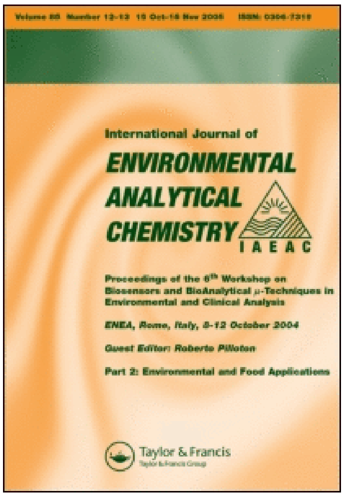

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Sample preparation and digestion considerations for determining metal deposition at small arms ranges

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Sample preparation and digestion considerations for determining metal deposition at small arms ranges

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Determining the metal content of soil collected from small arms training ranges (SARs) is difficult and controversial because the contamination consists of fine particulates abraded from bullets and larger fragments such as intact bullets and spent shell casings. This heterogeneous distribution of materials can be difficult to sample reproducibly and difficult to prepare for analysis. Similar issues are encountered with sampling and analysing solid residues of energetic compounds for which grinding to 75 microns is necessary to achieve excellent precision. Issues to be resolved for SAR metals include the necessity of sieving, the extent of contamination from grinding, and the proper digestion procedure for efficient recovery. The work reported in this manuscript employed field and laboratory sampling approaches developed for energetics and examined a variety of laboratory sample preparation techniques for SAR metals. Application of the sampling approaches used for energetics to metals was straightforward. The US Environmental Protection Agency (USEPA) nitric acid digestion procedure is effective for the recovery of three of the most important SAR metals, copper, lead and zinc, when analysing a 2 g portion of the <2 mm fraction of an unground soil sample. However, sieving the sample ignores a large portion of the total metal load and a total digestion with hydrofluoric acid is necessary to determine the concentration of all naturally-occurring metals in the sample. Finally, the USEPA-approved method for metal analysis is inappropriate for tungsten unless supplemented with phosphoric acid.

Keywords: soil contamination; tungsten; lead; copper; sample preparation

1. Introduction

Contamination from small arms ranges (SARs) is a problem of international significance [1–3] because large quantities of metals are deposited in surface and near-surface soil. For example, soil samples from the backstop berms at shooting ranges have contained as much as 60,600 mg kg^{-1} of lead [4].

At a typical military SAR, the soldier faces the target and fires the projectile towards a target and into a backstop berm. The two mechanisms at work to scrub energy to stop the projectile are displacement of soil particles and fragmentation. Although fragmentation

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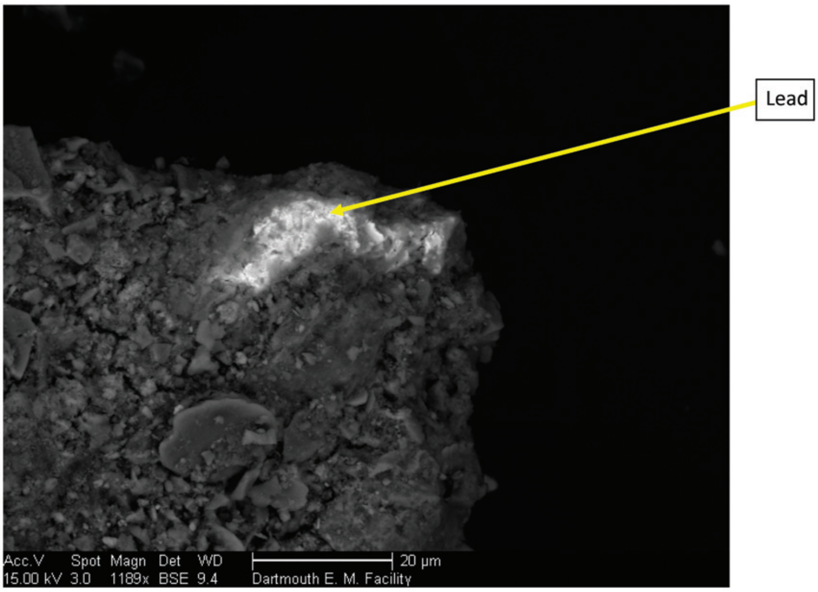

Figure 1. Scanning electron microscope photograph of lead fragment smeared onto soil grain surface.

may occur [5,6], the 5.56 mm round for the M-16, the most widely used projectile at military SARs in the USA, is designed to remain mostly intact upon impact, explaining why much of the metal on military ranges is found as particles >2 mm in diameter [5]. Concerns about lead, usually the SAR metal of most concern, have led to some recent use of tungsten projectiles. The latter consist of a steel penetrator followed by a tungsten/nylon slug, with a propellant cartridge and ignition cap. Both lead and tungsten bullets are jacketed with an alloy consisting primarily of copper and zinc [7,8]. Based on field reconnaissance, projectiles with intact jackets as well as fragments of jacket material, steel penetrators and chunks of projectiles can be found; however, a small quantity of fragments, too small to be readily visible, are also produced (Figure 1).

