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Soil intake in ruminants grazing on heavy-metal contaminated shooting ranges

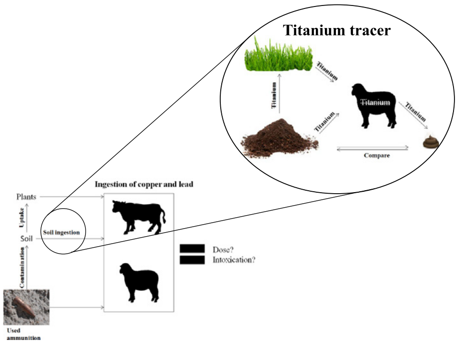
Ida Vaa Johnsen *, Jorunn Aaneby

Norwegian Defence Research Establishment (FFI), Instituttveien 20, NO-2007 Kjeller, Norway

HIGHLIGHTS

- Soil ingestion rates found in this study was <2% for both cattle and sheep.
- Soil ingestion rate did not vary between season and location.
- Lead but not copper concentration in soil and grass correlated.
- Calculated dose show little risk for ruminants grazing on soil with >1000 mg Pb/kg.

GRAPHICAL ABSTRACT



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ABSTRACT

Shooting ranges contain copper and lead from spent ammunition, this contamination can represent a risk for ruminants grazing there. The present study investigated the intake of copper and lead by sheep and cattle grazing on shooting ranges. Three factors are important for the ingested dose of metals: soil ingestion rate, accumulation of the metals in plants and grazing behavior. Up to 3700 mg Pb/kg dry weight (dw) and 1654 mg Cu/kg (dw) was found in soil and up to 52 mg Pb/kg (dw) and 35 mg Cu/kg (dw) was found in grass. The limit for sensitive land use set by the Norwegian Environment Agency is 60 mg Pb/kg and 100 mg Cu/kg, and the EU limit in fodder is 33.6 mg Pb/kg (dw). Soil ingestion was found by using titanium as a tracer, as titanium is abundant in soil, but not taken up in plants or animals. Low soil ingestion rates (<2%) were found in all investigated areas, including three shooting ranges and one cultivated pasture. There was no correlation between the copper concentration in soil and grass, such a correlation was found for lead. The risk of copper and lead poisoning by ruminants on shooting ranges was assessed based on the copper and lead concentration in the soil and grass, the soil ingestion rate and the grazing behavior. The risk assessment concluded that the calculated dose of copper (chronic sheep: 0.07, cattle: 0.08, acute sheep: 0.7, cattle: 0.8, mg/kg, body weight (bw), day) and lead (chronic sheep: 0.12, cattle: 0.12, acute sheep: 1.2, cattle: 1.2, mg/kg, bw, day) ingested by ruminants was much lower than both the assumed chronic (Cu sheep: 0.26–0.35 cattle: 8, Pb sheep and cattle:6, mg/kg, bw, day) and acute toxic doses (Cu sheep: 20–100, Pb sheep and cattle: 600–800, mg/kg bw) for sheep and cattle.

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* Corresponding author.
E-mail address: ida-vaa.johnsen@ffi.no (I.V. Johnsen).

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1. Introduction

The accumulation of metal residues from live firing of munitions in military training areas may represent a health risk to animals grazing on such areas (Braun et al., 1997). As an example, five calves grazing on an area containing an old shooting range in Switzerland, died from lead (Pb) poisoning. It was found that the calves had access to a strip of grass (2 m) between the bullet trap and the target (Braun et al., 1997). Beside the examples from shooting ranges, there are numerous accounts of ruminants dying from poisoning due to intake of toxic substances while grazing on rangeland pastures (Gudmundson, 1993; Guitart et al., 2010; Headley et al., 2008; Krametter-Froetscher et al., 2007; Oruc et al., 2009). In cattle, lead poisoning is the most frequent form of poisoning (≈50%), while copper (Cu) poisoning is the most frequent in sheep (≈70%) (based on data for Great Britain in 1999–2014) (Payne et al., 2004; VIDA, 2006a,b, 2014a,b).

Bullets used on small arms shooting ranges mainly contain lead, copper, zinc (Zn) and antimony (Sb) (Randich et al., 2002), while unleaded bullets contain steel (Mariussen et al., 2017). Concentrations of copper and lead on shooting range soil vary considerably, depending on use, soil properties and location in the shooting range. Previous studies have found concentrations of 17–5200 mg/kg copper and 44–33,600 mg/kg lead (Mozafar et al., 2002; Bannon et al., 2009; Mariussen et al., 2017) in soil on shooting ranges. In Norway, the average concentration of copper and lead in soil is 28 mg/kg and 67 mg/kg, respectively (Ottesen et al., 2000) and the limit for sensitive land use is 60 mg Pb/kg and 100 mg Cu/kg (Vik et al., 1999). The background level of copper and lead in soil through Norway varies from <5–380 mg/kg and from 2 to 219 mg/kg due to differences in soil property and regional variations, (Ottesen et al., 2000). Copper, and to some degree lead, has high affinity for organic matter (OM), and can form stable metal-organic complexes (Christl et al., 2005). Clay minerals and oxides, such as iron oxide, can bind copper and lead on the surface or as a complex (Sipos et al., 2008). Copper and lead binding in soil is highly dependent on pH, and a decrease in pH will decrease the extent of binding, and hence increase the mobility of the metals (Mariussen et al., 2017; Sanderson et al., 2012; Santillan-Medrano and Jurinak, 1975; Johnson et al., 2005; Gundersen and Steinnes, 2003).

