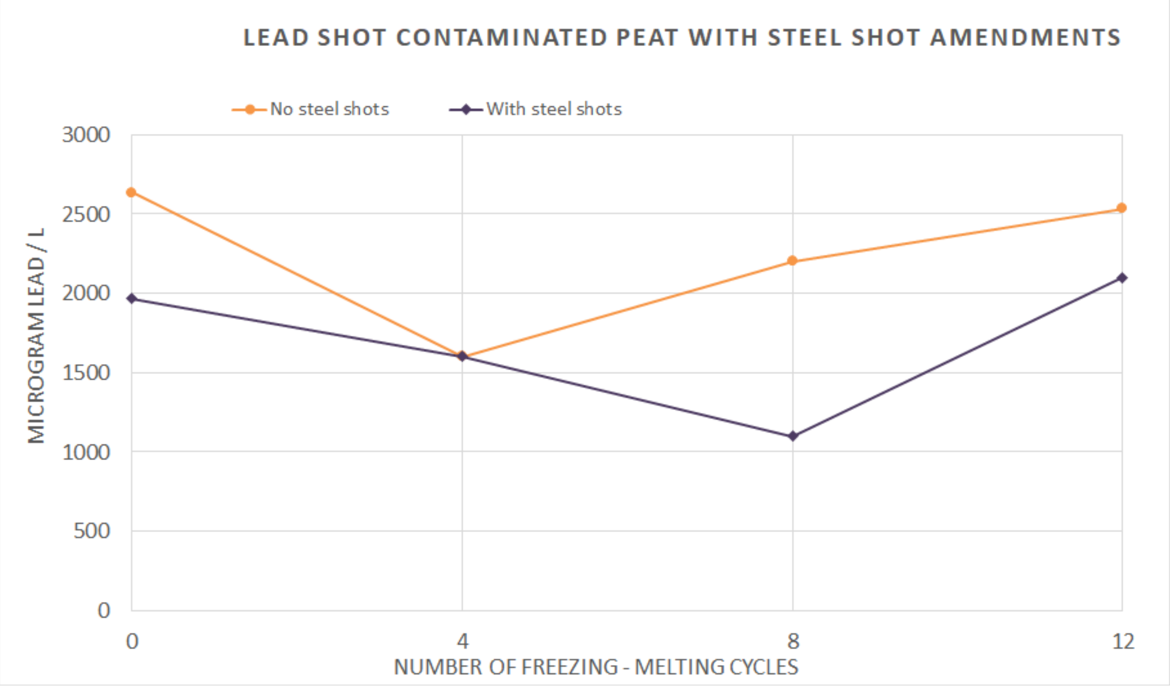


Figure 2. Soluble Pb (µg/L) in lead contaminated control soil (No steel shots) and lead contaminated soil with steel shots (With steel shots)