The range of particle sizes has resulted in controversy regarding how best to collect and prepare field samples for analysis – in particular because of previous work examining the heterogeneous distribution of energetic compounds such as RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and TNT (trinitrotoluene) on other types of military training ranges [9–11]. Besides the concerns regarding the particle size distribution, properly sampling, preparing, analysing and interpreting data from SARs is a problem exacerbated by the high level of deposition and the potential for change through time as the particles on the land surface corrode due to wind, rain and temperature [12,13]. For these reasons, the regulatory community has requested personnel at US military sites to apply techniques used for energetic residues to the determination of metal contamination. Sampling and sample preparation methodologies previously applied to energetics and used in this study were multi-*increment*® (multi-*increment*® is a registered trademark of EnviroStat, Inc. Fort Collins, Colorado) field sampling (typically 100-increments) [14] and multi-*increment*® (typically 20-increments) subsampling of the field sample to create the final subsample for preparation and analysis. Two grams was selected as the size for the analytical sample as representing the best compromise between using the largest sample possible and minimising problems with quantities of acid and size of sample digestion equipment. How best to obtain and prepare a 2 g sample from a SAR site, therefore, was the principal question addressed in this study.

2. Background

2.1 *Comparison of heterogeneity of distribution of small arms range metals and energetics*

The heterogeneity of munition residues on military training ranges has been recognised for some time. It had been suggested that agreement within a factor of four was adequate comparison criteria for energetics for sample splits or co-located samples submitted to different analytical labs [15]. But even this seemingly lenient criterion was difficult to accomplish. One study reported that the standard method with 2 g subsamples (sieved to <0.6 mm by hand-grinding), collected from a mortar impact area and analysed for the explosives RDX, and HMX, showed a factor of 25 variation for HMX while RDX results barely satisfied the factor of four criteria [11]. At a grenade range, these investigators reported RDX results varied by a factor of approximately seven, TNT by a factor of approximately five, and HMX was detected in only one third of the samples. Clearly, with this type of data, it is virtually impossible to make a decision regarding disposition of a contaminated site.

When these investigators used $\sim$50 g analytical subsamples (an increase by a factor of 25) of the aforementioned sample from the grenade-range with the samples ground or sieved to <2 mm, the mean Relative Standard Deviation (RSD) for RDX, TNT and HMX remained unacceptably high, ranging from approximately 70 to $>260\%$. Finally, the study reported that grinding a $\sim$4 kg field sample to approximately 75 microns and then analysing 10–50 g subsamples reduced the RSDs for RDX, HMX and TNT to $<10\%$.

Thus, before examining sample preparation techniques, it was critical for this investigation to evaluate whether 2 g analytical subsamples from SARs could yield sufficient reproducibility. In extensive sampling of nine SARs reported elsewhere [16,17], 76 pairs of subsamples were evaluated. The subsamples were obtained from 3–5 kg field samples (a similar sample size for which RSDs for energetics ranged from $\sim$24 to 60% [11]) obtained by combining 100 increments in the field. The field samples were sieved to <2 mm from which the 2 g analytical subsamples was obtained. The field samples, by means of separate subsampling, were subjected to duplicate or triplicate analyses, thus, average Relative Percent Differences (RPDs) were calculated because there were insufficient replicates of any single sample to calculate RSD. The RPDs for the metals of most interest at SARs were as follows: lead = 28%, antimony = 22%, tungsten = 23%, copper = 47% and zinc = 40%. The higher RPDs for copper and zinc are believed to be a consequence of the greater difficulty of sampling and analysing relatively large pieces of bullet jackets. In other words, nugget effects occasionally cause some unexpectedly high results. Nonetheless, these RPDs suggest similar or better precision than what was found for energetics when the analytical sample was 25 times larger (50 g) [11]. Consequently, metal distribution at SARS may not be as heterogeneous as the distribution of energetics at anti-tank and grenade ranges. The remaining questions, therefore, are whether alternate digestion approaches and/or finer grinding of the samples are warranted.

2.2 *SAR metal sample preparation issues*

Conventional, small-calibre, military bullets (5.56 mm [M16] and 7.62 mm) have spent projectiles composed of antimony-hardened lead in a copper jacket with masses ranging from 32 to 86 g per bullet, of which 96.4% by weight is lead [18]. In tungsten rounds, as noted previously, a tungsten/nylon core replaces the lead/antimony. Thus, other constituents are relatively minor in terms of mass when compared to lead or tungsten and copper. Arsenic and nickel are primarily used in shot, and tin, zinc, chromium and cobalt are present mostly as impurities [19,20]. A recent comprehensive review of antimony at SARs reported high concentrations (1,000–17,000 mg kg^{-1}) because of its association with lead as a hardening agent [2]. Copper and zinc are also abundant at SARs because they are the primary components of the bullet jacket. Although experiments have shown that many metals may be released from the detonation of some ordnance items (aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, phosphate, selenium and zinc [21–23]), this investigation focused on those elements of most interest at SARs: lead, antimony, copper, zinc and tungsten. Treatment of antimony data in this report is incomplete for two reasons. First, digestions using only nitric acid are known to yield variable recoveries [24] and second, some of the analyses were performed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and some by inductively coupled plasma-mass spectrometry (ICP-MS). The former had an antimony detection limit of approximately 20 mg kg^{-1} which was too high for most of these samples, rendering some of the comparisons problematic.

Controversies regarding how best to prepare and digest a SAR sample for metals can be framed by the following questions:

(1) Should the sample be ground and, if so, should it be sieved prior to grinding?
(2) If the sample is to be sieved, which sieve size is appropriate?
(3) If the sample is to be ground, what grinding equipment should be selected?
(4) Which approach should be used for sample digestion?
(5) Is it important to achieve total digestion of the sample?

Answers to these questions are not straightforward, as was illustrated by the range of soil digestions reported in a review from the European Union [25]. The nine countries providing data variously employed the following sample digestion approaches: aqua regia, hydrofluoric acid, lithium borate fusion and the microwave/nitric acid method approved by the US Environmental Protection Agency (USEPA SW846, Method 3051A) [26].