In Norway (and other countries such as Switzerland) it is uncommon that shooting ranges are fenced, and as a consequence they can be used as pasture for livestock (Tandy et al., 2017). This is considered positive, because the grazers reduce the need for maintenance of the ranges. In the last few years, a concern for whether livestock are at risk from metal poisoning by grazing on contaminated shooting ranges has emerged. Several factors play a role in the potential poisoning of grazing animals on shooting ranges, such as the degree of contamination in soil and vegetation, soil ingestion rate, grazing time on contaminated areas, transfer of metals from the GI (gastro intestinal) tract into blood circulation, species, breed, health status and age of the animal (Hill et al., 1998; Johnsen et al., 2018). Lead poisoning in ruminants are rarely chronic, but acute poisoning is fairly normal, especially in cattle, for instance after intake of old leaded paint or car batteries (NAS, 1980; Leary et al., 1970). In the case of acute lead poisoning, the highest concentration of lead is found in the liver and kidney. In the case of long term exposure and chronic poisoning, lead is stored in the bones (Zmudski et al., 1983; Wilkinson et al., 2003), where it replaces calcium (Ca) (Payne and Livesey, 2010). Acute lead poisoning often lead to symptoms such as blindness, ataxia, cramps, muscle tremors, aggression, teeth grinding, anorexia, diarrhea and constipation (Sharpe and Livesey, 2004). Lead poisoning harms red blood cells, the kidney, bones and central nervous system (Krametter-Froetscher et al., 2007). Copper poisoning is fairly normal in sheep, but is seldom seen in adult cattle, but acute copper poisoning has been observed in calves (Bradley, 1993; Minervino et al., 2009). Acute copper poisoning does occur amongst ruminants, but chronic poisoning is by far the most common type of copper poisoning (Sivertsen and Plassen, 2004; Froslie et al., 1985). Copper poisoning can be divided into two phases: copper accumulation in the liver, and an acute hepatic cell death when the liver storing capacity is reached and the copper is released into the blood stream (Minervino et al., 2009; Bradley, 1993). Symptoms of copper poisoning include anorexia, runny nose, stomach pain, icterus, anemia, asphyxia and fatigue (NAS, 1980; Minervino et al., 2009; Bradley, 1993; Roubies et al., 2008). Table 1 shows toxic doses of copper and lead for cattle and sheep, along with the threshold value for copper and lead in fodder. The toxicity of copper depends on the concentration of molybdenum (Mo) in the fodder. Molybdenum binds copper and makes it less available for uptake once ingested. A Cu/Mo-rate of 6/1 is optimal, while rates >10/1 can lead to copper poisoning (Hidiroglou et al., 1984; Buck and Sharma, 1969).

Ruminants mainly ingest contaminants such as copper and lead by consumption of soil, grass/plants and water. Typical concentrations of copper and lead in water on shooting ranges are not high enough to give a substantial contribution to the ingested dose. Using concentrations found by Mariussen et al. (2017) in a stream in a Norwegian shooting range, 176 μg Pb/l and 415 μg Cu/l, the intake for a cow drinking 150 l/day and a sheep drinking 10 l/day, is 44 μg Pb/kg body weight (bw) and 55 μg Cu/kg (bw), and 103 μg Cu/kg (bw) and 23 μg Pb/kg (bw) for the cow and sheep, respectively. The typical concentrations of copper and lead in soil on shooting ranges are several magnitudes higher than the concentrations in grass/plants (Braun et al., 1997; Johnsen et al., 2018; Robinson et al., 2008; Rooney et al., 1999). The amount of soil ingested by ruminants plays an important role in the risk of copper and lead intake. Johnsen et al. (2018) found soil ingestion rates of 0.1% and 0.4% in sheep in a study in Leksdalen, Norway (two different areas). These rates were lower than the soil ingestion rates found in previous studies, which typically ranged from 1.7 to 17.6% (Green et al., 1996; Green and Dodd, 1988; Smith et al., 2009; Vaithiyanathan and Singh, 1994; Abrahams and Steigmajer, 2003), and as high as 67.9% (Smith et al., 2009). Previous studies have suggested that soil ingestion in ruminants can depend on area, season, weather, climate, stocking density and pasture quality (Green et al., 1996; Herlin and Andersson, 1996; Healy, 1967; Smith et al., 2009). Plants growing on contaminated soil can take up and accumulate contaminants, and plants are a route for ingestion of contaminants by ruminants. It has been suggested that the metal content in plants can vary between seasons (Robinson et al., 2005; Deram et al., 2006).

Soil ingestion rates for sheep cannot be used for cattle, as these animals have different grazing behavior (Green et al., 1996). Soil ingestion rates for cattle have in previous studies been reported as: 1.5–8%, with variations through the season (Green and Dodd, 1988; Abrahams and Thornton, 1994; Thornton, 1974; Herlin and Andersson, 1996; Healy, 1968).

The main objective of the present study was to investigate: the risk of metal poisoning of ruminants grazing on typical Norwegian shooting ranges, the typical soil ingestion rates in Norway and the accumulation of metals in grass growing on contaminated areas. The study focused on investigating of the soil ingestion rate for sheep on four locations, and three times during the grazing season (in one of the locations). Accumulation of copper and lead in grass was investigated on all the locations

Table 1
Acute and chronic toxic doses for oral ingestion by sheep and cattle (Oruc et al., 2009; Perrin et al., 1990; NAS, 1980; Payne and Livesey, 2010) and threshold value for copper and lead in fodder (2002/32/EC, Rupflin and Krebs, 2015).

Mg/kg		Copper		Lead	
		Sheep	Cattle	Sheep	Cattle
Toxic dose	Acute (per kg bw)	20–100	–	600–800	600–800
	Chronic (per kg bw per day)	0.26–0.35[a]	8	6	6
Fodder	Green fodder 12% water content (EU)	–	–	30	30
	All fodder, Switzerland (dw)	17	40		

[a] When Mo concentration in the soil is low.

and dates. These data contribute to knowledge of soil ingestion and metal accumulation in grass, and the seasonal and geographical variations. The risk of poisoning of ruminants grazing on contaminated shooting ranges can be assessed by calculating a theoretical ingested dose. The ingested dose depends on the grazing behavior of the animals. Surveillance of the animals was therefore included in the study.

2. Materials and methods

2.1. Study areas

The areas included in this study were three shooting ranges: Melbu, Steinsjøen and Hengsvann, and one cultivated pasture in Kjeller (Fig. 1).

