

Analysis of antimony (Sb) in environmental samples

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Norwegian Defence Research Establishment (FFI)

28 February 2012

FFI-rapport 2012/00347

1197

P: ISBN 978-82-464-2048-6

E: ISBN 978-82-464-2049-3

Keywords

Skytebaner

Antimon

Tungmetaller

Mikrobølgeovnassistent syreoppslutning

Mineraljord

Fisk

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English summary

Metals and metalloids from ammunition residues in shooting ranges and landfills may leach into the soil and surrounding watercourses and may pose a threat to exposed wildlife and humans. To assess the mobility of metals in solid waste, classify hazardous waste and evaluate its leaching potential in a landfill, standard procedures of leaching tests are established. Such tests, both at our institute and elsewhere, have shown that antimony has a high mobility in soil. Therefore, solid waste containing Sb are often classified as hazardous materials. It is important to establish adequate methods for analysis of Sb to make proper evaluations of environmental fate of this compound, both in the field and in the laboratory. This work has evaluated some aspects about antimony analysis and fate in environmental samples compared with lead and copper.

The work has focused on three main objectives: a) Evaluate recovery of Sb in soils and biological materials after extraction with different digestion methods; b) Evaluate the leachability of Sb in soil from shooting ranges with standard leaching tests in order to determine the easily exchangeable fraction of Sb; c) Compare analyses of Sb, Cu and Pb in soil between a portable XRF instrument and an ICP-MS instrument. Recoveries of Sb from microwave assisted digestion of mineral soil and peat soil were determined for three different acids: nitric acid, a combination of nitric acid and HCL (Aqua Regia) and a combination of nitric acid and hydrofluoric acid (HF). A sample of cod were, in addition, spiked with Sb and subjected to different extraction procedures.

Extraction of mineral soil and peat soil with nitric acid was shown adequate for Pb and Cu, whereas Aqua Regia or HF have to be used for Sb. Approximately 5% of the total Sb-content was recovered from the mineral soil with nitric acid. HF is a highly toxic and corrosive acid and Aqua Regia is the preferable acid for Sb extraction. The recovery was dependent on extraction temperature. Biological material can be digested with nitric acid in combination with some hydrogen peroxide. The portable XRF instrument is convenient for use in the field for analysis of metals in soil. The study shows a very good correlation between actual level in mineral soils of Pb and Cu, measured with ICP-MS after Aqua Regia digestion, and XRF-analysis. The XRF tend to underestimate Pb and Cu concentration in mineral soil and overestimate the concentration in peat soil. This might be due to how the instrument is calibrated. The XRF is less suitable for Sb analysis, especially in peat soil, but may be used on grounded mineral soil if the concentration is higher than 50 mg/kg. The XRF is quite sensitive for Pb, and in shooting range soil Sb and Pb are expected to correlate. Standard leaching test shows that Sb is readily mobilized into the water fraction from contaminated soil. The mobility of Sb is higher than that of Cu and Pb and it appears that the Sb extracted with nitric acid is the mobile fraction. The concentration of Sb in the leachate was correlated with the concentration in soil.

Sammendrag

Det er deponert store mengder bly (Pb), kobber (Cu), antimon (Sb) og sink (Zn) fra håndvåpenammunisjon og disse metallene kan lekke ut i jorden og omkringliggende vassdrag og dermed utgjøre en trussel for utsatte dyr og mennesker. For å vurdere mobilitet av metaller i avfall, som for eksempel ammunisjonskontaminert jord fra skytefelt, benyttes standard utlekkings tester. Slike tester, både ved vårt institutt og andre steder, har vist at antimon fra ammunisjon har en høy mobilitet i jord. Derfor er avfall som inneholder Sb ofte klassifisert som farlig avfall. Det er derfor viktig å etablere pålitelige metoder for analyse av Sb for å gjøre riktige vurderinger av skjebnen til denne forbindelsen i miljøet, både i felt og på laboratoriet. Dette arbeidet har vurdert noen aspekter rundt antimonanalyse og skjebne i miljøprøver sammenlignet med bly og kobber. Arbeidet har fokusert på tre hovedmål: a) evaluere gjenvinning av Sb i jord og biologisk materiale etter ekstraksjon med forskjellige ekstraksjonsmetoder; b) Studere mobilitet av Sb i jord fra skytebaner med standard utlekkings tester for å vurdere andelen mobilt Sb; c) sammenligne analyseresultatene av Sb, Cu og Pb i jord utført med et bærbart XRF instrument og et ICP-MS instrument. Oppslutning av Sb i mineral- og torvjord ble gjort i mikrobølgeovn med tre forskjellige syreblandinger: salpetersyre (HNO_3), Kongevann (HNO_3 og saltsyre (HCl)), og en kombinasjon av salpetersyre og flussyre (HF). En prøve av torsk ble i tillegg tilsatt en kjent mengde Sb og ekstrahert med forskjellige ekstraksjonsmidler.

Gjenvinning av Pb og Cu i mineraljord og torv var tilstrekkelig med bruk av salpetersyre, mens kongevann eller flussyre måtte benyttes for ekstraksjon av Sb. Ca 5% Sb ble gjenvunnet i mineraljorda med salpetersyre. Flussyre er imidlertid både svært giftig og korrosivt og kongevann vil være den foretrukne syren for oppslutning av prøven. Gjenvinning av Sb var avhengig av temperatur. Biologisk materiale kan oppsluttes med en blanding av salpetersyre og hydrogenperoksid (H_2O_2). Et bærbart XRF-instrument er praktisk for måling av metaller i jord i felt. Denne studien viste en meget god korrelasjon mellom faktisk nivå av Pb og Cu i mineraljord, målt med ICP-MS og Aqua Regia oppslutning, og XRF-analyse. XRF-instrumentet underestimerte Pb og Cu-konsentrasjonen i mineraljord og overestimerte konsentrasjonen i torvjord. Dette kan skyldes hvordan instrumentet er kalibrert med hensyn på forholdet mellom jordprøvens tetthet og volum. XRF var mindre egnet for Sb-analyse, spesielt i torvjord, men viste tilfredsstillende resultater på oppmalt mineraljord ved jordkonsentrasjoner høyere enn 50 mg/kg. XRF-instrumentet er ganske følsomt for Pb, og i jord fra skytefelt er konsentrasjonen av Sb og Pb forventet å korrelere. Standard utlekkings test viste at Sb lett mobiliseres i vannfraksjonen fra forurenset jord. Mobiliteten av Sb var betydelig høyere enn for Cu og Pb. Det ser ut som om den salpetersyreløselige fraksjonen av Sb fra mikrobølgeovnoppslutningen, var den mobile fraksjonen. Konsentrasjonen av Sb i utlekkingsvannet korrelerte med konsentrasjonen i jord.

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Preface

This study was performed under the FFI-project 119702: “Effects of ammunition related pollutions on living organisms”. The object of the study was to increase knowledge about fate of antimony (Sb) in environmental samples, with particular emphasis on polluted soil and determination of Sb concentrations in soil. Sb is used as alloy in lead bullets and is an important pollutant at small arms shooting ranges. The author wishes to acknowledge Marita Ljønes and Arnljot Strømseng for their contribution in sample collection and chemical analysis. The students Ane Marie Beck and Thea Lund Read from Oslo University College (HiO) contributed to the preparation of spiked Sb-materials. The deputy Marianne Bergh from HiO contributed to the XRF-analysis and preparation of peat soil.

Kjeller, December 2011

Espen Mariussen

1 Introduction

1.1 Background

In Norway there are approximately 65 military areas for small arms training in which more than 500 shooting ranges are distributed. These areas are the major deposits of residues from use of small arms ammunition, and may pose a threat to wildlife and domestic animals drinking or grazing on the contaminated area. The composition of the bullets in small arms ammunition may vary, but the most frequently used ammunition consists typically of lead (Pb), copper (Cu), zinc (Zn) and antimony (Sb). It has been estimated a mean annual deposition of approximately 111, 68 and 13 metric tons of Pb, Cu and Sb respectively in Norwegian military small arms shooting ranges for the years 2004-2008 (Reistad et al., 2009). Recently, so-called environmentally friendly small arms ammunition, made primarily by steel and copper, has replaced the use of lead ammunition, but still most of the spent lead bullets are left untouched in the berms.

Antimony has been used as alloy in conventional lead bullets to increase the hardness of the bullets. The most frequently used small arms ammunition used by the Norwegian military contain approximately 8% Sb (Voie and Strømseng, 2000). Antimony is a metalloid belonging to the same subgroup in the periodic table as arsenic (As) and shares some of its physical and chemical properties (Gebel, 1997; de Boeck, 2003). This has made it a so-called pollutant of interest by the environmental authorities in U.S. and E.U. (Filella et al., 2002a). E.U. and U.S. EPA have established goals on maximum admissible concentrations of Sb in drinking water of 5 µg/l and 6 µg/l respectively (Filella et al., 2002a; McCarty et al., 2004). These estimates can be regarded conservative due to the lack of adequate toxicity studies. To assess the mobility of metals in solid waste, and to classify hazardous waste and evaluate its leaching potential in a landfill, standard procedures of leaching tests are established. Such tests, both at our institute and elsewhere, have shown that antimony apparently has a high mobility in soil. Therefore, solid wastes containing Sb are often classified as hazardous materials. It is therefore important to establish adequate methods for the analysis of Sb to make proper evaluations of environmental fate of this compound, both in the field and at the laboratory.