Typically, geologic samples collected for metals assaying are ground, although cross-contamination caused by grinding is a well-known phenomenon. As noted by Hartman [27], the 'geochemist must be concerned with sources of contamination in the sample preparation equipment. Grinding plates and blades of different composition are available so that the obvious contamination from chrome steel, tungsten carbide and other materials can be avoided. Similarly, loss of sample representativeness through ''smearing'' of native copper, native gold, molybdenite or other soft materials on pulveriser plates can be avoided in many instances by the selection of alternative equipment.' Others have also reported contamination with tungsten, iron and other metals, noting that grinding time and the amount of quartz in the sample affected the amount of contamination [28].

Classical techniques used for mining assays often employ a strong acid mixture and/or alkaline fusion to ensure dissolution of the entire sample. Environmental analyses typically employ digestions that are less harsh because the focus is usually on samples originally contaminated by an aqueous solution, so presumably the metals are adsorbed to the surface rather than bound in the silicate structures of primary minerals. For example, the USEPA method (3051A) for metals in soils employs a nitric acid leach [26] in order to dissolve the environmentally available fraction of the sample.

The choice of sample preparation method also has serious cost consequences. EPA Method 3051A is amenable to large sample batches and rapid throughput because only one reagent is added to the sieved sample. Grinding samples significantly lowers sample throughput and increases cost because most laboratories have only a few grinders. Grinding also introduces another sample-handling and decontamination step. Likewise, use of stronger acid mixtures increases reagent costs, the time required to prepare the samples for digestion and can require (as with the use of hydrofluoric acid) specialised and more expensive apparatus.

To examine the question of how to evaluate metal content on SARs, field samples were sieved to <2 mm and then prepared by the following techniques: (1) traditional USEPA method, that is, unground and leached with hot nitric acid; (2) traditional USEPA method, but leached with a hot nitric/phosphoric acid mixture; (3) ground with a ball mill using agate balls followed by digestion with the nitric/phosphoric acid mixture; (4) ground with a metallic ring mill followed by digestion with the nitric/phosphoric mixture; (5) total digestion of unground samples with hydrofluoric acid, nitric acid and boric acid. The use of the acid mixture (nitric alone versus nitric and phosphoric) may be necessary to maximise tungsten recovery [18]. Finally, the total metal content of the sample was compared to the amount in the <2 mm fraction.

3. Experimental

A total of 14 surface and subsurface samples collected from the Massachusetts Military Reservation (MMR) were used in the sample preparation experiments. Site characteristics of the MMR have been published elsewhere [17]. Ottawa sand was also ground and digested as a means of evaluating cross-contamination and grinding efficiency.

3.1 *Surface soil sampling*

Previous work has shown that multi-*increment*® soil sampling enhances sample representativeness at military training ranges [9]. The multi-*increment*® sampling strategy employed a stratified random design, the first step of which was dividing the study area into decision units (Figure 2). A decision unit is an area of interest or population (e.g. berm face) from which the average soil concentration is obtained with a specified level of confidence [14]. Hence, 100-increment soil samples (subsamples that comprise the final sample) of the top 5 cm were obtained at evenly-spaced locations throughout each decision unit. Prior to collecting the increments, the area was gridded in order to determine the number of lines and increments per line to achieve a 100-increment sample. A random starting location was selected and increments were collected on fixed intervals – typically along a line at every 3 to 5 paces while walking from one side of the decision unit to the other. Upon reaching the opposite side, the sampler typically moved 3 to 5 paces along the edge of the decision unit then returned to the opposite side while collecting increments parallel to the first line. This pattern was repeated until 100 increments were collected. Plastic syringes (1.25-cm ID), metal scoops, or a metal corer (5-cm ID) were used for

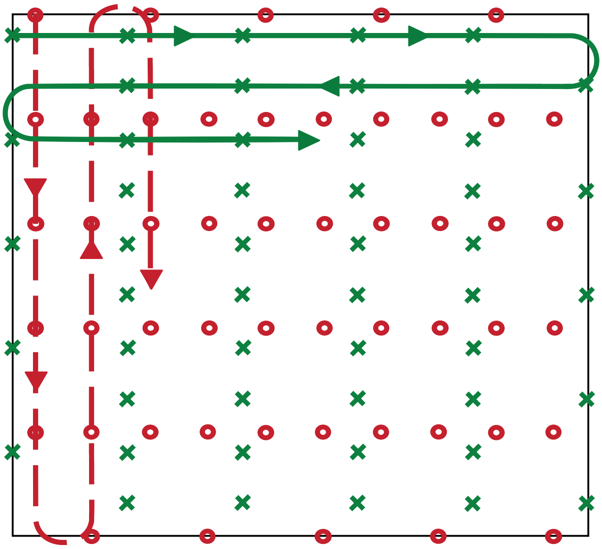

Figure 2. Multi-*increment*® sampling technique.
Note: The solid and dashed lines represent the paths of two different samplers. In this case duplicate samples were collected. The Xs correspond to the sample locations for the solid-line sampler and the Os to the sample locations for the dashed-line sampler.

sampling the surface soil. The multi-*increment*® samples typically weighed 3 to 5 kg. It is recognised that using any corer in this way may discriminate against an intact bullet or other large fragment which either does not fit in the corer or is excluded because it strikes the edge of the corer and is displaced rather than collected. Field observations during sampling, however, indicate this discrimination rarely happens and samples often contain visible fragments of spent bullets and casing. Besides the primary investigation samples, additional samples were collected, analysed and evaluated to document the achievement of quality assurance objectives [18].