Melbu shooting range is located in Hadsel municipal, Nordland county, Norway. The shooting range was established after the Second World War and has been used by the Norwegian Defence (Home Guard) until 2005. The range is 5 km^2 and 10% of the area is affected by shooting activity. Melbu was the main study area in the present study; several smaller areas inside Melbu shooting range were sampled, a description of the areas is presented in Table 2.

Steinsjøen shooting range is located in Østre Toten municipal, Oppland county, Norway. It consists mostly of pine forest with hills, marshes, ponds and lakes, and has been used since the late 1960's. Hengsvann shooting range is located in Kongsberg and Notodden municipal, Buskerud and Telemark county, Norway. The range has been used since after the Second World War, and is still in use today. The cultivated pasture is located in Kjeller in Skedsmo municipal, Akershus county, Norway. The pasture is located next to the runway on Kjeller airport. The cultivated pasture was included in the study because it has higher stocking density than the ranges, and could give an indication on the implication of stocking density on soil ingestion for sheep.

2.2. Sample collection

The technique that was used to collect grass, soil and feces is called "multi increment sampling (MIS)" or "incremental sample methodology (ISM)", described in ITRC (2012) and TR-AVT-197 (2016). The MIS/ISM technique produces a representative and reproducible sample for the average concentration (here of metals) in an area called the "decision unit (DU)", without having to process and analyze a large amount of samples for each area. In the DU, a number of increment samples (>30) is collected into a composite sample. The number of increment samples is not finite, but the more samples, lower the uncertainty. The technique ensures representative samples because increments (>30) are collected through the whole investigation area and variations in the concentration is therefore included in the sample. Drying, sieving and crushing, as described in "Sample preparation and analysis" further ensures representative and reproducible results. The size and description of the various DU's can be viewed in Table 2. In Melbu, the DU was the whole area for determination of soil ingestion. For determination of the accumulation of metals in grass, the DU was smaller areas: some areas where heavy contamination was expected and some where no contamination was expected. In Steinsjøen and Hengsvann, the DUs were the areas where sheep feces were found. In the cultivated pasture in Kjeller, the whole pasture was the DU. Soil samples were collected from the top 5 cm of the soil. Grass samples were cut 1–2 cm above the ground, to simulate grazing. The feces collected were fresh, and care was taken not to collect feces that had been in contact with

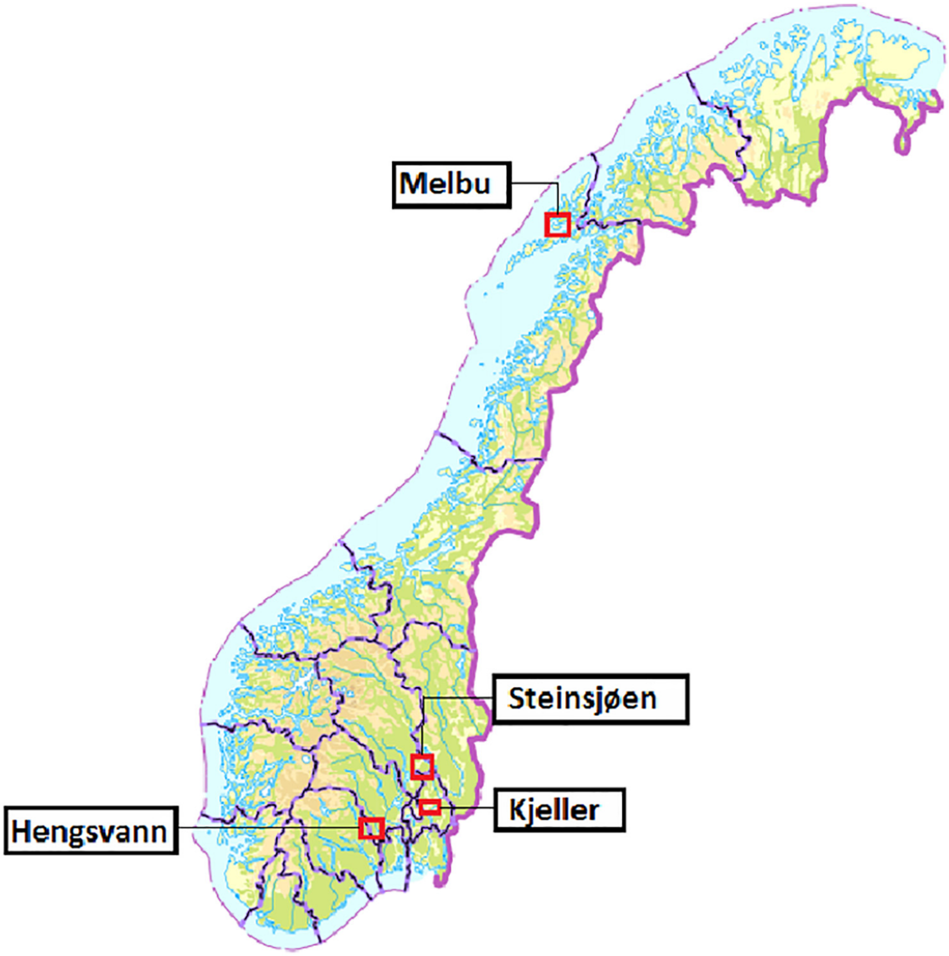

Fig. 1. Map of Norway with study areas marked (Kartverket.no).

Table 2
Description of sampling ranges and areas.