Standard methods to extract Cu and Pb in soil samples is microwave assisted digestion of the samples in concentrated nitric acid (HNO₃). Nitric acid is usually sufficient to obtain good recovery of a range of elements in soil, including Cu, Pb and Zn (e.g. Tighe et al., 2004). For some elements, however, nitric acid is not sufficient and other acids or combinations of acids must be applied, such as hydrochloric acid or hydrofluoric acid based digestion. Several reports have shown poor recovery of antimony in soil samples with the use of nitric acid, especially in samples with high silicate content (Tighe et al., 2004; Telford et al., 2008, Chen and Ma, 2001). It is known that Sb form insoluble complexes with silicates (Nash et al., 2000). Poor recoveries have also been reported due to the loss of volatile Sb compounds during the heating process of the digestion procedure (Tighe et al., 2004). Recovery of elements and other chemicals from an extraction procedure is dependent both on the matrix and the agents used for the extraction. To

avoid erroneous results and unnecessary use of hazardous extraction agents it is important to evaluate different procedures.

X-ray fluorescence (XRF) is a powerful method for element analysis, especially in soil and alloys. Handheld and portable XRF-instruments, such as Thermo Scientific Niton XRF, are convenient instruments to define the area that is influenced from pollution in the field. The portable instruments are, however, less sensitive and accurate than traditional laboratory equipment, such as ICP-MS. The sensitivity to different elements also varies substantially.. Other factors that can influence detection limits and accuracy are the content of moist, organic materials and particle size. It is therefore important to compare the analyses from the portable field instruments with more reliable and accurate in-house laboratory instruments.

1.2 Main Objectives

The main objectives of this work have been to evaluate some aspects about antimony analysis and fate in environmental samples, and compare with lead and copper. The work has focused on three main objectives:

- Evaluate recovery of Sb in soils and biological materials after extraction with different digestion methods.
- Evaluate the leachability of Sb in soil from shooting ranges with standard leaching tests in order to determine the easily exchangeable fraction of Sb.
- Compare analyses of Sb, Cu and Pb in soil between a portable XRF instrument and an ICP-MS instrument.

To evaluate recovery of Sb after extraction of soils we have in this report compared three different digestion methods. The extraction solutions tested were nitric acid, a combination of nitric acid and HCl (Aqua Regia) and a combination of nitric acid and hydrofluoric acid (HF). HF is used to completely dissolve the sample, but is a highly corrosive and toxic acid. Therefore, it would be convenient to avoid use of this acid. Two soil types, one with high and one with low content of organic materials, were spiked with known amounts of Sb. In addition to soil, a sample of cod were spiked with Sb and subjected to different extraction procedures.

It appears that Sb from small arms ammunition is very mobile. To evaluate the leachability of Sb in soil from shooting ranges, different soil types were subjected to standard leaching tests in order to determine the easily exchangeable fraction of Sb in the soil and compare it with total amount, assessed with Aqua Regia digestion. The same soil samples were, in addition, analyzed by XRF and subjected to microwave assisted digestion with nitric acid, Aqua Regia and HF followed by analysis on ICP-MS for comparison.

2 Materials and methods

2.1 Materials and Methods

2.1.1 Sample description

Six soil samples from Hjerkin firing range were collected summer 2007. The soil samples were taken from berms, which was a mixture of local soil and soil from a copper mine near the firing range. The soils sampled have, therefore, a natural high content of Cu. Some further details about the area and the sampling are reported in Strømseng et al., (2008). The soil samples were sieved and the fractions < 2mm were subjected to further analysis and investigations. The soils were subjected to ignition loss analysis and had less than 2.5% organic matter (Strømseng et al., 2008). Peat samples were collected summer 2011 at Avgrunnsdalen and Steinsjøen small arms shooting ranges. The peat samples were dried at 105°C for approximately 24 hours and grounded by hand in plastic zip lock bags and subjected to XRF analysis and prepared for ICP-MS analysis as described below.

2.2 Sample preparation

2.2.1 Preparation of soils for leaching test

The < 2mm fractions of the mineral soil collected from Hjerkin shooting range were grounded to powder with a crushing mill. 100 g of the soil was added 1 L of deionized water (liquid – solid ration of 10) in a Duran flask and put into a Reax overhead mixer. An aliquot of 25 ml water was taken out and filtered through a 0.45 µm filter after approximately 1, 3, 8, 24, 36 and 48 hour. pH of the soil-water mixture was measured ahead of each water sampling. This time lag also enabled the coarser particles to settle. The water samples were conserved with 0.5% nitric acid and analyzed for Sb, Cu and Pb on ICP-MS. After the last sampling, the soil was dried at 105°C for approximately 24 hours and homogenized in a porcelain mortar. To estimate loss of Sb, Cu and Pb the soils were subjected to element analysis on ICP-MS after micro wave digestion with two different extraction methods, nitric acid and Aqua Regia digestion respectively, as described in detail below.

2.2.2 Spiking of soils with Sb

An aliquot of a < 2 mm fraction of mineral soil, collected near our institute at Kjeller and assumed not to be contaminated with Sb, was crushed in a mill and burned at 550°C over night to remove organic materials. The soil was then spiked with a standard solution of Sb (Sb-tartaric acid, Spectrascan certified reference material) to concentrations corresponding to 0.1, 1, 10 and 100 mg/kg respectively. To ensure that the Sb solution was properly dispersed into the soil material, the soil was added excess deionized water and mixed for approximately 2 hours. The spiked soil was then dried at 105°C for approximately 24 hours and homogenized in a crushing mill. A peat sample, assumed not to be contaminated with Sb, was collected from a bog near the town of Lillehammer, Norway. The peat was dried at 105°C for approximately 24 hours and homogenized in a porcelain mortar and then spiked with 0.1, 1, 10 mg/kg Sb as described for the

mineral soil. The spiked peat samples were dried at 105°C for approximately 24 hours and homogenized in a crushing mill.

2.2.3 Spiking of a cod sample with Sb

Filets of frozen cod were purchased from a grocery store and homogenized in a food processor. The cod sample was then spiked with a standard solution of Sb (Sb-tartaric acid, Spectrascan certified reference material) to a concentration corresponding 5 mg/kg (final concentration on a dry weight basis). To ensure that the Sb solution was properly dispersed into the material it was added excess deionized water and mixed for approximately 2 hours. The spiked cod was added to a porcelain mortar and dried at 105°C for approximately 24 hours and then homogenized in the mortar.

2.3 Digestions procedures

2.3.1 Digestion of soils

Aliquots of approximately 0.3-0.4 g of soil and peat were subjected to micro wave assisted digestion with different acids with a final volume of 10 ml of nitric acid (1:1 mixture of water and concentrated nitric acid respectively), Aqua Regia (1:3 mixture of concentrated nitric acid and HCl respectively) or HF (1:3 concentrated HF and nitric acid respectively). The samples were digested in a micro wave oven with the following temperature program: 9°C/min to 180°C, followed by 5 min at 180°C, 2°C/min to 200°C followed by 10 min at 200°C. After digestion, the samples were allowed to cool down to room temperature into their vessels before transfer to 50 ml polyethylene vials (Sarstedt) with deionized water. To assess recovery of Sb, a certified soil reference material (GBW07406, Institute of Geophysical and Geochemical Exploration) was subjected to micro wave assisted digestion with Aqua Regia at different temperatures. Similar program as described above was used, however, the peak temperature was adjusted to 130°C, 150°C and 160°C respectively.

2.3.2 Digestion of fish

Approximately 0.5g of cod samples were subjected to digestion with final volume of 10 ml of nitric acid (1:1 mixture of water and concentrated nitric acid respectively), nitric acid and hydrogenperoxide (1:1 mixture of concentrated nitric acid and 25% hydrogen peroxide respectively) and Aqua Regia (1:3 mixture of concentrated nitric acid and HCl respectively). The digestion was performed in Teflon coated vessels in microwave oven as described for soil and peat, or at room temperature in the ventilation hood at the laboratory.

2.4 Analysis of elements on ICP-MS

The elements Sb, Cu and Pb were analyzed on ICP-MS (Thermo X-series II). The samples were added internal standard for correct quantification. A four point standard curve was prepared (0.1-1000 ppm) for quantification. Procedure blanks were regularly prepared to control background contamination, and reference materials of water (Analytical reference material, TM 23.4, Lot no. 1010 and TMDA 61.2, Lot no. 0510 from Environment Canada, Canada), and soil (GBW07406,

Institute of Geophysical and Geochemical Exploration) were prepared and analyzed to ensure correct estimate of the element concentrations.