3.2 *Subsurface soil sampling*

Subsurface soil samples were not collected with the multi-increment method, but were obtained by combining the soils from the same depth intervals for four cores collected within a decision unit. Twenty-five centimetres was selected as the sample interval based on field X-Ray Fluorescence (XRF Model # Alpha-4000s, Innov-X systems, Woburn, MA) measurements of several 60 cm cores and test pits sampled on 5 cm intervals. It was not always possible, however, to achieve the maximum desired depth of 150 cm with the available sampling equipment. Therefore, in some cases, the final combined sample consisted of fewer than four increments.

3.3 *Sample preparation*

USEPA Method 3051A was used as the basis for comparison and for modification. Prior to digestion, the ~5 kg field samples were air-dried. A portion of each sample was

Table 1. Metal content[a] of steel bowls used with the Labtech Essa ring mill.

	Average (mg kg^{-1})	Maximum (mg kg^{-1})
Antimony	15.2	18.4
Arsenic	62	64
Chromium	103,700	112,000 (~10%)
Copper	1,735	1,990
Lead	6	7
Manganese	3,000	3,700
Molybdenum	1,620	2,110
Nickel	2,880	3,030
Vanadium	863	1,140
Tungsten	809	1,210
Zinc	29	52

[a] Data provided by the manufacturer.

then set aside prior to sieving in order to qualitatively evaluate the total metal load in the soil. The remaining sample was then sieved using a USS #10 sieve (2 mm) which yielded ~3 kg. Samples were then either ground or not, and subsampled by spreading the soil onto aluminum foil and collecting 100-increments to make a final 2 g subsample for the <2 mm soil fraction and 20-increments for the >2 mm size fraction. The subsamples were then digested with one of the three different acids or acid mixtures.

3.4 *Laboratory grinding of soil samples*

Grinding was performed with a Lab Tech International ball mill (Model PM400, East Sussex, United Kingdom) utilising 50 metal-free agate balls and bowl or a Lab Tech Essa steel ring mill grinder (Model LM2, Belmont, Australia) which has a steel puck and bowl with a combined weight of 40 lb. The composition of the stainless steel bowl and puck in contact with the soil, as provided by the manufacturer, is shown in Table 1. Of immediate interest are the high concentrations of antimony, copper and tungsten – elements of particular interest at SARs. Lead and zinc, usual elements of interest at SARs, are low. This steel ring mill grinder has been used at the Cold Regions Research and Engineering Laboratory for three years, grinding thousands of soil samples for the analysis of energetic residues, and there is clear visual evidence of metal loss on the bowl as well as the puck, suggesting this could be an issue for metals analysis.

The stainless steel bowl and puck were cleaned after each use by washing with soapy water, followed by an acetone rinse and air drying. To assess cross-contamination, Ottawa sand, EMD Chemicals Inc. Lot 46298651, was ground to determine whether there was carryover after grinding 14 environmental field samples. The sample designated ‘aliquot 1’ was ground first, followed by ‘aliquot 2’ – both representing fresh aliquots of Ottawa sand.

A timed grinding test was also conducted to assess contamination from the metal grinder. This test used the same metal grinder and the same puck and ball used previously with the assumption that contamination from the grinder would increase with time. In this case, two aliquots of Ottawa sand obtained from a different vendor, Restek Corp.

Lot 203010-AA, were ground; the first for 90 seconds and the second for 330 seconds. These two samples were compared to unground Ottawa sand.

The ground portion of the samples, now approximately 3 kg, was spread out in a thin layer on a sheet of aluminum foil. The sample aliquot for digestion was obtained by randomly collecting and then combining 20 increments of approximately 0.1–0.25 g each. Triplicate subsample aliquots were obtained for each of the 14 field soil samples used in the study. Thus, 42 individual subsamples were available for analysis.

3.5 *Sample digestions*

Most of the sample digestions were performed using a modification of USEPA SW-846, Method 3051A which employs microwave heating. The method was modified for several of the treatments by adding phosphoric acid to the digestion process and changing the composition of the solution used to rinse the filter media. The modified method uses 8 mL of concentrated nitric acid and 2 mL of concentrated phosphoric acid (both trace metal grade) as the digestion solution for 2 g of ground soil. This change in digestion acid prevents formation of tungstates and polytungstates thereby maintaining tungsten in a soluble form [18]. Method 3051A specifies digestion of 0.5 g; however, as noted previously, research with energetics has demonstrated that larger samples yield a more representative value [11,14]. Samples as large as 50 g have been evaluated for analysis of energetics, but such large analytical samples would be impractical for metals because of the large volumes of acid and the size of the equipment that would be needed. Thus, as described previously (Section 2.1), 2 g was selected as the largest practical sample size considering the acid volume and equipment constraints. Following digestion and filtration as described in Method 3051A, the sample and filter paper were washed with concentrated phosphoric acid. The volume of the digested sample was then adjusted to 100 mL with ultra-pure water. Finally, one set of unground samples was digested with a nitric acid, hydrofluoric acid and boric acid mixture intended to dissolve refractory minerals.

3.6 *Analytical*

Samples were analysed primarily by ICP-MS, although some data were obtained with ICP-OES and XRF. Considerable method development and quality assurance were included to ensure data quality. These efforts are described elsewhere [18,29].

4. Results

4.1 *Ottawa sand*

Table 2 compares the analysis of unground Ottawa sand (average of three replicates) to two subsequent aliquots of Ottawa sand ground after the environmental samples. For the purpose of all of the treatment comparisons, results within 40% are considered acceptable agreement. Aliquot 1 was analysed in duplicate. The generally good agreement among the Aliquot 1 duplicates and Aliquot 2 (Table 2) demonstrates the increase in metal content from unground to ground was not caused by cross-contamination from the environmental samples. Otherwise, the Aliquot 2 sample would have a significantly lower metal content than Aliquot 1. The increase from unground to ground, therefore, results from more efficient digestion of the smaller particles produced by grinding, contamination

Table 2. Comparison of analytical results[a] for unground Ottawa sand to Ottawa sand ground (60 seconds/metal ring mill grinder) after grinding the 14 environmental samples.