	Range	Sampling area	DU size (m^2)
Melbu			
1	Range 1, situated on mire, has not been in use for several years, little intervention in terrain.	Middle of the range	15 × 17
2	Range 2, situated on mire, and has not been in use for several years, little intervention in terrain.	On the edge of the range	12 × 7
3–1	Range 3/4, in-house firing point, built up bullet trap. Mostly mineral soil, but a small part in the middle of the lane was mire.	Bullet trap, mineral soil	24 × 9
3–2		Target area but not bullet trap, mineral soil	16 × 10
3–3		In front of firing point, mineral soil	13 × 31
3–4		Middle of range, on the mire area	30 × 10
4	Range 8 and 9, situated on mire, have not been in use for several years, little intervention in terrain.	Middle of range	30 × 23
5	Reference area, outside the shooting range area, mineral soil		10 × 10
6	The whole area	From the reference area downrange, and the whole shooting range area	
Hengsvann			
7	Below a shooting range, mineral soil		5 × 10
8	Alongside road inside range area		3 × 35
Steinsjøen			
9	Range 4, samples collected from firing point, mid-range and target area, mostly mineral soil.		
10	Range 5, samples collected from target area, mineral soil.		
Kjeller			
11	Cultivated pasture, mineral soil.		

soil. Feces and grass samples were collected on three dates in Melbu (June 27th, August 2nd and August 30th). Soil samples were only collected once (August 2nd), as metal contamination in soil does not vary through the season. In Kjeller (August 8th), Steinsjøen (July 31st) and Hengsvann (July 28th), soil, grass and feces samples were collected once.

2.3. Surveillance

The sheep and cattle in Melbu were monitored using wildlife cameras. 8 cameras were placed in areas known to be contaminated with metals. The animals were monitored to observe the grazing behavior on contaminated areas and to get an idea of the amount of time the animals grazed on contaminated areas (on the specific range). The sheep in Hengsvann, Steinsjøen and Kjeller were not monitored.

2.4. Sample preparation and analysis

The soil samples were dried at 105 °C for approximately 24 h (until stable weight). The samples were then sieved through a 2 mm sieve (Fritsch) and crushed with a ballmill until visual homogeneity (Retsch RM100, 300 rpm for 5–10 min). The soil sample preparation was in accordance with the procedure described by Clausen et al. (2013), with some minor alterations. Feces samples were dried and crushed in the same manner as the soil., Soil and feces samples were digested in triplicates (0.2–0.4 g) with 5 ml HNO_3 (Ultrapure 67%, Merck) and 1 ml HF (puriss 38–40%, Merck) in Teflon vials. The samples were heated to 260 °C in a pressurized microwave (UltraWave, Milestone) and the temperature was maintained at 260 °C for 10 min. With every 12 samples, two blanks and one certified reference material (soil) (GBW07407, Institute of Geophysical and Geochemical Exploration, Langfang China) was included.

Half of the grass in each composite sample was washed. The grass was first rinsed in running water (Milli q), and then placed in a vial (Nalgene) filled with purified water (milli q) and placed in a rotator for 24 h. The water was changed twice during this period. The grass samples were dried at 60 °C for approximately 48 h (until stable weight) and crushed in a ballmill until visual homogeneity (Retsch RM100, 400 rpm 10–20 min). The grass samples were digested in triplicates (0.2–0.4 g) with 3 ml HNO_3 (Ultrapure 67%, Merck), 6 ml HCl (Suprapure 30%, Merck) and 0.25 ml H_2O_2 (Suprapure 30%, Merck). The samples were heated to 260 °C under pressure. With every 12 samples, two blanks and one certified reference material (rye grass) (ERM – CD28, institute of reference materials and measurements) was digested.

The samples, blanks and the certified reference materials were diluted and analyzed for metals using ICP-MS (inductively coupled plasma mass spectrometry) (Thermo x-series 2). A four point standard curve was used for quantification of the elements, an internal standard was used to assure precision and certified standards (soil [Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Ti, Zn] and rye grass [As, B, Cd, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Zn], TMDA-53.3, TM-23.4 [Al, Sb, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ti, Zn] and AES-07 [Al, Ca, Mg, K, Na], from Environmental Canada) were used to assure accuracy.

Organic and mineral content in soil, feces and grass was determined by loss on ignition (LOI) according to the method described in Chambers et al. (2011).

2.5. Calculations

The titanium (Ti) concentration in the soil was used for calculation of soil ingestion rates (Eq. 1). The copper and lead concentrations in soil and grass were used to calculate theoretical ingested doses (Eq. (2)) and metal accumulation in grass. Soil ingestion rate was calculated according to the method described in Mayland et al. (1975) and Smith et al. (2009). This method (Eq. (1)) uses titanium as a tracer because titanium is abundant in soil, but not taken up by plants.

$$\%\text{soil ingestion} = \frac{(1-Pd)Ti_f * 100}{Ti_s - Pd * Ti_f} \qquad (1)$$

Pd – Plant digestibility
Ti_f – Ti concentration in feces (mg/kg)

Ti_s – Ti concentration in soil (mg/kg)

Metal dose ingestion was calculated as described in Johnsen et al. (2018), taking into account grazing time on the contaminated areas (found by monitoring) and the soil ingestion rate.

$$D = \frac{S * F * Si}{Bw} * G \tag{2}$$

D – Dose per day (mg/kg, bw, per day)
S – Metal concentration in soil (mg/kg)
F – Amount of fodder ingested per day (kg dry weight [dw])
Si – Soil ingestion rate
Bw – Body weight (kg)
G – Part of the time the animal grazed on contaminated area

Eq. (2) can also be used to calculate dose from grass by exchanging S for metal concentration in grass, and Si for 1-Si.

2.6. Statistics

The data was tested for normality by using the "Shapiro-Wilk test of normality" (SPSS). The specific tests used to compare groups are mentioned along with the results.