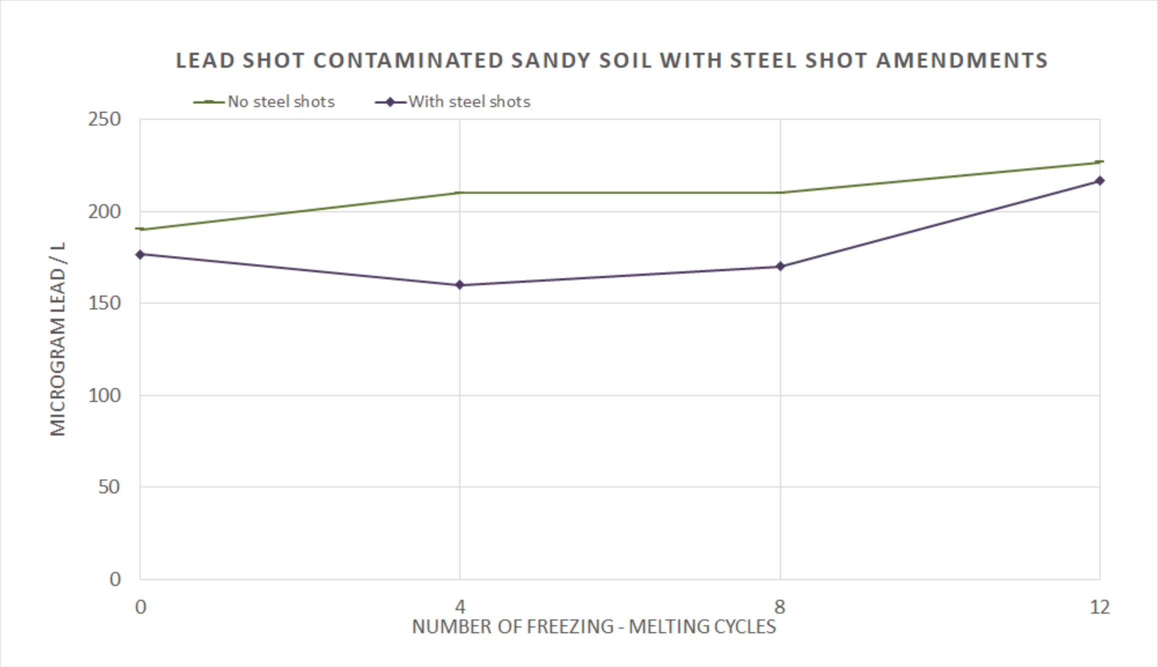


Figure 3. Soluble Pb (µg/L) in lead contaminated control sandy soil (No steel shots) and lead contaminated sandy soil with steel shots (With steel shots)

According to the field evidence in one month leaching test period (after 12 cycles) and in liquid-solid ratio 10, lead leaching was not elevated after steel shot amendments. The twelfth test cycle was statistically tested. One factor t-test did not show statistical difference ($p>0.05$) between the control and the steel shot amended soils.

In Figures 4 and 5 iron leaching in both soil types are presented. Iron leaching from steel shot amendment peat soil (With steel shots) exceeded the control soil (No steel shots) between the 8 and 12 cycles.

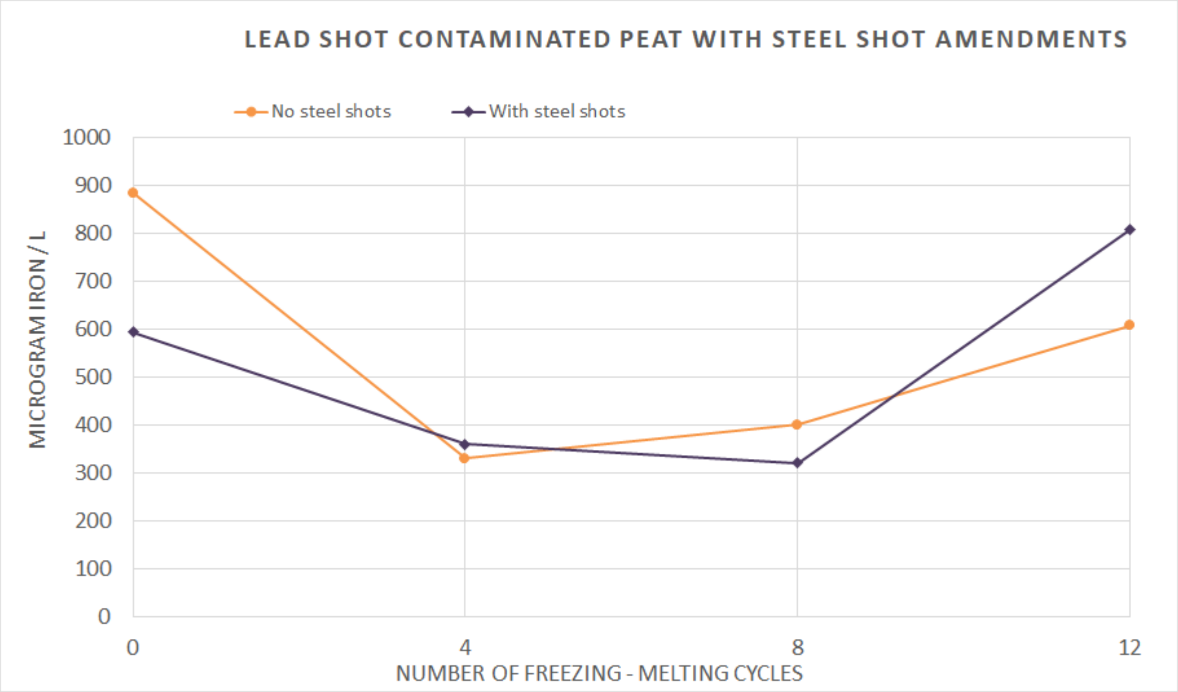


Figure 4. Soluble iron (µg/L) in lead contaminated control peat (No steel shots) and lead contaminated peat with steel shots (With steel shots)