	Average unground sample ($mg\,kg^{-1}$)	Aliquot 1 ground sample ($mg\,kg^{-1}$)	Aliquot 1 duplicate ($mg\,kg^{-1}$)	Aliquot 2 ground sample ($mg\,kg^{-1}$)	Apparent mass increase from grinding ($mg\,kg^{-1}$)	Soil crustal average value[b] ($mg\,kg^{-1}$)	Apparent mass increase from grinding as % of soil crustal average
Chromium	1.1	115	113	102	107	100	107
Copper	2.4	7.7	7.4	6.5	4.7	30	16
Iron	1120	2760	2700	2540	1510	38000	4
Manganese	2.8	8.9	8.7	8.3	5.7	600	1
Molybdenum	0.7	<2.5	2.8	2.7	0.7	2	35
Nickel	1.7	4.4	4.3	4.2	2.5	40	6.25
Lead	2.8	5.5	4.8	4.5	2.0	10	20
Vanadium	0.3	<2.5	<2.5	<2.5	None	100	0
Tungsten	2.4	16	9.8	7.2	7.5	1.5	500
Zinc	2.3	28	27	24	23	50	47

[a] All samples digested with the nitric acid/phosphoric acid mixture (modified EPA 3051a).

[b] Soil crustal average values from Lindsay [30] except for molybdenum and tungsten which are from Pais and Jones [31].

from the grinding equipment itself, or a combination of the two. As shown previously in Table 1, the grinding equipment is composed of approximately 10% chromium which has been reported as a primary contaminant that can be introduced by metal grinding [32].

The actual effect of grinding on data interpretation will, of course, depend on the magnitude of contamination being assessed. At a typical SAR, the primary contaminants are lead, antimony, copper and zinc and, recently at a few ranges, tungsten. Antimony could not be assessed because the detection limit was too high. Lead, copper and zinc values at SARs range from hundreds to thousands of $\mathrm{mg\,kg^{-1}}$. Thus, these metals could not be seriously affected by the small metal introduction possible from grinding when evaluating the extent of contamination at a SAR. Similarly, tungsten values also range to hundreds and even thousands of $\mathrm{mg\,kg^{-1}}$ [18] and would not be significantly affected by grinding.

Table 3 shows how grinding for longer periods increases apparent metal concentrations. Note that this aliquot of Ottawa sand was from a different vendor than that shown in Table 2 and contained more metal. The increases from the 90 second to the 330 second grind (Table 3) suggest two possibilities; increased metal recovery from within the crystalline structure of the soil matrix or metal contributed from the grinder. These two mechanisms are further explored later in this paper. Using the 90 second grind data as a conservative value, the amount of metal added, if assumed from the metallic grinder, would be insignificant when evaluating a SAR soil except for chromium and possibly iron. However, depending on local geology, background determinations could be affected assuming the increased metal concentrations are due to the grinder.

4.2 *Small arms range samples*

4.2.1 *Total analysis versus sieved (<2 mm) fraction*

This paper focuses on 2 gram subsamples of the <2 mm fraction because it is both the standard preparation technique and previous work demonstrated acceptable precision (Section 2.1). However, the >2 mm fraction may be of significance at SAR sites, particularly for tungsten which has been shown to leach in significant amounts from large particles [17]. The >2 mm fraction for the 14 environmental field samples used in this study represented between 12% and 39% of the total sample mass and often contained visible pieces of bullets and bullet jackets. The analytical subsamples for these analyses were built with 20-increments, but the greater range in particle size causes large subsampling error. These results, therefore, are only useful for demonstrating that a potentially significant amount of metal is excluded when samples are sieved.

A preliminary evaluation of the potential importance of the >2 mm fraction was performed by analysing this fraction from all 14 samples for tungsten and from six samples for copper and lead. Multiple subsamples were obtained and analysed from these field samples. The >2 mm fraction contained 18–64% of the total tungsten mass [18]. For both copper and lead, an obvious issue was the lack of precision among the replicates. In some cases, differences among replicates were several orders of magnitude. For copper only 5 of 35 results were not one to two orders of magnitude greater than the corresponding <2 mm result.

Lead values often ranged from double to several orders of magnitude greater than the corresponding result determined for the <2 mm fraction. Conventional wisdom is that only the small particles are of environmental significance, but bullets and bullet jackets are

Table 3. Apparent increase in metal content[a] in Ottawa sand from grinding longer (metal ring mill grinder).

	90 sec grind	330 sec grind			
	Concentration increase as compared to unground sample (mg kg^{-1})	Concentration increase as compared to unground sample (mg kg^{-1})	Concentration increase from grinding 90s versus 330s (mg kg^{-1})	Soil crustal average value[b] (mg kg^{-1})	Mass increase from 90s to 330s grind as % of soil crustal average
Chromium	220	460	240	100	240
Copper	3.3	4.7	1.4	30	5
Iron	2270	4970	2700	38000	7
Manganese	9.8	21	10.8	600	2
Molybdenum	1.4	3.2	1.7	2	85
Nickel	3.4	7	3.5	40	9
Lead	0	−0.4	−0.4	10	0
Vanadium	0	0	0	100	0
Tungsten	2.8	2.6	−0.2	1.5	0
Zinc	1.7	2.1	0.4	50	1

[a] Average values were used when there were two or more analyses of a sample.