2.5 Ignition loss

The organic matter in the soil was determined gravimetrically. Aliquots of approximately 5 g of the soil, predried at 105°C for approximately 24 hours, were burned at 550°C over night to remove organic materials. The residue was considered as the mineral portion of the samples.

3 Results and Discussion

3.1 Micro wave assisted digestion of antimony in soil

3.1.1 Spiked soil samples

Two soils, one peat soil and one mineral soil, were spiked with 0.1-100mg/kg Sb and subjected to Aqua Regia and nitric acid digestion. It was revealed with Aqua Regia digestion that the soil control contained some Sb (Table 3.1), approximately 1 mg/kg in both soil types. Due to the content of Sb in the control soil we were not able to evaluate reliable recovery data in the 0.1 and 1 mg/kg spiked soils. The soils added 10 and 100mg/kg Sb, in addition to the soil reference material (GBW07406) gave more reliable results. Recovery of Sb depended both on soil type and digestion method. With nitric acid, only 3% and 5% recovery of Sb in the mineral soil was obtained (Table 3.2). With use of Aqua Regia it was obtained recoveries between 66 and 91% of the nominal Sb concentrations. An interesting observation was that nitric acid obtained much better recovery in peat than in mineral soil. The peat used in this study had a high organic content, approximately 90%, showing that Sb adsorbed to organic material is more available for release than Sb in mineral soil. Humic and fulvic acids, which are the principle components in peat, are low and high molecular weight aromatic substances with primarily carboxylic and phenolic substituents, in addition to sugar and ether moieties. The carboxylic and phenolic functional groups contribute to a negative surface charge enabling complexation with cations. Sb primarily exists as the negatively charged SbOH_6^- (Filella et al., 2002) and is probably less adsorbed to the peat surface. Mineral soil contains different silicates minerals and less organic matter and it is known that Sb may form insoluble complexes with silicates (Nash et al., 2000). In addition, Sb is associated with iron oxyhydroxides and sulfides. HCl may, at elevated temperatures and pressure, dissolve silicate, iron and sulfide minerals (Telford et al., 2008). Apparently, however, some nitric acid is needed to release Sb from organic materials (Telford et al, 2008).

Hydrofluoric acid is often used to completely dissolve soil samples, even samples with high silica content. HF is proven effective in releasing Sb from silicates (Tighe et al., 2004; Telford et al., 2008, Chen and Ma, 2001). HF is, however, extremely toxic and corrosive making it advantageous to use alternatives, such as Aqua Regia. The HF digestion of spiked material and reference soil gave recoveries of approximately 120% in both the 100 mg/kg soil and the reference soil (Table 3.2). Whether the high recovery was due to coincidences or indicates that

HF-digestion is a more sensitive method to systematic errors remains to be elucidated. However, digestion of soil from Hjerkin firing range, as presented below (Table 3.4), showed no significantly difference in recovery of Sb in soil between Aqua Regia digestion and HF-digestion indicating that Aqua Regia is adequate for measuring total Sb in soil samples. Some precautions must, however, be taken when using Aqua Regia. It has been shown that Sb may be lost due to volatilization of SbCl₃ and SbCl₅ from the HCl media (Nash et al., 2000; Hjortenkrans, et al., 2009). It is, therefore, important to keep the vessels closed until they have reached approximate room temperature, enabling the Sb components to condense. The relative standard deviations of the analyses of the spiked samples from Aqua Regia digestion were below 15% indicating high precision and repeatability of the methods used (Table 3.2).

Table 3.1 Concentrations of Sb (mean ± Sd (median)) in the control soils (n = 4), used for the spiking experiments, after microwave oven assisted digestion with Aqua Regia and HNO₃.

Control soil	Aqua regia	HNO ₃	Ignition loss
Mineral soil (mg/kg)	1.1 ± 1.1 (0.7)	0.02 ± 0.01 (0.02)	
Peat soil (mg/kg)	0.9 ± 0.2 (0.9)	0.5 ± 0.1 (0.5)	91 %

Table 3.2 Recovery of Sb in soils (mean ± Sd (median)) spiked with Sb and reference soil (GBW) and relative standard deviations (%) of the analyses. The soils (n = 4) were subjected to microwave oven assisted digested on with three different acids.

Recovery	HF	Aqua regia	HNO ₃
Mineral soil (10 mg/kg)	68 ± 9.3 (66) 14%	66 ± 4.4 (66) 6.7%	2.8 ± 2.4 (3.0) 84%
Mineral soil (100 mg/kg)	118 ± 20 (111) 17%	82 ± 4.1 (82) 5.0%	5.1 ± 0.6 (5.1) 12%
Peat soil (10 mg/kg)		80 ± 1.4 (80) 1.6%	52 ± 3.4 (52) 6.5%
GBW soil (60 mg/kg)	120 ± 2.5 (120) 2.1%	91 ± 4.8 (91) 5.2%	4.8 ± 1.4 (4.2) 29%

3.1.2 Spiked fish samples

Fish fillet was homogenized, added Sb and dried to a nominal concentration of 5.1 mg/kg. The control sample contained only minor amount of Sb, approximately 0.2 mg/kg, prepared for analysis with the use of Aqua Regia as digestion method. The spiked fish was digested in a microwave oven with HNO₃, HNO₃ + H₂O₂ and Aqua Regia respectively. In addition, the fish sample was digested in room temperature over night with HNO₃ + H₂O₂. Recovery between 82 and 86% of nominal concentration of Sb was achieved for the samples digested in the microwave oven (Table 3.3). There were no significantly differences in recovery between the three digestion methods prepared in microwave oven (Table 3.3). Recovery of the fish sample digested over

night in room temperature was, however, significantly less than recovery obtained with use of microwave oven ($p < 0.001$, two sided student-t, different variance). Aqua Regia is a very corrosive acid mixture and other acid mixtures, such as HNO_3 , are preferred if possible. With the use of HNO_3 as digestion acid gaseous NO_x are formed. A mixture of $\text{HNO}_3 + \text{H}_2\text{O}_2$ is, therefore, convenient since the presence of H_2O_2 removes the gaseous NO_x that is formed and reoxidizes it to NO_3^- . In addition H_2O_2 increase the oxidation potential of the mixture. One major challenge, however, with biological materials is often a low content of metals making the material vulnerable to laboratory contamination. Estimated limits of quantification (defined as standard deviation of 11-13 analyses of blanks multiplied with 10) for Cu, Pb, Sb and Zn were 0,07; 0,14; 0,13 and 0,32 mg/kg respectively. One way to avoid contamination is to prepare the material in a clean-room and use dedicated equipment for trace analysis. In addition, the analytical instrument must have low and reliable detection limits.

Table 3.3 Recovery of Sb in fish (mean \pm Sd (median)) spiked with Sb and relative standard deviations (%) of the analyses. The fish fillet ($n \geq 4$) with a nominal concentration of 5.06 mg/kg was digested on microwave oven with three different acid mixtures.

Recovery	Aqua regia	$\text{HNO}_3 + \text{H}_2\text{O}_2$	HNO_3	$\text{HNO}_3 + \text{H}_2\text{O}_2^*$
Fish (5.06 mg/kg)	82 \pm 3.9 (82) 4.8%	85 \pm 1.6 (87) 1.9%	86 \pm 3.2 (87) 3.8%	70 \pm 3.2 (72) 4.7%

*The samples ($n = 3$) were left on the table in the acid mixture over night and then analyzed without microwave assisted extraction.

3.1.3 Soil samples from Hjerkin firing range analyzed with ICP-MS

In addition to spiked samples and reference materials, the soil samples collected from Hjerkin firing range were analyzed for Sb, Pb and Cu. The seven soil samples were digested with Aqua Regia, nitric acid and HF, six from Hjerkin firing range and one soli from Sessvoll that was assumed to be clean (Table 3.4). The analyzed concentrations of the different soils are summarized in Table 3.5. With the use of nitric acid, recovery of Sb was approximately 4% and 5% of the Aqua Regia and HF-extraction respectively, confirming that nitric acid is not suitable to extract Sb from mineral soil. HF is believed to completely dissolve the elements in the soil and represents the actual content of elements in the soil. Mean recoveries of Aqua Regia digested soil compared to HF were 92% \pm 4.2, 95% \pm 8.2 and 91% \pm 6.7 for Pb, Cu and Sb respectively. The differences in recovery between Aqua Regia and HF-digestion were not significant. Mean recoveries of nitric acid compared to Aqua Regia digested soil were 104, 104 and 5% of Pb, Cu and Sb respectively. These findings show that nitric acid is adequate for Pb and Cu extraction, whereas Aqua Regia or HF digestion should be used if Sb is included. HF is, however, a more hazardous chemical and Aqua Regia digestion should be preferred. As stated above, some precautions must, however, be taken when using Aqua Regia due to volatilization of SbCl_3 and SbCl_5 from the HCl media (Nash et al., 2000; Hjortenkrans, et al., 2009).