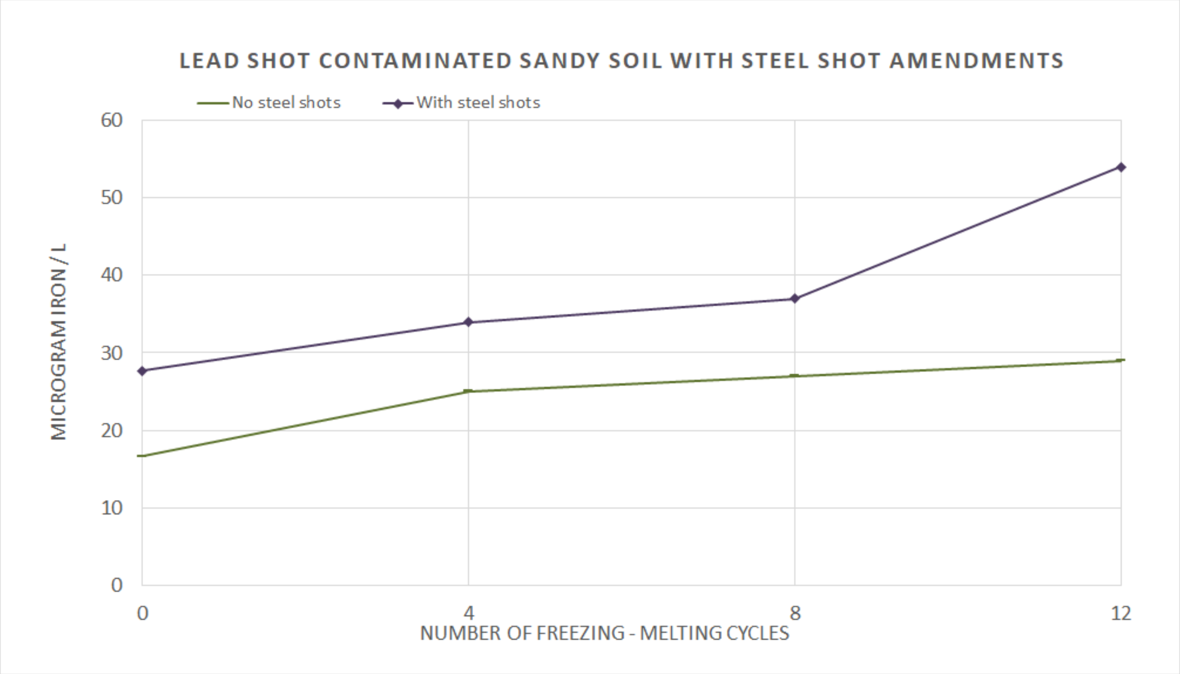


Figure 5. Soluble iron (µg/L) in lead contaminated control sandy soil (No steel shots) and lead contaminated sandy soil with steel shots (With steel shots).

According to the field evidence in one-month leaching test period (after 12 cycles) and in liquid-solid ratio 10, iron leaching appeared to be elevated after steel shot amendments. The twelfth test cycle was statistically tested. One factor t-test did not show statistical difference between the control and the steel shot added. For peat land the significance of t-test was $p=0.06$ and for sandy soil $p=0.08$.

Soil pH and EC values are presented in Tables 7 and 8 for peat and sandy soils, respectively. The pH or EC in soils amended with steel shot did not differ from that of soils without steel shot, neither in peat or sandy soil. The differences were statistically tested for the whole test period and for the 12-week freezing cycle ($p>0.05$). Although, after 12 weeks freezing cycles the solubility of iron appeared slightly higher in steel shot treated soil samples (Figure 4 and Figure 5) this was not reflected in the EC. It means that the solubility of iron was insignificant in respect to the overall EC in soil.

The tested soils represent two shooting range types that are very challenging considering the management of metal mobility. Peat is very acidic, and the soil sorption capacity of lead relies mainly on the amount and quality of soil organic matter. In sandy soil the amount of organic matter was low, only 0.64% total organic carbon and the mineral fraction was coarse (low in clay). Consequently, the sorption capacity of sandy soil is low.