[b] Soil crustal average values from Lindsay [30] except for molybdenum and tungsten which are from Pais and Jones [31].

coated with dirt and small particles that surely contain minute particles abraded from the bullets. In addition, the bullets and bullet jackets corrode with time and eventually release additional metal for environmental transport [12,13,17]. These data demonstrate that measuring only the small particle (<2 mm) fraction seriously underestimates the total metal load. How much environmental risk is underestimated by using only the <2 mm fraction is unknown and could be the subject of further research.

4.3 *Comparison of preparation techniques*

Summary data for the 14 environmental samples are presented in Table 4. Three of the field samples were subsampled additionally in order to obtain replicate analyses. In those instances, the average values were used. Comparing minimum values and averages from the various methods to the crustal average suggests each of the samples is contaminated with lead and tungsten. Inspection of individual results (not shown) indicates only one or two samples are not obviously contaminated with copper. Those samples with the highest values for copper are also obviously contaminated with zinc. Hence, these data show contamination patterns consistent with their collection from a military SAR [16–18]. Table 4 shows the general trends for the methods and the metal results to be the following: nitric acid leach < nitric/phosphoric leach < metal ground < total digestion with HF. The results from the ceramic ground samples were intermediate; some of the results approximated the nitric/phosphoric leach while others were more similar to the metal ground samples.

Despite the approach taken in sample collection and processing, nugget effects were not avoided (Table 5). Nugget effects occurred at a rate of approximately 5% or less in this data set. These would not, however, have caused erroneous decision-making regarding whether or not a sample was contaminated. Even if the ‘nugget’ values are excluded, two of the three samples with copper nugget effects are still obviously contaminated with copper. Moreover, lead and tungsten are elevated in all three samples where there are copper and zinc nugget effects. Lead contamination, as well as copper and tungsten, is still evident in each sample for which a lead nugget effect was apparent. The sample with the tungsten nugget effect is still somewhat contaminated with tungsten and clearly has elevated lead. These ‘nugget effect’ values, when included in mathematical comparisons of the methods, masked or distorted overall data trends in some cases. Because excluding these results would not have affected decision-making regarding whether or not a sample was contaminated, deleting the ‘nugget’ results from the method comparisons was deemed appropriate. The resulting ratios between the various preparation techniques for the environmental samples are shown in Tables 6 and 7. In addition, paired t-tests, >95% level of confidence, were performed between the USEPA standard method (sieved/unground/nitric acid digestion) and both (1) ceramic and (2) metal ground samples digested with the nitric/phosphoric acid mixture, and (3) with the nitric acid/hydrofluoric acid/boric acid mixture.

4.3.1 *Unground USEPA Method-HNO_3 digestion versus unground modified USEPA Method-HNO_3/H_3PO_4 digestion*

The addition of phosphoric acid caused an increase of approximately a factor of three in apparent tungsten recovery (Table 6, column 1) while results for copper, lead and zinc, three prominent SAR metals, were within 20% of the value obtained with nitric acid alone.

Table 4. Summary data (mg kg^{-1}) for the 14 environmental samples.

Grind status	Unground				Unground				Ceramic ground				Metal ground				Unground				
	HNO_3 digestion (EPA 3051A)				$HNO_3 + H_3PO_4$ digestion (modified EPA 3051A)				$HNO_3 + H_3PO_4$ digestion (modified EPA 3051A)				$HNO_3 + H_3PO_4$ digestion (modified EPA 3051A)				$HF + HNO_3 + H_3B0_3$ digestion				
Digestion method	N[a]	Min	Ave	Max	N	Min	Ave	Max	N	Min	Ave	Max	N	Min	Ave	Max	N	Min	Ave	Max	Soil crustal average[b]
Chromium	14	4	7	10	11	6	11	15	14	59	69	84	14	70	105	147	14	23	237	448	100
Copper	14	33	220	686	11	35	619	3435	14	19	207	643	14	33	216	702	14	23	577	4950	30
Iron	14	2613	4266	5587	11	4331	5868	7393	14	3467	4734	6356	14	5902	7182	8178	14	9900	11167	12800	38000
Manganese	14	26	49	104	11	36	70	156	14	26	50	89	14	38	64	129	14	140	178	230	600
Nickel	14	2.5	3.1	3.8	11	2.9	5.1	6.7	14	2.5	3.7	4.9	14	4.3	5.5	6.6	14	4.3	6.5	8.7	40
Lead	14	70	347	850	11	71	314	736	14	55	409	1092	14	71	488	1277	14	130	404	650	10
Antimony	14	6	13	30	11	nd[c]	nd	23	14	10	13	22	14	21	28	38	14	1	7	12	<1
Vanadium	14	4	8	12	11	9	13	20	14	7	10	14	14	10	13	16	14	17	23	29	100
Tungsten	14	12	174	1434	11	16	364	1090	14	6	314	1396	14	9	349	1591	14	5	310	679	1.5
Zinc	14	18	33	87	11	22	72	341	14	9	32	85	14	20	31	54	14	24	78	565	50

[a] N is number of samples.

[b] Soil crustal average values from Lindsay [30] except for tungsten which is from Pais and Jones [31].

[c] nd = not detected.

Table 5. Apparent nugget effects. "Nugget" value ($\mathrm{mg\,kg^{-1}}$) is underlined and the average of the other four digestion methods is provided in parentheses.