3.1.4 Peat samples from Avgrunnsdalen and Steinsjøen small arms shooting ranges analyzed with ICP-MS

Avgrunnsdalen and Steinsjøen small arms shooting range is located at peatland, and most of the ammunition residues are deposited in peat soil. The mineral fraction in peat might be less than 10% and the sorption behavior of the metals probably differs from that of mineral soil. Peat soils from Avgrunnsdalen and Steinsjøen were digested with nitric acid and Aqua Regia to compare yield of Pb, Cu and Sb. Compared to mineral soil the yield of Sb was much higher in nitric acid digested peat, confirming the findings from spiked peat showing that Sb adsorbed to organic material is more available for release than Sb in mineral soil (Table 3.5). Compared to Aqua Regia digestion, however, the recovery varied substantially and Aqua Regia is still the preferable acid for the digestion of Sb in peat soil.

Table 3.4 Concentrations (mg/kg) of Sb, Pb and Cu (mean \pm SD) in the soils from Hjerkin demolition area after microwave oven digestion with three different acids. Each soil sample was assayed in triplicate.

	Sb (HNO₃)	Sb (Aqua Regia)	Sb (HF)
Haukberget 1 (2), 07-028	23 \pm 2,7	239 \pm 26	258 \pm 37
Haukberget 2 (2), 07-029	10 \pm 0,4	201 \pm 21	211 \pm 33
Haukberget 4 (2), 07-031	2,2 \pm 0,5	45 \pm 15	58 \pm 30
Haukberget 5 (2), 07-032	5,3 \pm 1,9	1205 \pm 132	1192 \pm 223
Haukberget 8 (2), 07-035	1,5 \pm 0,7	19 \pm 11	21 \pm 8,9
Haukberget 20 (1), 07-162	3,2 \pm 0,8	832 \pm 34	939 \pm 77
Sessvoll	0,09 \pm 0,1	0,7 \pm 0,5	1.7 \pm 1.3

	Pb (HNO₃)	Pb (Aqua Regia)	Pb (HF)
Haukberget 1 (2), 07-028	2234 \pm 95	2265 \pm 220	2591 \pm 293
Haukberget 2 (2), 07-029	2061 \pm 293	1842 \pm 203	1878 \pm 267
Haukberget 4 (2), 07-031	374 \pm 32	494 \pm 169	561 \pm 252
Haukberget 5 (2), 07-032	10388 \pm 827	11192 \pm 1298	12286 \pm 2330
Haukberget 8 (2), 07-035	342 \pm 201	226 \pm 93	240 \pm 98
Haukberget 20 (1), 07-162	7403 \pm 433	7821 \pm 327	8843 \pm 685
Sessvoll	9,3 \pm 5,0	9,0 \pm 4,7	33 \pm 2.0

	Cu (HNO₃)	Cu (Aqua Regia)	Cu (HF)
Haukberget 1 (2), 07-028	782 \pm 55	737 \pm 14	652 \pm 14
Haukberget 2 (2), 07-029	1452 \pm 38	1381 \pm 90	1452 \pm 13
Haukberget 4 (2), 07-031	643 \pm 123	803 \pm 116	799 \pm 18
Haukberget 5 (2), 07-032	1505 \pm 541	1203 \pm 49	1019 \pm 30
Haukberget 8 (2), 07-035	1294 \pm 42	1090 \pm 21	1226 \pm 229
Haukberget 20 (1), 07-162	760 \pm 30	912 \pm 36	1082 \pm 342
Sessvoll	11 \pm 1,6	14 \pm 1,3	12 \pm 1.0

Table 3.5 Concentrations (mg/kg) of Sb, Pb and Cu (mean \pm SD) in peat soils from Avgrunnsdalen (A) and Steinsjøen (S) small arms shooting ranges after microwave oven digestion with two different acids. Each soil sample was assayed in triplicate.

Sample id.	Sb (Aqua Regia)	Sb (HNO ₃)	Cu (Aqua Regia)	Cu (HNO ₃)	Pb (Aqua Regia)	Pb (HNO ₃)
A11 0-15*	123	110	622 \pm 77	630	5577	4723
A23 0-15	197 \pm 57	157 \pm 15	278 \pm 69	242 \pm 48	1268 \pm 409	1085 \pm 215
A33 0-15	241 \pm 15	127 \pm 79	1730 \pm 57	1736 \pm 77	11062 \pm 572	11880 \pm 3181
A41 0-15	28 \pm 0.6	27 \pm 0.2	715 \pm 14	765 \pm 23	4393 \pm 95	4238 \pm 241
S03 0-15**	502 \pm 5.2	25 \pm 4.3	6833 \pm 205	5970 \pm 96	9538 \pm 278	8022 \pm 59
S13 0-15	631 \pm 20	125 \pm 65	5317 \pm 135	4660 \pm 257	12919 \pm 481	10756 \pm 583
S18 0-15	279 \pm 10	221 \pm 55	2896 \pm 7.3	3129 \pm 118	4780 \pm 96	5360 \pm 185

* A11 0-15 Aqua Regia extraction, Sb and Cu concentrations are presented as median. HNO₃ extractions are assayed only once. **S03 0-15 HNO₃ extraction is assayed in duplicate.

3.1.5 Analysis of Sb in mineral soil as a function of temperature

Microwave assisted digestion of soil for extraction of metals is dependent on temperature. HCl is shown to dissolve silicate, iron and sulfide minerals at elevated temperatures facilitating the dissolution of less soluble elements, such as Sb (Telford et al., 2008). To assess recovery of a soil reference material, the soil reference was subjected to microwave assisted digestion with Aqua Regia at different temperatures, 150°C, 160°C and 180°C respectively. Recovery of Sb was significantly reduced at lower temperatures (Figure 3.1).

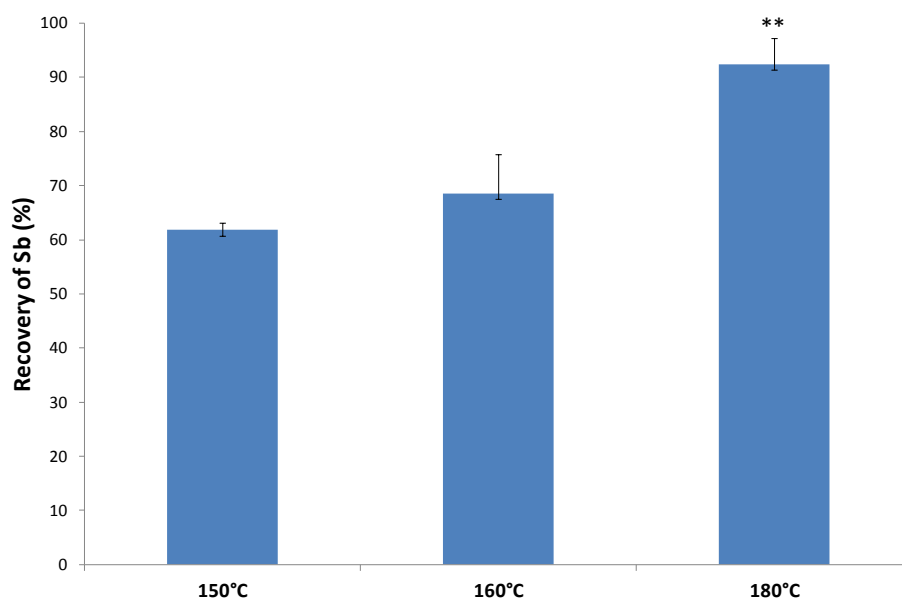


Figure 3.1 Recovery (%) of Sb from reference soil as a function of temperature. The results are presented as mean \pm SD from at least 4 replicates. The soil was extracted with Aqua Regia and has a nominal concentration of 60 mg/kg.

3.1.6 Other elements

The reference soil has known concentrations of a range of elements. In addition to Sb, Pb and Cu the recovery of 12 other elements from Aqua Regia and HNO₃ digestion were compared. The elements molybdenum (Mo), tin (Sn), titan (Ti) and tungsten (W) had significantly poorer recovery with HNO₃ than with Aqua Regia (Table 3.6). The recoveries of Ti and W were, however, low even with the use of Aqua Regia and further investigations must be performed to elucidate suitable extraction methods. Tungsten is widely used in ammunition and is an emerging contaminant in shooting ranges and demolition areas. Recovery of cadmium (Cd) was approximately 150%, which may be due to analytical interferences or laboratory contamination. This remains to be elucidated.