3. Results and discussion

3.1. Soil

Metal (Cu, Pb and Ti) and organic matter (OM) concentration in the soil samples is showed in Table 3. The titanium concentrations in the soil samples are presented alongside with the titanium concentration in the feces samples. The metal concentration in the soil gives information about the degree of contamination in the area. The highest concentrations of lead (>1000 ppm) was found in area 1, 3–1, 3–4, 4 and 9. These areas were either target areas (3–1 and 9) expected to be highly contaminated, or areas situated on mire (1, 3–4 and 4). The lead concentrations were high (up to 3700 mg/kg) compared to what has been suggested, by the Norwegian Veterinary Institute, as the upper safe limit (300 mg/kg) for lead in soil where ruminants are grazing (Bernhoft, 2011). The highest concentration of lead was measured in Melbu (3700 mg/kg). However, this concentration was considerably lower than the lead concentration (229,550 mg/kg) that caused acute poisoning and death of 6 calves in Switzerland (Braun et al., 1997). The highest copper concentrations (>1000 ppm) were found in area 1 and 4, both on mire. Mire/peat has high content of OM which is known to bind copper and lead (Christl et al., 2005). Five of the areas (area 2, 5, 7, 8 and 11) had copper concentrations in soil below the considered background level in Norway (28 mg/kg), and nine of the areas (2, 3–2, 3–3, 5, 6, 7, 8, 10 and 11) had copper concentrations below what is considered safe for sensitive land use (100 mg/kg) by the soil quality guidelines set by the Norwegian Pollution Control Authority (now the Norwegian Environment Agency) (Vik et al., 1999). Five areas had copper concentrations above what is considered safe for sensitive land use (area 1, 3–1, 3–4, 4 and 9). On average, the lead concentrations were higher than the copper concentrations on the sites contaminated by shooting activity. On the sites where the soil was less affected by shooting activity (area 2, 5, 7, 8 and 11), the copper and lead concentrations were similar. On these sites, the lead concentrations were below the background level in Norway 67 mg/kg (Ottesen et al., 2000) and the limit for sensitive land use (60 mg/kg), set by the Norwegian Pollution Control Authority (now the Norwegian Environment Agency) (Vik et al., 1999). By comparison, measurements of lead in areas throughout Norway by Ottesen et al. (2000), indicates background concentrations of: Hengsvann and Kjeller: 70 mg/kg, Steinsjøen: 111 mg/kg, Melbu: 50 mg/kg. Higher lead concentration compared to copper concentration is expected on small arms shooting ranges, as the ammunition contains more lead than copper. Usually, the ammunition used for small arms consists of a lead and antimony alloy core, covered with a copper and zinc alloy (Randich et al., 2002). The Shapiro-Wilk-test (SPSS) of normality found that metal concentration in soil was not normally distributed. Two non-parametric tests (Kendall's tau-b and Spearman's rho, SPSS) were performed to look for correlations between copper and lead concentration in soil. A correlation coefficient of 0.817 (Kendall's tau-b) and 0.941 (Spearman's rho) was found, both with a statistical significance >99%. The correlation indicates that the copper and lead contamination on the investigated areas is caused by shooting activity. Generally, elevated copper and/or lead concentration in soil (>800 mg/kg) was found in areas with high shooting activity (bullet traps, mid-range, target areas etc.). The concentrations were several magnitudes higher than the concentrations found in the reference area (<30 mg/kg). This supports that the copper and lead in the soil mainly stems from shooting activity.

Table 3
Cu, Pb, dry weight and organic matter content measured in soil, N (increments) was between 50 and 120, except for sample area 6 where N was 250.

Area	Cu	Pb	DW	OM
1	1164 ± 139	1930 ± 239	14%	98%
2	28 ± 0.3	26 ± 0.5	14%	82%
3–1	156 ± 6	2171 ± 116	85%	6%
3–2	91 ± 8	808 ± 64	84%	4%
3–3	61 ± 2	150 ± 6	74%	11%
3–4	977 ± 125	3700 ± 684	14%	97%
4	1654 ± 556	1779 ± 325	17%	82%
5	20 ± 1	23 ± 4	64%	13%
6	41 ± 2	260 ± 17	–	–
7	24 ± 5	45 ± 10	68%	16%
8	22 ± 2	24 ± 3	89%	2%
9	110 ± 13	1034 ± 192	86%	3%
10	57 ± 11	663 ± 591	86%	3%
11	25 ± 0.5	25 ± 1	62%	16%

3.2. Grass

The mean lead and copper concentrations in the grass samples can be viewed in Table 4 (dry weight of the grass is included in attachment Table A1). Concentrations of 2–5 mg Pb/kg and 3–20 mg Cu/kg (dw) is considered normal in grass (Chaney, 1989; Robinson et al., 2008). In the unwashed grass samples, the considered normal level of lead was exceeded in 8 of the 28 samples. These grass samples were collected from area 3–1, 3–2 (all three dates), area 1 (6.27) and area 10, all areas with high lead concentrations in the soil (>600 mg/kg). For copper, the considered normal level was exceeded in 3 of the 28 washed samples, two from area 5 (6.27 and 8.29) and one from area 7, none of these sites had high concentrations of copper in the soil (<50 mg/kg).

3.2.1. Soil contamination on grass

To determine whether soil particles were attached to the grass, metal concentration (Cu, Pb and Ti) was measured both in washed and unwashed grass samples (Table 3). The Shapiro-Wilk-test (SPSS) of normality found that the data was not normally distributed (sig. < 0.05). A non-parametric test (Wilcoxon signed ranks test [SPSS]) was conducted to determine whether there was a difference in the metal (Cu and Pb) concentration in the washed and unwashed grass. No statistical significant difference between the copper concentration in washed and unwashed grass was found (Asymp. Sig. [2-tailed] = 0.399). A statistical significant difference was found between the mean lead concentration in washed and unwashed grass (Asymp. Sig. [2-tailed] = 0.043). The mean lead concentration was higher in the washed (9.6 mg/kg) than the unwashed grass (8.4 mg/kg). This

Table 4
Ti, Cu, Pb concentrations and Cu/Mo-rates measured in washed (w) and unwashed (u) grass, N (increments) was between 50 and 120.