Sample #/Method	Copper	Zinc	Lead	Tungsten
68B/$HF + HNO_3 + H_3B0_3$ digestion	$\underline{4950}$ (45)	$\underline{565}$ (22)	430	436
10S/$HNO_3 + H_3PO_4$ digestion	$\underline{1910}$ (359)	$\underline{180}$ (26)	169	438
5S/$HNO_3 + H_3PO_4$ digestion	$\underline{3435}$ (519)	$\underline{341}$ (72)	736	1090
11S/metal ground	702	27	$\underline{286}$ (88)	468
11S/$HF + HNO_3 + H_3B0_3$ digestion	710	37	$\underline{630}$ (88)	559
4S/ceramic ground	588	23	$\underline{1092}$ (402)	524
4S/metal ground	702	27	$\underline{1277}$ (402)	468
13S/$HF + HNO_3 + H_3B0_3$ digestion	23	32	203	$\underline{51}$ (27)

There was insufficient data to judge antimony, the other SAR metal. For the non-SAR contaminants (Table 7, column 1), concentrations increased 50–90%, indicating the addition of phosphoric acid may enhance dissolution of recalcitrant minerals. The use of phosphoric acid is necessary to achieve a reasonable recovery of tungsten because it inhibits the formation of solid polytungstate compounds [18]. The increases in manganese, nickel, and vanadium may not be important because the natural values in these particular samples are quite low when compared to soil crustal averages (Table 4).

4.3.2 *Unground USEPA Method-HNO_3 digestion versus modified (HNO_3/H_3PO_4 digestion) USEPA Method with ceramic grinder*

Lead, copper and zinc results, with the inclusion of ceramic grinding, were within approximately 10% of the standard EPA method and antimony values were within approximately 30% (Table 6, column 3). The tungsten result was approximately 10% lower than the nitric/phosphoric acid method, which, as shown in the previous paragraph, is the method of choice for tungsten. For chromium, iron, nickel and vanadium, the ceramic grind and phosphoric acid/nitric acid digest had a higher apparent recovery (t-test with >95% confidence) than the standard USEPA method (Table 7), but except for chromium results were less than the modified EPA method with unground samples. Chromium, however, typically increased by an order of magnitude relative to the unground sample. Vanadium and nickel values were always higher when the sample was ground but only by a few $\mathrm{mg\,kg^{-1}}$ for these samples with low natural concentrations. The reason for the larger relative increase in chromium may be a consequence of being more easily released from recalcitrant minerals when the samples were ground finer. As will be discussed later, a greater percentage of chromium was recovered with the metal grinder and more still with the aggressive HF digestion. (Agate may also contain chromium and be a source itself. Data to examine this possibility were not obtained in this study.) Taken as a whole, therefore, ceramic grinding appears to offer little or no improvement over digesting an unground SAR sample with the modified USEPA method.

4.3.3 *Unground USEPA Method-HNO_3 digestion versus modified USEPA Method with metal grinder*

Copper, lead, zinc and tungsten values are higher with the metal grind but within 30% of the results for the unground samples (Table 6, column 4). Although low-level antimony

Table 6. Average ratios of results from various preparation techniques for SAR metal contaminants.

	# of values in calculations[a]	# of values excluded[b] because of nugget effect	$HNO_3 + H_3PO_4$ digestion versus HNO_3 digestion (EPA 3051A)	Ceramic ground/$HNO_3 + H_3PO_4$ digestion versus HNO_3 digestion (EPA 3051A)	Metal ground/$HNO_3 + H_3PO_4$ digestion versus HNO_3 digestion (EPA 3051A)	$HF + HNO_3 + H_3BO_3$ digestion versus HNO_3 digestion (EPA 3051A)
Copper	64	3	0.8	0.9	1.2	1.2
Lead	63	4	1	1.1	1.3	1.2
Zinc	64	3	1	1	1.1	1.4
Tungsten	66	1	2.9	2.5	2.9	3.7
Antimony (Values with '<' not included in calculations)	67	0	0.6[c]	1.3	2.9	0.6

[a] The original data set consisted of 67 results.

[b] Results believed to be a consequence of 'nugget effects', as shown in Table 5, were excluded.

[c] Only three samples had numerical values for the $HNO_3 + H_3PO_4$ digestion. The remainder were reported as below the detection limit.

Table 7. Average ratios[a] of results from various preparation techniques for metals not typically considered SAR contaminants.

	$HNO_3 + H_3PO_4$ digestion versus HNO_3 digestion (EPA 3051A)	Ceramic ground/ $HNO_3 + H_3PO_4$ digestion versus HNO_3 digestion (EPA 3051A)	Metal ground/ $HNO_3 + H_3PO_4$ digestion versus HNO_3 digestion (EPA 3051A)	$HF + HNO_3 + H_3B0_3$ digestion versus HNO_3 digestion (EPA 3051A)
Chromium	1.7	10.9	16.6	37.4
Iron	1.5	1.1	1.7	2.7
Manganese	1.5	1	1.3	4
Nickel	1.7	1.2	1.8	2.1
Vanadium	1.9	1.3	1.7	3

[a]All 67 results were used because there were no apparent nugget effects.