*Table 3.6 Recovery of 15 different elements after Aqua Regia and HNO₃ digestion respectively. The results are presented as mean recovery (% ± SD) from at least 4 replicates. The nominal concentrations are shown in brackets behind each element (**p<0.01, paired Student-t).*

Recovery (%) reference soil	Aqua Regia	HNO ₃
As (220 mg/kg)	91 ± 2 (91)	88 ± 2 (87)
Ba (118 mg/kg)	103 ± 7 (103)	103 ± 8 (100)
Cd (0,13 mg/kg)	146 ± 51 (155)	145 ± 43 (154)
Cr (75 mg/kg)	92 ± 6 (91)	88 ± 3 (87)
Cu (390 mg/kg)	100 ± 2 (100)	98 ± 3 (100)
Mn (1450 mg/kg)	95 ± 2 (96)	96 ± 2 (96)
Mo (18 mg/kg)	102 ± 8 (104)	66 ± 6 (66)**
Ni (53 mg/kg)	102 ± 3 (103)	100 ± 4 (101)
Pb (314 mg/kg)	95 ± 3 (95)	92 ± 3 (92)
Sb (60 mg/kg)	91 ± 5 (91)	5 ± 1 (4)**
Sn (72 mg/kg)	87 ± 2 (87)	40 ± 4 (41)**
Ti (4390 mg/kg)	38 ± 3 (37)	13 ± 1 (13)**
V (130 mg/kg)	95 ± 3 (95)	90 ± 2 (89)
W (90 mg/kg)	46 ± 17 (49)	1 ± 1 (1)**
Zn (97 mg/kg)	91 ± 4 (90)	90 ± 3 (90)

3.2 Soil samples analyzed with ICP-MS compared with a portable XRF

3.2.1 XRF-analysis of mineral soil from Hjerkinn firing range

The dried soil samples from Hjerkinn firing range were analyzed by XRF in order to compare with the data from the ICP-MS analysis. Both the < 2 mm fraction and the grounded fractions of the mineral soil from Hjerkinn were subjected to XRF analysis of Cu, Pb and Sb to evaluate the significance of particle size. There were generally a very good correlation between the XRF-analyses and the ICP-MS analyses of the elements analyzed in the mineral soils (Figure 3.2-3.4). However, provided that the ICP-MS analyses give the correct concentrations in the soil sample, the XRF underestimated the element concentration in mineral soil, particularly when analyzing on the < 2 mm fraction. An exception was the analyses of Cu in mineral soil of which the XRF-analyses of grounded and the < 2 mm fraction did not differ (Figure 3.4). The soil from Hjerkinn used in these experiments had a high natural content of Cu, which may lead to a different outcome with the XRF than if the soil only was influenced by Cu-containing ammunition. This remains to be elucidated. The XRF underestimated the Cu, Pb and Sb concentrations with a factor of approximately 1.3, 1.4 and 1.2 respectively in the grounded mineral soil fraction. The improved results with the grounded material may be due to a more homogenous sample or how the XRF is calibrated with regards to weight and density ratio. Analysis on grounded soil also reduced the detection limit of the elements tested. For example, Sb was not detected in the < 2 mm fraction of 3 of the soil samples, whereas it was detected in all of the grounded samples. The accuracy of the XRF-analysis was, however, low in the soil samples with less than 45 mg/kg Sb, as analyzed with Agua Regia digestion on ICP-MS. XRF should, therefore, not be used on mineral soil containing less than approximately 50 mg/kg Sb. More investigations are, therefore, needed to determine accurate detection limits, not only for Sb, but for the other elements as well.

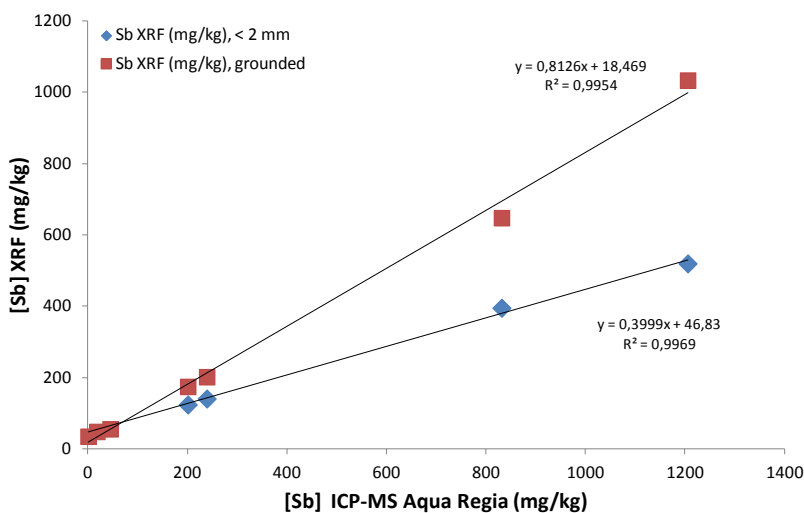


Figure 3.2 Correlation between ICP-MS analyses of Sb after Aqua Regia digestion and XRF analyses of Sb in soils from Hjerkinn firing range . XRF analyses were performed on both the < 2 mm soil fraction and grounded fraction. The results from the ICP-MS analyses are mean concentration of three independent digestions. The XRF analyses are mean concentrations from five independent measures.

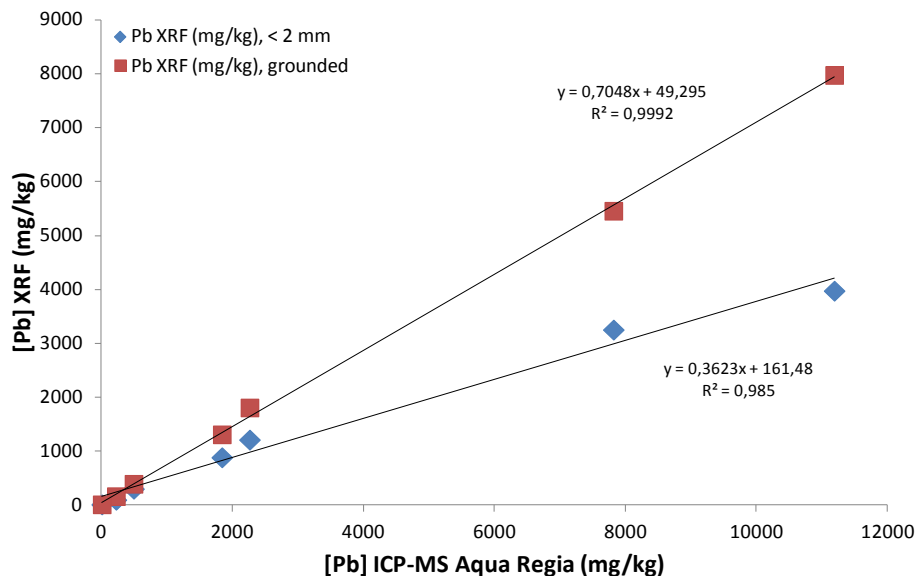


Figure 3.3 Correlation between ICP-MS analyses of Pb after Aqua Regia digestion and XRF analyses of Pb in soils from Hjerkind firing range. XRF analyses were performed on both the < 2 mm soil fraction and grounded fraction. The results from the ICP-MS analyses are mean concentration of three independent digestions. The XRF analyses are mean concentrations from five independent measures.

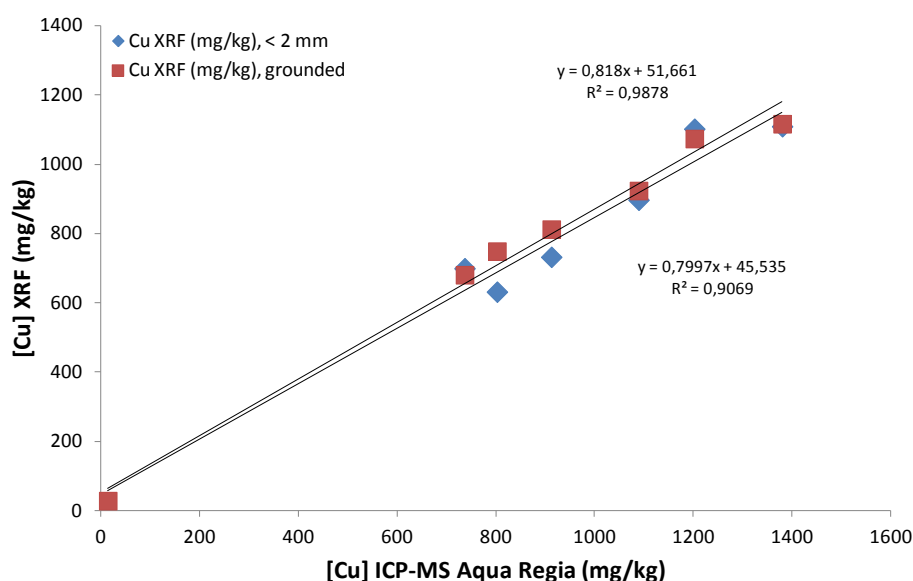


Figure 3.4 Correlation between ICP-MS analyses of Cu after Aqua Regia digestion and XRF analyses of Cu in soils from Hjerkind firing range. XRF analyses were performed on both the < 2 mm soil fraction and grounded fraction. The results from the ICP-MS analyses are mean concentration of three independent digestions. The XRF analyses are mean concentrations from five independent measures.