Area			Ti (mg/kg)			Cu (mg/kg)			Pb (mg/kg)			Cu/Mo		
			6.27	8.2	8.29	6.27	8.2	8.29	6.27	8.2	8.29	6.27	8.2	8.29
1	U	Av	3.9	2.1	1.8	20	15	8.6	5.8	2.0	0.69	25	37	14
		SD	0.21	0.42	0.10	1.5	1.2	0.76	0.21	0.20	0.060			
	W	Av	1.7	1.3	1.4	18	8.1	12	6.2	0.81	0.76	19	14	9
		SD	0.13	0.28	0.10	2.4	0.28	0.79	0.52	0.036	0.057			
2	U	Av	27	4.9	5.7	6.7	5.9	5.3	0.35	0.39	0.122	13	3	4
		SD	5.8	0.54	0.38	0.50	0.16	0.16	0.038	0.038	0.0085			
	W	Av	20	3.6	3.2	11	6.4	15	0.39	0.72	0.16	5	4	4
		SD	7.1	0.68	0.59	3.2	0.45	2.4	0.095	0.051	0.021			
3–1	U	Av	10	110	1432	9.4	14	15	31	43	44	5	8	7
		SD	1.8	29	69	0.82	2.0	1.4	2.7	4.1	3.6			
	W	Av	24	58	411	10.9	8.1	20	21	30	53	11	6	5
		SD	4.4	5.4	152	0.25	0.46	8.7	1.1	1.2	25			
3–2	U	Av	12	16	138	13	13	13	12	20	52	11	4	5
		SD	2.4	2.4	27	1.4	1.9	1.6	2.9	3.0	5.1			
	W	Av	5.9	21	49	10	9.2	9	31	24	41	4	4	4
		SD	1.2	2.0	7.0	1.1	0.79	1.4	1.7	1.6	3.7			
3–3	U	Av	14.7	16	17.6	14.7	13	12	0.80	20	1.9	8	7	6
		SD	0.44	2.4	0.50	0.62	1.9	1.4	0.063	3.0	0.20			
	W	Av	4	21	6.6	30	9.2	11	1.4	24	3.2	5	7	4
		SD	1.4	2.0	0.83	7.1	0.79	1.0	0.39	1.6	0.29			
3–4	U	Av	1.3	2.4	13	15	6.3	8.8	2.5	3.6	1.38	10	15	10
		SD	0.08	0.36	1.5	3.5	0.94	0.63	0.55	0.53	0.064			
	W	Av	1.7	1.9	14	13.7	8.3	14	3.0	2.32	3.6	11	12	8
		SD	0.18	0.16	2.9	0.76	0.31	1.6	0.56	0.073	0.45			
4	U	Av	1.3	1.9	1.4	14.0	11.7	10.9	1.83	0.40	0.47	17	23	10
		SD	0.22	0.29	0.30	0.76	0.78	0.80	0.069	0.042	0.020			
	W	Av	–	2.7	1.7	–	14	12	–	0.79	1.00	–	12	9
		SD	–	0.31	0.24	–	1.8	1.0	–	0.091	0.074			
5	U	Av	15	26	358	35	11.3	28.2	0.36	0.47	0.5	7	6	5
		SD	1.9	2.1	6.0	7.5	0.62	0.32	0.058	0.010	0.10			
	W	Av	5.4	12	119	14.6	8.8	27	1.1	0.25	0.49	5	5	4
		SD	0.73	1.7	8.6	0.82	0.70	2.9	0.17	0.027	0.040			
7	U	Av			19			30			1.6			4
		SD			2.2			3.6			0.17			
	W	Av			13			21			2.3			3
		SD			1.5			3.7			0.42			
8	U	Av			80			20			0.64			4
		SD			16			3.7			0.040			
	W	Av			24			19			3.7			3
		SD			3.3			2.4			0.38			
9	U	Av			4.8			8.8			4.6			1
		SD			0.31			0.69			0.43			
	W	Av			8.5			18			14.5			1
		SD			0.17			2.0			0.45			
10	U	Av			10.7			9.2			8.4			0.3
		SD			0.95			0.20			0.61			
	W	Av			11			15			17.2			0.4
		SD			2.3			1.5			0.47			
11	U	Av			57			14			0.465			4
		SD			8.5			1.4			0.0039			
	W	Av			37			21			0.57			3
		SD			4.8			1.1			0.035			

indicates that the grass was contaminated in the washing procedure. The results showed that little or no soil was attached to the sampled grass, or that the potential soil on the grass was not washed away by the washing procedure.

The amount of soil particles attached to grass can also be assessed by analyzing the titanium concentration in the grass. Titanium is not taken up by plants, and any titanium found on grass is from soil. A non-parametric test (Wilcoxon signed ranks test [SPSS]) showed a significant difference between titanium concentration in washed and unwashed grass (mean washed = 31.6 mg/kg, mean unwashed = 85.8 mg/kg, $p = 0.006$). This indicates that some soil was removed during the washing procedure. It was challenging to compare the soil content on the grass from different areas as some grass grew on mire where the soil contained little titanium, and other grass grew on mineral rich soil with high concentration of titanium. Titanium concentrations ranging from 110 to 1432 mg/kg (3–1, 3–2, 5 29th of August, 3–1 2nd of August) indicated high soil contamination of some of the grass samples. All the grass samples with elevated titanium concentration were found on areas with mineral rich soil. There was no significant difference between the titanium content in grass samples from different areas or dates (Related-samples Friedman's two-way analysis of variance by rank [SPSS], sig. > 0.05). Most of the grass samples with elevated lead concentration (>5 mg/kg), had elevated titanium concentration (>10 mg/kg), except for the grass collected from area 1 on mire. This indicates that the lead in the grass samples may originate from soil particles on the grass.

3.2.2. Accumulation in grass

The lead concentration in grass was compared to regulations for lead concentration in green fodder (30 mg/kg 12% water content, 33.6 mg/kg [dw]) in EU (2002/32/EC and DIRECTIVE, 2002). The EU (and Norway) does not have any restrictions for copper in animal fodder. The concentration of copper in the grass was therefore compared to the guidelines for copper in fodder in Switzerland (sheep: 17 mg/kg, cattle: 40 mg/kg [dw]) (Rupflin and Krebs, 2015).