measurements, as noted previously, were unreliable in this study, all of the metal ground samples had significantly higher reported values than those from any other method. These data indicate either antimony was more easily released from more finely ground samples or is contributed by the grinding equipment, as suggested by the data in Table 1. Chromium, iron, manganese, nickel, and vanadium had higher apparent recoveries (t-test with >95% confidence) than the standard USEPA method (Table 7, column 4) when samples were subjected to the metal grinder and the modified EPA method. Not shown in the table but also significant at the 95% confidence level were aluminum, barium, potassium, magnesium, sodium, and titanium. Chromium is one to two orders of magnitude greater with metal grinding as compared to the unground sample and approximately 50% greater than the ceramic grind sample. Manganese is consistently 30–50% higher. Nickel is only a few $mg\,kg^{-1}$ higher but all values are naturally low. Similarly, although vanadium values are often a factor of two higher, all results are relatively low. Aluminum is also 30–50% higher after the grind (~3,000–5000 $mg\,kg^{-1}$, unground). Barium was usually a few $mg\,kg^{-1}$ higher but values were naturally low (<10 $mg\,kg^{-1}$, unground). Potassium was two to three times higher but for relatively low natural values (</= 200 $mg\,kg^{-1}$, unground). Magnesium (~400–700 $mg\,kg^{-1}$, unground) and sodium (~40–60 m/kg-unground) were both about 1.5 times higher, but again, values were not high relative to most environmental samples. As with antimony, the metals highest in Table 1, chromium, manganese and nickel, showed the greatest increases.

4.3.4 *Unground USEPA Method-HNO_3 digestion versus unground-$HF/HNO_{34}/H_3BO_3$ digestion*

The nitric acid/hydrofluoric acid/boric acid digest released more metal (t-test with 95% confidence) than any other method, but copper, lead and zinc results remained within 30% of the standard EPA method (Table 6). Increases were also modest for tungsten in terms of total $mg\,kg^{-1}$. Digestions using hydrofluoric acid for antimony should probably be performed in a closed container such as an acid digestion bomb as these values tended to be of the lowest recorded. Increases for the non-SAR metals nickel and vanadium were quite low in terms of total $mg\,kg^{-1}$. Iron and manganese values increased by approximately a factor of two and four over the standard EPA method while chromium results were almost three times higher than the metal ground sample. The fact that the highest results were obtained from an unground sample implies the increases with grinding were not due to contamination from the grinding apparatus but rather due to more efficient digestion of smaller particles.

4.3.5 *Discussion*

Examining the five sample preparation methods from the standpoint of cost-effectiveness provides a clear conclusion. The use of the standard EPA method is sufficient for the usual SAR metal contaminants: lead, copper and zinc. Where tungsten is a concern, phosphoric acid must be added to the standard EPA method. Higher results for these metals were obtained when samples were ground finer using a metallic grinder and higher still when total digestions employing HF were used. Nonetheless, all results were within a range of 10–30% indicating subsequent decision-making during a site investigation would be the same whichever method was selected. Considering that additional sample handling steps and specialised equipment significantly increase the cost of the grinding and total digestion methods, the approximately 10% additional metal measured is not worth the extra cost. These data are consistent with the EPA method description which notes that the 'this method is not intended to accomplish total decomposition of the sample; the extracted analyte concentrations may not reflect the total content in the sample' [26].

In contrast, for non-SAR, presumably residual metals such as chromium and nickel, total digestion employing HF yields substantially higher concentrations than any other method. Where site investigation requires accurate quantification of these metals, a simple leach is inadequate. Indeed, these results suggest additional cost savings. Traditionally, a lengthy list of metals is determined in SAR samples. Most of that data is so inaccurate that collecting and interpreting it is not cost-effective.

5. Conclusions

Although much has been learned from this study, a number of important questions remain. Chief among these is the large amount of metal in the >2 mm fraction. SAR samples frequently contain malleable brass bullet jackets, in some cases with adhering bullet fragments. Is it proper to exclude these from the analyses by sieving? If not, how best to obtain a representative sample? Also, are sample collection and analyses performed when deposition is fresh a reasonable predictor of the available or mobile metal burden in future years? While these questions require additional research, the following conclusions are apparent for the <2 mm soil fraction:

Results for copper, lead and zinc, three of the most important SAR metals, were within a sufficiently narrow range that decision-making for a particular set of site investigation data would not be affected by the sample preparation approach. In particular, adequate results can be obtained simply by sieving to <2 mm and following with USEPA Method 3051A, nitric acid digestion with microwave apparatus. Nugget effects for copper and zinc, apparently from pieces of bullet jackets, were evident in three of 65 results or 4.6% of the time. A nugget effect for lead was apparent in 6.3% of the results (4 of 63) and for tungsten in 1.5% (1 in 65) results. Each of these samples was obviously contaminated with the same and/or other elements even if the 'nugget' result was excluded.

- Additional investigation is needed to determine the appropriate method for antimony which has been increasingly identified as an important SAR contaminant [2,16]. These data indicate, however, that losses are significant when a total digestion employing HF in an open container is used.

- Contamination from grinding with conventional steel apparatus was not evident from this data set. Owing to the fact that results for metals apparently present in residual, recalcitrant minerals (e.g. Cr, Ni, V), were higher when ground in a metallic ring mill versus ball mill suggests the former method produces a smaller particle size than the ceramic agate bowl system.
- The heavy and focused usage of a SAR apparently results in a lower distributional heterogeneity of metal in the <2 mm size fraction as compared to samples collected for energetic compounds. Hence, unlike energetics, when determining concentrations of the SAR metals copper, zinc, lead, tungsten and antimony, there is no significant advantage to grinding the samples prior to digestion if a multi- *increment*® soil sampling methodology is utilised.
- Tungsten determinations require addition of phosphoric acid to prevent low recovery.
- Increasing the reactivity of the digestion acid, $HNO_3 \rightarrow HNO_3 + HPO_4 \rightarrow HNO_3 + HF + H_3BO_3$ resulted in increased recovery of all metals. Iron, manganese and vanadium values are significantly increased by the use of hydrofluoric acid in the digestion. However, as noted by many, there is a controversy in regards to which digestion procedures are reflective of the metal bioavailable [33].

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