Table 7. Soil pH and EC in lead shot contaminated peat with and without steel shot

	pH [-]		**EC [µS/cm]**	
Freezing cycle (weeks)	Lead shot contaminated peat	Lead shot contaminated peat with steel shot amendments	Lead shot contaminated peat	Lead shot contaminated peat with steel shot amendments
0	3.99	4.07	252.0	248.0
0	4.01	4.05	268.0	224.0
0	4.08	3.98	266.0	270.0
4	4.10	4.09	159.1	153.9
4	4.17	4.13	188.6	185.6
4	4.17	4.05	196.5	170.5
8	4.28	4.36	131.1	107.4
8	4.30	4.31	168.1	138.5
8	4.27	4.29	153.0	136.0
12	4.24	4.32	152.1	138.4
12	4.51	4.24	160.4	168.5
12	4.37	4.34	131.7	154.0

Table 8. Soil pH and EC in lead shot contaminated sandy soil with and without steel shot

	pH [-]		**EC [µS/cm]**	
Freezing cycle (weeks)	Lead shot contaminated sandy soil	Lead shot contaminated sandy soil with steel shot amendments	Lead shot contaminated sandy soil	Lead shot contaminated sandy soil with steel shot amendments
0	5.65	5.84	6.8	8.6
0	5.67	5.50	6.9	6.7
0	5.84	5.69	6.2	8.1
4	6.06	5.94	7.8	7.1
4	6.15	5.85	7.5	8.9

4	5.81	5.82	20.2	10.1
8	5.96	6.00	8.3	7.2
8	5.80	5.96	7.9	7.7
8	5.80	5.74	7.4	7.3
12	6.2	6.25	8.4	6.9
12	6.08	6.23	7.7	7.9
12	6.12	6.07	11.2	7.4

3.2.4 Field evidence of ferrous remediation strategies

Given the high concentration of lead and other metals currently found in shooting range soils (Dinake et al, 2019), the need to manage ranges to minimise adverse environmental impacts has been recognised and best management practices (BMPs) for managing lead have been developed (USEPA, 2001). The BMPs can be deployed to meet four general objectives:

1. Control and containment of lead bullets and bullet fragments;
2. Prevention of migration of lead through the soil profile and to surface-water bodies;
3. Removal and recycling of lead from the range; and
4. Documentation of activities and record keeping.

Achieving the second objective of BMP prevents lead migration by monitoring the soil, deploying soil amendments (to adjust characteristics such as pH) and using erosion controls to prevent the displacement of contaminated soil. Manipulating metal bioavailability with the addition of chemical amendments represents an effective mitigation strategy, which avoids the high costs associated with unsustainable traditional remediation alternatives (e.g. excavation, treatment and disposal) (Bolan et al, 2008; Martin and Ruby, 2004). In an ideal situation, chemical amendments are applied to the soil to induce specific reactions within the soil matrix to render the metal contaminant inert, without substantially altering soil properties. One common mechanism of co-precipitation of metals (including the oxyanions antimony and arsenic) uses iron and aluminium oxyhydroxides (Basta et al, 2005; Bolan et al, 2003). More generally, these reactions include specific adsorption to the mineral matrix, ion exchange, precipitation of sparingly soluble compounds, and complexation with soil organic matter and inorganic constituents, and can be achieved though several measures (Sanderson et al, 2012).

It is important to note that a large body of research exists for the use of ferrous chemical amendments, in the form of industrial by-products, as potential stabilisers of metal contaminants (Berti and Cunningham, 1997; Aboulroos et al, 2006; Bertocchi et al, 2006; Kumpiene et al, 2007; Spuller et al, 2007). Such by-products include fly ash, beringite, bauxite and birnessite, which contain not only iron, but also aluminium and manganese oxides, have been shown to be effective in stabilising lead and other metals through different mechanisms to varying degrees, depending on their chemical composition (Sanderson et al, 2012).

Other ferrous soil amendments include intentionally engineered products such as nanoparticles. Liu and Zhao (2007) prepared and tested a new class of stabilised iron phosphate nanoparticles that reduced lead leachability by 85 to 95% and bioaccessible lead by 31 to 47%. Similarly, a study by Ponder et al (2000) used zero valent iron nanoparticles to immobilise CrVI and PbII by reducing them to CrIII and Pb0, respectively. The zero valent nanoparticles achieved metal removal rates more than four times greater than commercial iron filings. Okkenhaug (2013) studies show that metallic iron adsorbs heavy metals when oxidised and creates binding sites in the form of iron oxyhydroxides. The process is known to be pH dependent (e.g. iron oxyhydroxides adsorbed lead only when lime was added) and pH did not decrease. In the soil many reactions are occurring simultaneously, with other metals and organic matter in competition for binding sites available with organic matter.