The lead concentration in the grass exceeded the threshold limit for lead in fodder in 5 of the 49 grass samples (both washed and unwashed). These 5 grass samples were all collected from areas highly contaminated with lead (in soil). The concentrations of lead in the grass from the reference area was low (<1.1 mg/kg). None of the grass samples had copper concentrations exceeding the Swiss limit for copper in cattle fodder. However, 13 (of 49) grass samples (washed and unwashed) had copper concentrations exceeding the Swiss limit for copper in sheep fodder. Unlike the lead contaminated grass, these samples had not consistently been collected from areas with heavy copper contamination in the soil. Two of the (unwashed) grass samples with high concentrations of copper (>17 mg/kg) were collected from the reference area in Melbu, four from Hengsvann and one from the cultivated pasture, which were all areas where the soil samples had low copper concentration (<30 mg Cu/kg in soil). This indicates that the copper concentration in grass was not dependent on the copper concentration in the soil.

Two statistical tests were performed to investigate the null hypothesis: the copper and lead concentration in the grass is independent of the copper and lead concentration in the soil from the same area. The Shapiro-Wilk-test (SPSS) could not prove that the data was normally distributed. Two non-parametric tests (Kendall's tau-b or Spearman's rho, SPSS) were performed to test for significant correlation between the copper and lead concentration in the grass and soil. Data for unwashed grass samples was used for the calculations, partly because ruminants will graze unwashed grass and partly because of the suspected contamination of samples during washing. A statistical significant positive correlation (Kendall's tau_b: 0.432 and Spearman's rho: 0.588) was found between the lead concentration in soil and grass (99% confidence in both tests). Such a correlation was not found for copper. This study indicates that the copper accumulation in grass is independent of the copper concentration in the soil. This is probably because copper is an essential element and the uptake in plants is regulated. Lead is not an essential element, and the uptake in plants is therefore more dependent on the concentration of lead in the soil (Evangelou et al., 2012).

3.2.3. Seasonal fluctuation

To determine whether the metal concentration in grass fluctuated during the grazing season, samples were collected on three different dates. The data was tested for normality using the Shapiro-Wilk-test of normality (SPSS). Normality could be assumed for the copper concentration in the grass (Sig. >0.05), but not for the lead concentration in the grass (Sig. <0.05). For copper, a parametric test (ANOVA: Two-Factor without replication, Excel), was performed and for lead, a non-parametric (Friedman-test [SPSS]) was performed. No statistical difference in the copper ($P = 0.199$) or lead (Asymp. Sig. = 0.648) concentration in the grass on the three dates was found. The results showed no significant seasonal fluctuation in metal (Cu and Pb) concentration in grass, at least in this site. This implies that an assessment of the grass contamination once during the grazing season (which in this site is from late May to mid-September) would give sufficient information for the whole season. The copper and lead ruminants ingest from grass can be assumed to be quite constant during the grazing season.

3.2.4. Cu/Mo-rate

Elevated Cu/Mo-rates (>10) were found in 6 locations at one or more of the sampling dates. All the locations were in Melbu, and the highest rates (>15) were found in the grass growing on mire (area 1, 3–4 and 4). All these areas had high concentration of copper in soil. The high Cu/Mo-rate could be attributed to both the high copper concentration in the soil, and that the grass grew on mire, which is naturally low in molybdenum. A high Cu/Mo-rate can cause copper poisoning even when the copper concentration in the fodder is below the recommended value. Some of the areas could therefore be of concern to grazing animals, especially for sheep as they are very susceptible to copper poisoning.

3.3. Soil ingestion rate

Soil ingestion rates were calculated using Eq. (1) and the titanium concentrations measured in feces and soil (Table 4). The titanium concentrations in feces in Table 6 are average concentrations in feces samples (composite samples containing about 10 subsamples) (complete table of titanium concentrations in feces in attachment Table A2). The soil ingestion rates found in all the four areas, at different times of the season, and in different weather, was <2% for both sheep and cattle. This was comparable to a similar study performed in Leksdal, Norway (Johnsen et al., 2018) where soil ingestion rates of 0.1% and 0.4% were found. The findings in the present study and in the study by Johnsen et al. (2018) supports the assumption made by Johnsen et al. (2018) that the soil ingestion rates previously used (5% (Eriksen et al., 2009) and 10–30% (Rupflin and Krebs, 2015)) are too high (at least for Norwegian conditions). The Shapiro-Wilk-test of normality (SPSS) showed that the soil ingestion rate data was normally distributed. A non-parametric test (one way ANOVA [Excel]) was performed to determine whether the soil ingestion rates found for sheep on the three different dates in Melbu were significantly different from each other. There was no significant difference between soil ingestion rates on the three dates ($p = 0.157$). This indicates that the soil ingestion was stable through the Norwegian grazing season, and contradicts previous studies which have shown that the soil ingestion has varied a lot through the season (Abrahams and Steigmajer, 2003; Smith et al., 2009; Herlin and Andersson, 1996). In most other countries, the grazing season lasts all year. For instance; Abrahams and Steigmajer (2003) and Thornton (1974) both measured soil ingestion all throughout the year. In Norway the grazing season only lasts for 3–6 months, depending on the location.

There was not sufficient data to perform statistical analyses on the differences in soil ingestion rates between the sites; however, the results indicated small or no differences. Since soil ingestion previously has been shown to increase with increasing stocking density (Russel, 1988; Herlin and Andersson, 1996; Healy, 1967), it was assumed that the soil ingestion on the cultivated pasture would be higher than the soil ingestion on the shooting ranges. The soil ingestion rate in the cultivated pasture (1.4%) was slightly higher than the soil ingestion rate found on the shooting ranges (<0.6%). However, no definite conclusion can be made, as only one sample was collected from the cultivated pasture.

The small variations found in soil ingestion rates in Norway, both from this study and the study by Johnsen et al. (2018), indicate that the soil ingestion by ruminants in Norway is low and shows small variations between areas, stocking density, weather and season. It can be speculated that this is because the Norwegian grazing quality is generally good with a high degree of vegetation cover.