3.2.2 XRF-analysis in peat soil from Avgrunnsdalen and Steinsjøen small arms shooting range

There was a very good correlation between the XRF-analyses and the ICP-MS analyses of the peat soil. The XRF, however, overestimated considerably the Cu and Pb concentrations with a factor of approximately 1.5 and 2.5 respectively (Figure 3.5, 3.6). The reason for the discrepancy between mineral soil and peat soil might be how the XRF is calibrated. The ratio between volume and weight is much higher in dried peat soil than in mineral soil, which may lead to less accurate data. The XRF was not very suitable for Sb detection in the peat soil. Nevertheless, the XRF is quite sensitive for Pb, and in shooting range soil Sb and Pb are expected to correlate. Especially in the mineral soil from Hjerkin, the results showed that these two elements are correlated (Figure 3.7), but also in the peat soil from Avgrunnsdalen there was an increased Sb concentration as a function of the Pb-concentration (Figure 3.8). As an approximate rule the level of Sb in mineral soil is about one tenth of the Pb concentration, which is in agreement with the ratio of Pb/Sb in the bullets that was used by the Norwegian military (Strømseng and Voie, 2000). The concentration of Pb in the soil as measured with XRF, may, therefore, be used to estimate approximate concentrations of Sb. In peat soil, the Pb/Sb proportion was much higher, indicating less sorption of Sb in peat soil compared to mineral soil.

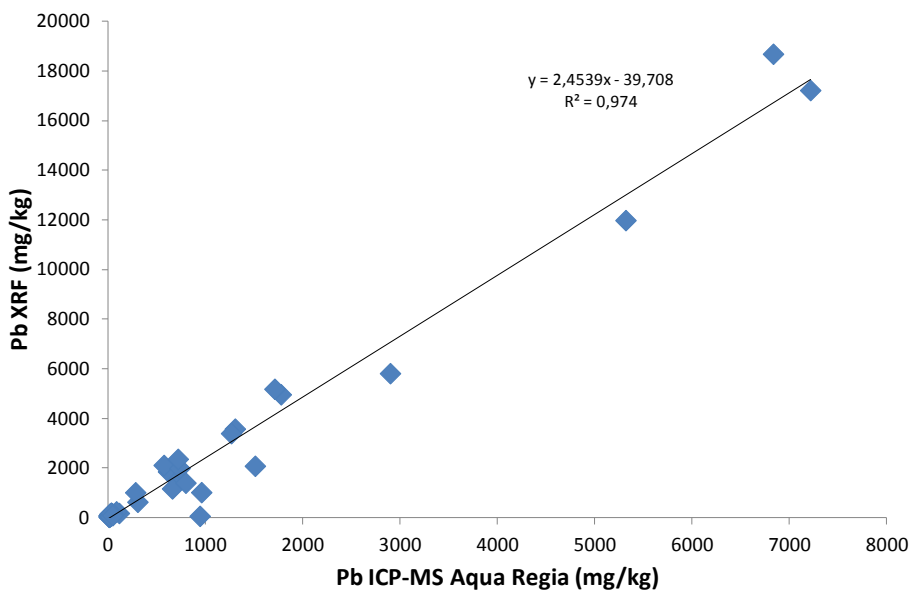


Figure 3.5 Correlation between ICP-MS analyses of Pb after Aqua Regia digestion and XRF analyses of Pb in peat soils from Avgrunnsdalen and Steinsjøen small arms shooting range. The results from the ICP-MS analyses are mean concentration of three independent extractions. The XRF analyses are mean concentrations from five independent measures.

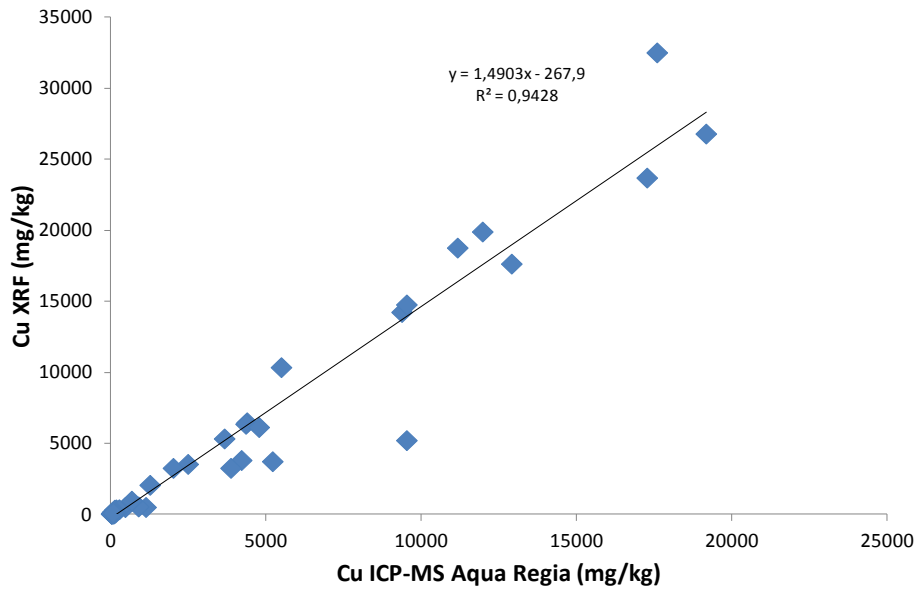


Figure 3.6 Correlation between ICP-MS analyses of Cu after Aqua Regia digestion and XRF analyses of Cu in peat soils from Avgrunnsdalen and Stensjøen small arms shooting range. The results from the ICP-MS analyses are mean concentration of three independent extractions. The XRF analyses are mean concentrations from five independent measures.

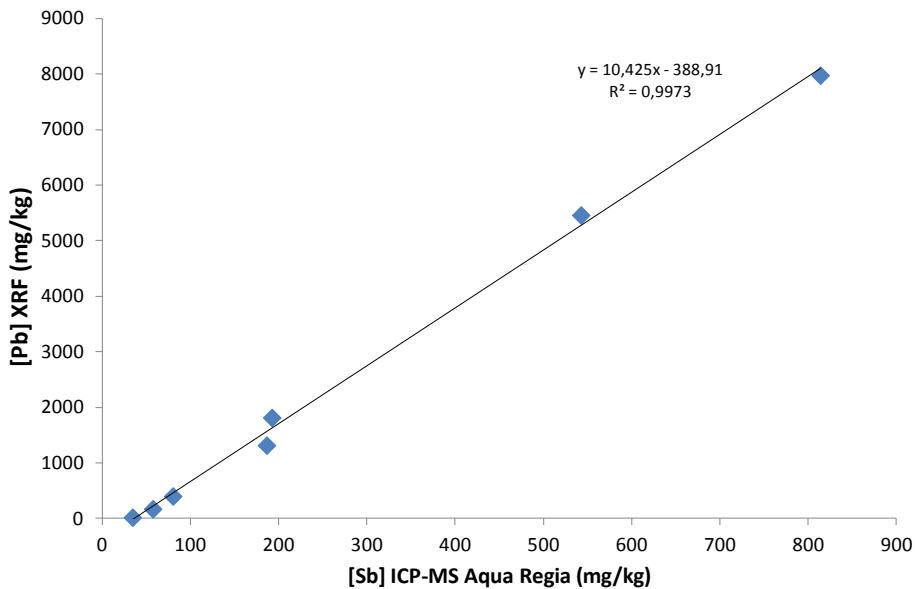


Figure 3.7 Correlation between ICP-MS analyses of Sb after Aqua Regia digestion and XRF analyses of Pb in mineral soils from Hjerkin firing range. The results from the ICP-MS analyses are mean concentration of three independent extractions. The XRF analyses are mean concentrations from five independent measures.

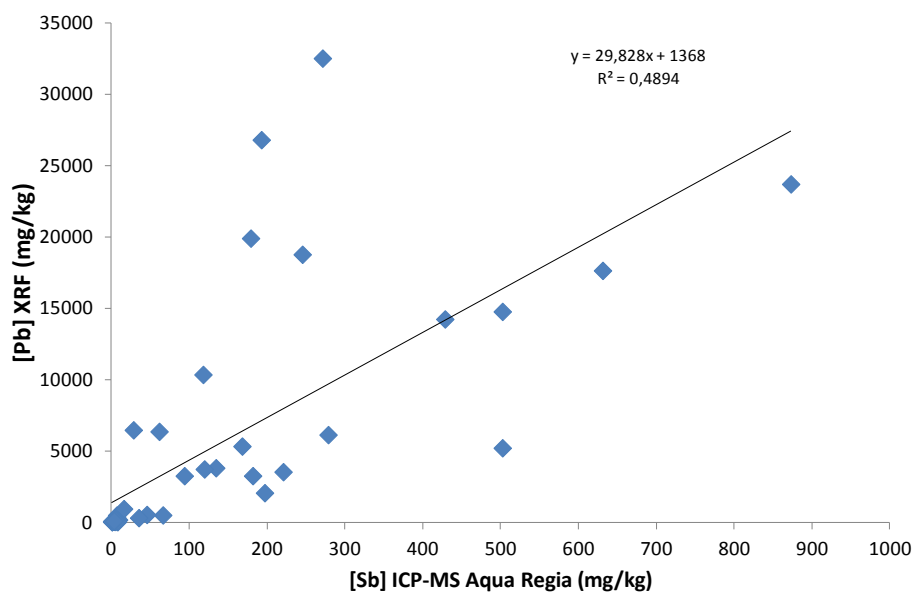


Figure 3.8 Correlation between ICP-MS analyses of Sb after Aqua Regia digestion and XRF analyses of Pb in peat soils from Avgrunnsdalen and Steinsjøen small arms shooting range. The results from the ICP-MS analyses are mean concentration of three independent extractions. The XRF analyses are mean concentrations from 5 independent measures.