Ultimately the effectiveness of each of these amendments are modified by soil properties, such as pH, texture, clay content, organic matter, as well as naturally occurring iron and manganese oxides (Dayton et al, 2006). A clear understanding of metal reactions with soil components opens the door for managing contamination in situ, promoting the formation of stable forms of metal strongly bound to the soil matrix.

Although this report is not suggesting that steel shot will provide a ready-made remediation solution to existing lead contamination, there appears to be sufficient evidence that ferrous remediation strategies exist which may inform the potential integration of steel shot into broader BMPs in the future. Future research should focus on the possibility of not merely replacing lead shot with less toxic steel, but adding value to this regulatory decision by investigating the added potential advantages of incorporating steel shot into ferrous remediation strategies to actively manage historical contamination.

4. CONCLUSIONS

Ramboll has reviewed the literature provided by ECHA, primarily the FITASC report (2020), but also published literature on the chemistry, fate and behaviour of iron and lead shot in soil and water and predicted the potential for changes to the mobilisation and availability of these metals through predictive modelling using the VisualMinteq model and reported field studies.

This report considered worst case scenarios of both existing lead shot, and expected steel shot contamination. When field evidence from two lead-contaminated soil types with different soil chemistries (peatland with low pH and high organic matter; sandy moraine with neutral pH low organic matter) was investigated, though differences in soil chemistry were predicted the addition of steel shot had no significant effect on lead mobilisation, compared to steel-free samples. Although shooting ranges are present across a high variability in soil types, such example soils studied represent two very different case, increasing the confidence in the observed effects.

The FITASC report (namely pages 75-80, FITASC, 2020) claimed the following influences of steel shot at lead-contaminated firing ranges:

- Pristine lead shot in the environment is rapidly covered by a stable layer of lead oxide, which prevents further oxidation until environmental conditions change;
- Shooting steel shot in areas where lead shot has previously been fired can be disastrous for the environment;
- Lead shot can last 1,000-10,000+ years in soils; and
- Steel shot can be protected against corrosion by applying an electro-galvanised coating, but such coatings may add toxic metals into the environment.

Ramboll’s research in this report can make the following conclusions .

4.1 Steel and lead corrosion rates

The lead oxide protective layer mechanism stated on page 77 of the FITASC report offers justification for the longevity of lead, but relies on stable environmental conditions being maintained. Indeed, as presented in section 2.2.1 of this report, a similar protective oxidation mechanism could occur for steel shot, but the required stable conditions are unlikely to be present in natural/semi-natural environments at shooting ranges. Surface soils in particular are dynamic environments, as they are exposed to weathering process (rainfall, freezing, windscour, etc) calling into question the stability required for “optimum” corrosion rates. While the information presented in this report is generally in agreement with lead shot being likely to corrode more slowly than steel shot, in both air and in soils, corrosion rates are only one part of the picture – factors such as speciation, fate and toxicity should also be considered relative to lead.

4.2 The behaviour of steel shot over existing lead

Claims made by the FITASC report of the “disastrous” results of shooting steel shot over lead are underpinned entirely by studies made in the absence of any soil component. Both corrosion (Hurley, 2004) and toxicity (Fäth et al, 2018) studies cited in the FITASC report make explicit statements to the fact that their results are made in aquatic experiments without soil, yet the authors of the FITASC report use these studies as their primary evidence for soil compartment. While this report finds such studies informative, we acknowledge their lack of environmental relevance and instead provide both detailed theoretical modelling (sections 3.2.1 and 3.2.2) and field studies (section 3.2.3) to refute the claims made by the FITASC report.

There is no significant theoretical evidence of soil acidification related to the chemical reactions of iron in steel shots, due to both the fundamental chemistry of iron oxidation, the buffering capacity of soils and the greater contribution of other natural processes to soil acidification (e.g. microbes and acid rain). Ultimately there is little evidence that steel-induced acidity in soils would promote the mobility of lead. This report also briefly investigated electrical conductivity that could theoretically promote lead corrosion in soils, but the contribution of iron from steel shot in this scenario was also considered to be limited.