3.4. Risk assessment

The risk of metal contamination for animals grazing on a shooting range depends on the metal dose the animals ingest. The metal dose ingested from soil and grass was calculated using Eq. (2). The surveillance study concluded that average time per day spent on all contaminated areas on the ranges combined was 7.3% for sheep and 1.4% for cattle. This included all sheep and cattle observed on the ranges (by wildlife cameras), and is not an estimate for one particular animal. The observed visit times are rough estimates, and to get a safety margin and for simplicity, both numbers were increased to 10% for calculations. As there is no data for each particular animal, a scenario where one animal grazes at the most contaminated area for 10% of its time was used for the dose calculations. This will overestimate the dose, but serves as a worst case scenario. In the calculations, the following parameters were

Table 5
Ti concentration in soil and feces (average) and calculated soil ingestion rate.

Area		Ti (mg/kg)				Soil ingestion rate (%)		
		Soil	Feces					
			June 27	Aug 2	Aug 29	June 27	Aug 2	Aug 29
Melbu	Sheep	7936	88	154	36	0.3	0.6	0.1
	Cattle		–	166	89	–	0.6	0.3
Hengsvann		4964			58			0.4
Steinsjøen		3080			49			0.5
Kjeller		3411			150			1.4

used: the highest concentration of copper and lead in grass (35 mg Cu/kg and 52 mg Pb/kg) and soil (1654 mg Cu/kg and 3700 mg Pb/kg) (Table 3 and Table 4), the average soil ingestion rate for cattle (0.3%) and sheep (0.48%) (Table 5), body weight of 75 kg (sheep) and 600 kg (cattle) and fodder intake per day of 1.3 kg (sheep) and 12 kg (cattle). The results of the calculations are presented in Table 6. The limit for chronic copper (sheep: 0.26 mg/kg, bw, day, cattle: 8 mg/kg, bw, day) (Oruc et al., 2009; Perrin et al., 1990) and lead (6 mg/kg, bw, day) (Payne and Livesey, 2010) poisoning was not exceeded. This indicates that there will be no risks for cattle or sheep grazing on a Norwegian shooting range contaminated with up to 3700 mg Pb/kg and 1600 mg Cu/kg. Similar calculations were done for acute poisoning (one day exposure), except it was assumed that the animals grazed only on the most contaminated areas for 24 h. The calculated doses (Table 6) were 20–600 times lower than the acute toxic doses of copper (Oruc et al., 2009) and lead (Payne and Livesey, 2010) (Table 1). Thus, acute and chronic poisoning of cattle and sheep in Melbu shooting range is highly unlikely.

The sheep and cattle in Melbu will be used for human consumption, including meat and milk production, and for breeding. Based on the low calculated doses of lead ingested by sheep and cattle, there is no reason to believe that there is any risk in consuming meat from animals that has grazed on Melbu shooting range. In addition, meat seldom contains high lead concentrations as lead is usually stored in bone, liver and/or kidney (Rudy, 2009; Lopez Alonso et al., 2000). A former study found that as long as the lead level in the blood was “normal”, <0.2 mg/kg, the level in milk was stable (Swarup et al., 2005) and under the limit value for human consumption, 0.02 mg/kg (EC-Regulation-1881/2006, 2006). It is unlikely that the lead consumed by the ruminants is high enough to elevate the concentration of lead in the blood to above “normal”. However, the level for “normal” lead content in the liver and kidney in sheep and cattle is <3 mg/kg (dw) (NAS, 1980), which is higher than the limit for lead in offal for human consumption (2 mg/kg dw) (EC-Regulation-1881/2006, 2006). For people consuming large amounts of offal, the lead content could pose a risk. The risk for humans consuming liver or kidney from the animals that have grazed in Melbu is unlikely to be particularly higher than consuming liver or kidney from elsewhere, as the calculated ingested metal doses for the ruminants were very low. There is no limit for copper in food for human consumption.

Table 6
Calculated average ingested Cu and Pb dose. Calculations performed using Eq. (2), soil ingestion rate (Table 5) and Cu and Pb concentrations in soil and grass (Tables 3 and 4).

Mg/kg, bw, day		Sheep			Cattle		
		Soil	Grass	Total	Soil	grass	Total
Chronic	Cu	0.01	0.06	0.07	0.01	0.07	0.08
	Pb	0.03	0.09	0.12	0.02	0.10	0.12
Acute	Cu	0.1	0.6	0.7	0.1	0.7	0.8
	Pb	0.3	0.9	1.2	0.2	1	1.2

4. Conclusion

The results from this study support the findings made by Johnsen et al. (2018): the soil ingestion rate in sheep (and cattle) in Norway is much lower than previously assumed and used for calculations in Norway (Herlin and Andersson, 1996; Bernhoft, 2011; Rupflin and Krebs, 2015). The low soil ingestion rate leads to low calculated doses of copper and lead ingested by ruminants. The results indicate that the risk of metal poisoning from contaminated soil for ruminants is unlikely, at least in the areas in this study (and areas with similar conditions). Ruminants can be poisoned from ingesting grass with high concentrations of copper and/or lead. The present study found a positive correlation between the lead concentration in soil and grass. This implies that there can be a risk of poisoning for ruminants grazing on shooting ranges heavily contaminated with lead because they can ingest a toxic dose from grass. There was no correlation between the copper concentration in soil and grass. Based on this, there is a very low risk of poisoning for ruminants grazing on copper contaminated areas. The theoretical calculated ingested doses of lead and copper for sheep and cattle grazing on the most contaminated parts of the study area were well below the chronic and acute toxicity doses found in literature. This suggests that shooting ranges with comparable contamination to Melbu are safe for ruminants to graze on.

No significant difference in the soil ingestion between the three sampling dates in this study was found. The variations between the sites were minimal (all <2%), indicating a stable soil ingestion rate through season, weather and area.

This study, and the study in Leksdalen (Johnsen et al., 2018), are the first studies to assess soil ingestion for ruminants in Norway. They are, to our knowledge, the first studies to assess the risk for ruminants grazing on contaminated areas by using site specific soil ingestion rates and metal uptake in plants. The results give valuable information that can be used in risk assessments in the future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.06.086.

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