3.3 Leaching tests of soil from berms at small arm shooting ranges

The seven different soil samples, six from Hjerkin and the one presumed non-polluted soil sample from Sessvoll were subjected to a leaching test. The soils contained different concentrations of elements and were analyzed for metals before and after the leaching test. Aliquots of 25 ml water was taken out and filtered through a 0.45µm filter after approximately 1, 3, 8, 24, 36 and 48 hour followed by analysis of Sb, Pb and Cu by ICP-MS. As shown in Figure 3.9, Sb was easily mobilized from the soil with a fast increase in the water Sb concentration followed by stabilization after approximately 24 hours. Table 3.7 shows the concentration in the extracts after 48 hours. The concentrations of Pb and Cu in the leachates were much lower and especially the Pb levels varied substantially. There was a significant correlation between the analyzed levels of Pb and Sb in the leachate and the soils (Figure 3.8), but no correlation was observed with Cu (Figure 3.9). It is known that soil used in berms at Hjerkin shooting range has a high natural content of Cu, which may reduce the significance of the contribution from the ammunition residues. The soil leachates had a relatively high pH of approximately 8.5. pH is perhaps the most important factor governing element mobility in soil. The mobility of Sb is expected to increase with pH, whereas mobility of Cu and Pb is expected to decrease with pH and the experimental conditions may have favored dissolution of Sb. The experiment is, however, performed according to standard procedure to evaluate leaching potential of waste (CEN 2005), with the exception that in this experiment grounded materials have been used. Grounding the materials increase the surface-volume ration of the soil. This probably will

favor increased release of the metals. In addition, grounding may have created conditions that increased the pH, but this remains to be elucidated.

Table 3.7 Concentration of Pb, Cu and Sb in leachates (µg/L) after 48h shaking on a Reax overhead mixer. The results are presented as mean ± SD from three separate experiments.

	Pb (ug/L)	Cu (ug/L)	Sb (ug/L)	pH
Haukberget 1 (2), 07-028	6.3 ± 0.3	84 ± 5.3	1670 ± 176	8.9
Haukberget 2 (2), 07-029	2.5 ± 0.4	38 ± 2.0	1020 ± 178	8.8
Haukberget 4 (2), 07-031	0.26 ± 0.1	34 ± 2.0	308 ± 97	8.9
Haukberget 5 (2), 07-032	85 ± 1.7	58 ± 0.8	2328 ± 87	8.8
Haukberget 8 (2), 07-035	0.12 ± 0.02	42 ± 1.4	97 ± 46	8.8
Haukberget 20 (1), 07-162	96 ± 13	117 ± 9.0	3817 ± 231	8.6
Sessvoll	1.6 ± 0.6	14 ± 1.2	1.2 ± 1.1	8.8

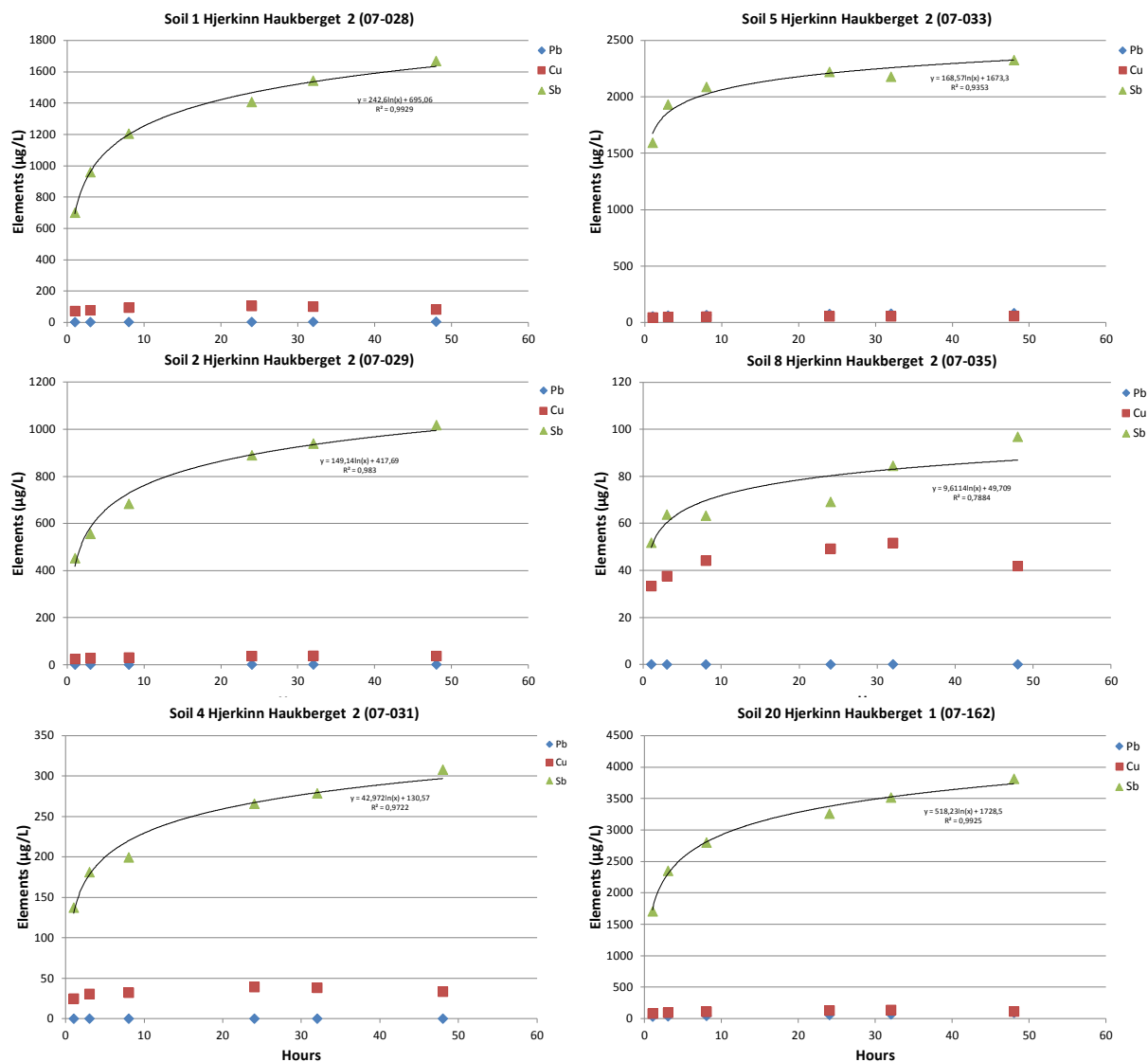


Figure 3.9 Concentrations of Sb, Cu and Pb as a function of time in leachates from the leaching tests of soils from Hjerkin demolition area. Each point is the mean of three independent experiments.

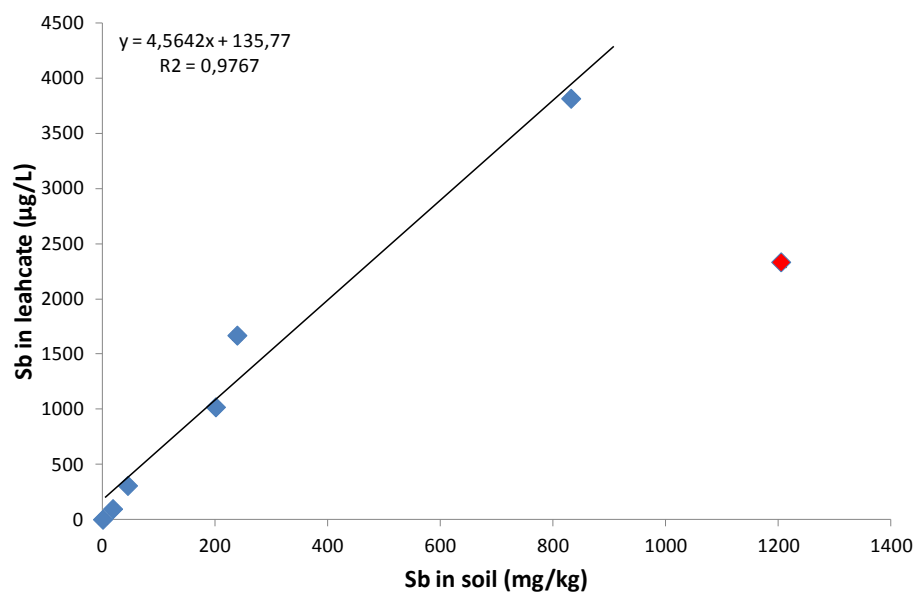


Figure 3.10 Correlation between Sb in leachates after 48 hours leaching test and the concentration of Sb in the soils analyzed after Aqua Regia digestion. The point in red is regarded as an outlier and was not included in the regression analysis. The results are mean concentration of three independent extractions.