This report also presents a selection of field evidence across different soil types that supports the theoretical evidence that iron from sheet shot does not mobilise lead in already contaminated soils. Furthermore, a selection of ferrous shooting range remediation strategies were briefly considered to contextualise the potential of steel shot to be incorporated into BMPs not as a merely less toxic alternative to lead, but also a potential strategy to remediate historical metal pollution at these sites.

4.3 Timescales of lead in soil

The FITASC report makes a number of claims as to the longevity of lead and other metals in a variety of soils with figures of 1,000-10,000+ years for lead often quoted. However, from examining the evidence provided along with this report it was often not possible to find the original reference for such claims; in instances where a reference could be found this was usually to an unreferenced source. As corrosion rate depends on highly variable factors such as soil type and climate, it is our professional opinion the evidence for variable corrosion rates in soil is too complex to make reliable long term estimates that are broadly applicable across different shooting ranges. Further detailed study could enumerate some corrosion rates in specific instances (in addition to giving further consideration if future remediation strategies are to be deployed on contaminated shooting ranges), but such a task is beyond the scope of this report.

4.4 Toxic metals associated with steel shot

This report suggests that from an environmental perspective, steel is likely to be a suitable alternative shot to lead. Although continued release of any toxic metal into the environment will likely have undesirable consequences, such approaches may be effectively managed starting with a reduction in toxicity of the metal in question (i.e. from lead to iron; section 2.3). One aspect that the FITASC study does raise is the variability of steel shot composition, especially when manufacturers may coat the shot with more toxic metals such as zinc or copper, in order to prevent corrosion. Although such coatings may be used in smaller amounts than the main constituting metal, studies suggest that zinc and copper may both be more toxic to aquatic species than lead (Khangarot and Ray, 1989). Future regulatory decisions should consider the prevalence of electro-galvanised steels to ensure more toxic metals are not being introduced to shooting range soils unintentionally.

With specific reference to the project aims in section 1.2, Ramboll has reached the following conclusions:

1) Is there available field evidence that steel shot acidifies soil and accelerates lead corrosion at shooting ranges?

   Although there is little theoretical evidence that supports this claim, pH change is highly dependent on the oxidation state of the steel being introduced to the system, with oxidised forms of steel more likely to acidify soils. However, in field studies with intentionally oxidised steel shot (presented in section 3.2.3), this effect did not ultimately result accelerated lead corrosion compared to steel-free controls. While steel induced pH change may be theoretically possible, the properties of soil (e.g. buffering capacity, organic matter) may ultimately result in little effect on resultant lead corrosion. The FITASC report's justification of pH/corrosion claims based on aquatic studies without a soil component are of limited environmental relevance.

2) Review the theoretical evidence that could support or refute the claims, specifically in relation to understanding of the fate and behaviour of metals (including Fe, Pb, Ni, As and Mn) in soils under different physico-chemical conditions, with particular emphasis on how speciation affects fate and behaviour in the environment;

   The results of theoretical speciation modelling reveal the although differences in soil chemistry (pH, dissolved organic matter) may affect the fate and behaviour of metals, metals are typically bound to organic matter or present in insoluble forms. Though a detailed investigation of each metal element in the highly variable soil environment is beyond the scope of this report, it offers some preliminary evidence for further investigation. This report takes a more even handed approach to metals in soils than that presented in FITASC (2020), which focussed mostly on lead and did not apply equal considerations (with respect to speciation, fate and behaviour) to other potential replacement metals.

3) What is the relative expected contribution of iron from steel shot (under reasonably foreseeable conditions of use) to soil acidification from all relevant sources that may contribute to acidify soil (including rain, microorganisms, metabolism, etc)?

   Although iron can contribute to soil acidification in some conditions (driven by oxidation state), there is limited evidence that such a process would contribute significantly to overall soil acidification relative to other sources such as acid rain or microorganism activity.