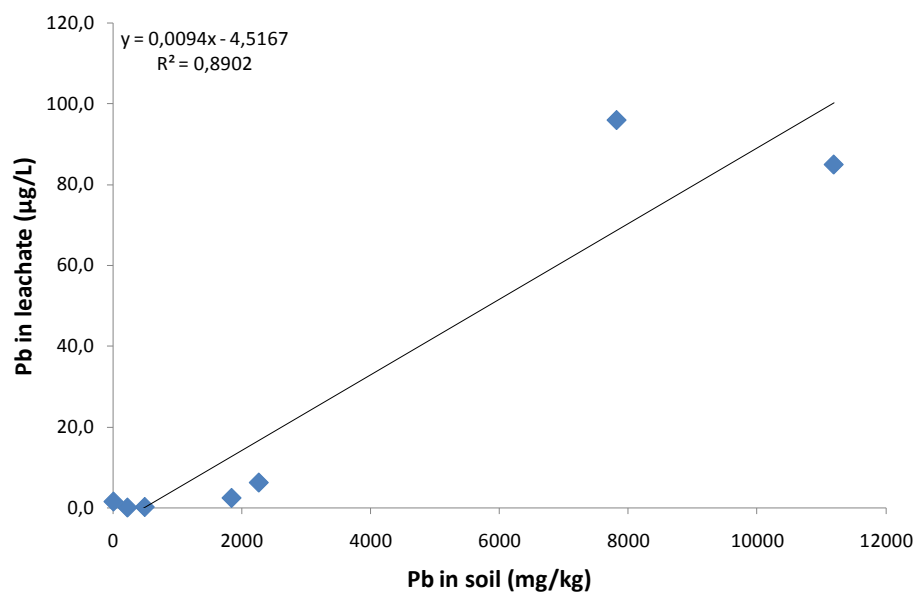


Figure 3.11 Correlation between Pb in leachates after 48 hours leaching test and the concentration of Pb in the soils analyzed after Aqua Regia digestion. The results are mean concentration of three independent extractions.

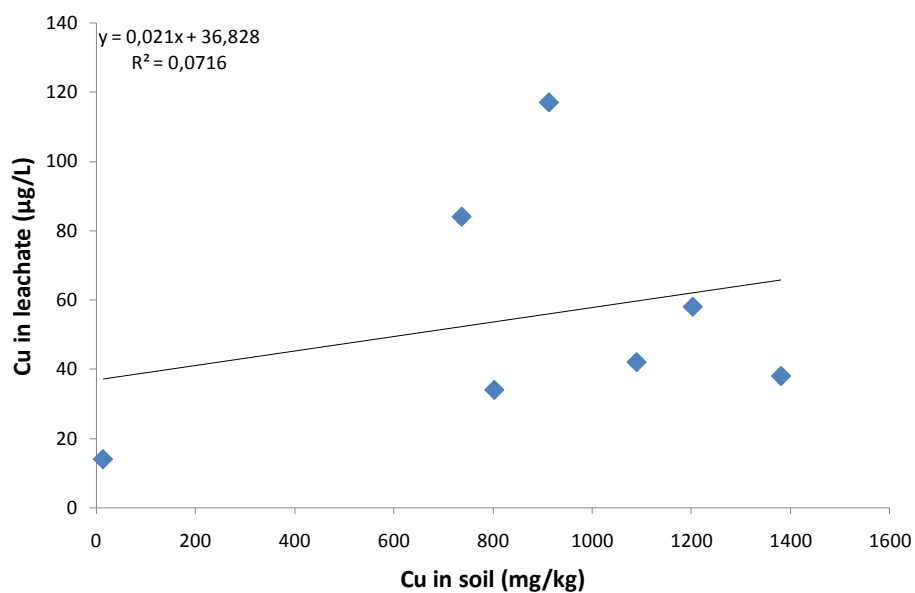


Figure 3.12 Correlation between Cu in leachates after 48 hours leaching test and the concentration of Cu in the soils analyzed after Aqua Regia digestion. The results are mean concentration of three independent extractions.

To indicate the proportion of elements that were lost during the leaching test, the soil samples were dried and subjected to analysis after Aqua Regia digestion. Based on the total amount of elements that leaked out from the soils and total element concentrations in the soil, the proportion of element concentration lost during the leaching test were estimated. The proportion of Pb, Cu and Sb that leaked was estimated to 0.004% (± 0.004 SD), 0.07% (± 0.04 SD) and 4.8% (± 1.8 SD) respectively. There was, however, no significant difference between concentrations in the soil samples before and after the leaching test (data not shown), indicating that the loss is too small to be detected by regular digestion procedures. Nevertheless, these findings show that a considerable portion of Sb was mobilized, whereas only a small fraction of Pb and Cu were released from the soil during the leaching test. An interesting observation was that the estimated leachable portion of Sb is very similar to the proportion of Sb extracted with nitric acid digestion, which was estimated to 4.9 % (± 3.9 SD). Whether the nitric acid digestible amount of Sb can be regarded as the mobile portion in soil remains to be elucidated, for example by sequential extraction or extractions of soil subjected to repeated leaching tests. A preliminary experiment of the latter was performed by doing leaching test of two of the soils that already had been subjected to leaching test. The experiment was repeated two additional times. The proportion of Pb and Cu that was mobilized varied. A higher proportion of Pb was mobilized, whereas similar amount of Cu was mobilized (Table 3.8). Although less compared to the first leaching test, a considerable amount of Sb was still mobilized, indicating that Sb in contaminated soil has a considerable shorter half-life compared to Cu and Pb. In the second leaching test, the pH of the water, percolating the soils, was even higher than in the previous experiment, between 9.1 and 9.3, indicating that the soil properties were changed. These findings indicate a complex adsorption behavior in the soil of the elements tested, which may e.g. include saturation conditions, pH, ion-exchange and contact time between water and soil.

A column experiment with analysis of water fractions should be performed to test mobilization of elements as a function of water volume percolating the soil.

Table 3.8 Concentrations of elements in leachates after three successive 24 hours leaching tests (ext) of soils from Hjerkin firing range. The results are mean \pm SD concentration of three independent experiments.

	1. ext	2. ext	3.ext
	Pb (ug/L)		
Haukberget 1	4.8 \pm 0.2	14 \pm 5.6	52 \pm 1.5
Haukberget 20	62 \pm 7.3	167 \pm 13	177 \pm 25
	Cu (ug/L)		
Haukberget 1	107 \pm 4.3	56 \pm 4.3	65 \pm 10
Haukberget 20	133 \pm 5.1	125 \pm 10	104 \pm 12
	Sb (ug/L)		
Haukberget 1	1408 \pm 91	315 \pm 8.0	319 \pm 3,3
Haukberget 20	3263 \pm 210	1281 \pm 128	1157 \pm 43

4 Conclusions

Mineral soil and peat soil were subjected to micro wave assisted digestion with different acids. Digestion of mineral soil with nitric acid is adequate for Pb and Cu extraction, whereas Aqua Regia or HF have to be used for Sb. HF is a highly toxic and corrosive acid, and Aqua Regia is, therefore, the preferable acid for Sb extraction. The recovery is dependent on extraction temperature. Although the recovery of Sb in peat soil with the use of nitric acid was much higher than in mineral soil, peat soils should also be extracted with Aqua Regia. Sb form insoluble complexes with silicates and an increased portion of the mineral fraction in the soil will reduce Sb-recovery with the use of nitric acid as digestive. Biological material can be digested with nitric acid in combination with some hydrogen peroxide. When preparing biological materials for analysis one should be particular aware of laboratory contamination since biological materials often contain only trace amount of certain metals.

The portable XRF instrument is convenient for use in the field for analysis of metals in soil. This study shows a very good correlation between actual level in mineral soils of Pb and Cu, measured with ICP-MS and Aqua Regia digestion, and XRF-analysis. The XRF tend to underestimate Pb and Cu concentration in mineral soil and overestimate the concentration in peat soil. This might be due to how the instrument is calibrated.

The XRF is less suitable for Sb analysis, especially in peat soil, but may be used on grounded mineral soil if the concentration is higher than 50 mg/kg. Nevertheless, the XRF is quite sensitive for Pb, and in shooting range soil Sb and Pb are expected to correlate.

Standard leaching test shows that Sb is readily mobilized into the water fraction from contaminated soil. The mobility of Sb is considerable higher than that of Cu and Pb and it appears that the Sb extracted with nitric acid is the mobile fraction. The amount of Sb in the leachate correlated with the amount in soil.

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