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APPENDIX 1 TABULATED REVIEW OF FITASC EVIDENCE

Author	**Date**	**Title**	**Article type**	**Acknowledgements/Funding sources**
Fäth *et al*	2018	Leaching behaviour and ecotoxicological effects of different game shot materials in freshwater	Peer reviewed journal article	The study was funded by the hunting licence fee of the Bavarian State Ministry for Nutrition, Agriculture and Forestry (StMELF). The authors also acknowledged support by the Bavarian Hunting Association (BJV) in selecting different types of game shot.
Dr Corinne Rooney	No date	Contamination at Shooting Ranges	Unreferenced fact sheet	The Lead Education and Abatement Design Group (LEAD) is a not-for-profit community organisation which develops and provides information and referrals on lead poisoning and lead contamination prevention and management (https://lead.org.au/au.html).
Lisin *et al*	2020	Management of Environmental Risks Related to the Use of Lead Ammunition at Outdoor Sports Facilities (Shooting Ranges)	Referenced presentation	International Shooting Sport Federation (ISSF) is the governing body of the Olympic Shooting events, and prepared at the request of ECHA
Hurley	2004	The Structure, Redox Corrosion and Protection of Commercial Lead-Antimony Shot.	Consultancy report	The author acknowledged the following organisations/individuals in assisting the preparation of this report: Analytical & Environment Services Ltd (UK); Hull Cartridge Company (UK); Winchester Ammunition Inc. (USA); Dr Theodore Sall; Beech Group Remediation Services (UK); Solucorp Industries Limited (USA); Capcis Limited (UK); Dept. Material Science UMIST (UK).

APPENDIX 2 CALCULATION AND JUSTIFICATION OF THE PARAMETERS IN VISUAL MINTEQ MODELLING

Conditions in VisualMinteq demonstrate maximum contamination for Pb reported in literature (Dinake et ak., 2019) and a subsequent deposition of steel shots relative to the amount of Pb contamination. Estimation for the amount of steel was calculated by using the mass ratio of steel and Pb in 2.4 mm pellets. In addition, the possible maximum amount of Mn and Ni impurities in steel were considered in the modelling. The contamination values demonstrate intensive use of firing ranges for over 35 years with Pb shots, followed by similar use with same time scale with steel shots. For Fe and Mn, soil background concentrations were added to their total concentrations. The possible impurities in Pb shots were not included. The soluble concentration of metals was calculated the from total concentrations with Kd-values.

Justification for the parameters

- pH: acidic soil= pH 4 and neutral soil= pH 7 (low pH was tested as it is known to enhance the predominance of soluble metal species).
- Steel shot composition, information provided by ECHA, upper limit % w/w)
- DOC: the concentration in organic soils high in DOC can amount to 55.7-62 mg/l (Leroy et al, 2017)
- Fe range in soils 2000-550 000 mg/kg, 100 000 mg/kg for Kd background calculations (Bohn et al,2005)
- Mn range in soil 20-10 000 mg/kg, 2000 mg/kg for Kd (soil-water partitioning coefficient) background calculations (Bohn et al,2005)
- Kd-values: low Kd values were used to demonstrate maximum solubility. The Kd values were representative for sandy soil (Sheppard et al, 2009). Suitability of the Kd's were also by comparing them to theoretical values (Thibault et al 1990 and Carlon et al, 2004)

Calculations

Firing range surface soil contaminated with Pb 100 000 mg/kg (Dinake et al, 2019).

- steel shot composition: Fe 98.8 % and impurities Mn 1.2 % (values present ECHA upper limit % w/w) and Ni 1.2 % (hypothetical value based on assumption of nickel plated steel)
- with similar use and time scale (decades) the amount of steel with 2.4 mm pellets (FITASC 2020, table 3):
    - 100 000 mg Pb/kg x (0.056 g steel pellet /0.082 g Pb pellet)=68 293 mg steel/kg
        - 68 293 mg steel/kg x 98.8 % Fe=67 473 mg Fe/kg
        - 68 293 mg steel/kg x 1.2 % Mn=820 mg Mn/kg
        - 68 293 mg steel/kg x 1.2 % Ni=820 mg Mn/kg

Estimates for soil solution metal concentrations based on measured Kd (Kd=Csolid/Csolution) values for sandy soil:

- Pb
    - Csolution=100 000 mg Pb/kg /2000 L/kg=**50 mg Pb/l**
- Fe
    - Csolution=(68 293 + 100 000 background) mg Fe/kg/4900 L/kg=**34 mg Fe/l**
- Mn
    - Csolution=(820 mg + 2000 background) mg Mn/kg /1800 L/kg=**1.6 mg Mn/l**
- Ni

Csolution=820 mg Mn/kg /530 L/kg=**1.5 mg Ni/l**