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Sequential Extraction Versus Comprehensive Characterization of Heavy Metal Species in Brownfield Soils

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The applicability of sequential extraction as a means to determine species of heavy-metals was examined by a study on soil samples from two Superfund sites: the National Lead Company site in Pedricktown, NJ, and the Roebling Steel, Inc., site in Florence, NJ. Data from a standard sequential extraction procedure were compared to those from a comprehensive study that combined optical- and scanning-electron microscopy, X-ray diffraction, and chemical analyses. The study shows that larger particles of contaminants, encapsulated contaminants, and/or man-made materials such as slags, coke, metals, and plastics are subject to incasement, non-selectivity, and redistribution in the sequential extraction process. The results indicate that standard sequential extraction procedures that were developed for characterizing species of contaminants in river sediments may be unsuitable for stand-alone determinative evaluations of contaminant species in industrial-site materials. However, if employed as part of a comprehensive, site-specific characterization study, sequential extraction could be a very useful tool.

Keywords: lead contamination; heavy-metals; superfund; chemical fractionation; phase characterization; speciation; scanning-electron microscopy.

Introduction

Identification of the chemical forms (speciation) and distribution of heavy-metals that are liberated, locked, or adsorbed on soil particles is fundamental to understanding the chemical and physical characteristics of these metals in soils. These characteristics control the degree to which the metals and their compounds are mobile, extractable, and plant-available. Consequently, speciation impacts the success of remediation efforts at contaminated sites, both from a characterization standpoint in understanding the relationship of the contaminants with their environment, and in development and evaluation of workable remediation strategies.

Speciation does not simply identify particles as specific chemical compounds, but also defines the phases by determining their variations in chemistry, size, associations, host materials, porosity, liberation, alterations, etc. Interpretation of all of these characteristics is key to making predictions about how contaminant particles exist and react in an environment.

The U.S. Environmental Protection Agency (EPA) Superfund Technology Demonstration Division funded a joint study with the U.S. Department of Energy (DOE), Albany Research Center (ARC) to find methods to accurately characterize inorganic contaminant species from two EPA-listed Superfund sites.

The study had two objectives. The first objective was to thoroughly characterize the species and modes of occurrence of the contaminant elements in soil samples from the two sites. The second objective was to compare the species data derived from the comprehensive characterization study with species data obtained from a standard sequential extraction procedure in order to judge the value of the methods for characterization of contaminated brownfield soils.

EPA selected the National Lead Company (NL) site in Pedricktown, NJ, and the Roebling Steel site in Florence, NJ, for this investigation, and collected two soil samples from each site for the study. Researchers at ARC combined chemical analysis, scanning-electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX) and wavelength-dispersive X-ray analysis (WDX), X-ray diffraction analysis (XRD), optical microscopy (OM) with image analysis, and size distribution analyses to identify inorganic contaminants and characterize host materials, in a comprehensive characterization of the two contaminated soil samples from each of the two sites. A standard sequential extraction procedure (Tessier, Campbell and Bission, 1979) was also conducted on each sample to provide extractability data. The results of the two methods of characterization were compared to determine the applicability of sequential extraction data to accurately define species to aid remediation efforts.

Studies of the viability of various sequential extraction methods (also identified in the literature as chemical fractionation, phase characterization, chemical form analysis, or speciation) have been documented extensively in the literature. Investigations measuring the reliability of sequential extraction have traditionally used artificially mixed minerals or artificial compounds in different soil types (Xiao-Quan and Chen, 1993; Yong and Galvez-Cloutier, 1993; Cabral and Lafebvre, 1998; Davidson *et al.*, 1998; Lin *et al.*, 1998; Keon *et al.*, 2001). A volume of work has been done to determine the reliability of sequential extraction methods to ascertain mixed heavy-metal and radioactive species in soils (Schultz *et al.*, 1995; Trautmannsheimer *et al.*,

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1998). In order to increase the reliability of the method, studies have been done comparing sequential extraction results between competing procedures (Nirel and Mord, 1990; Ma and Uren, 1998; Mester *et al.*, 1998; Usero *et al.*, 1998; Hall and Pelchat, 1999; Maiz *et al.*, 2000), to modeled predictions (Van Herck *et al.*, 2000), or to bioavailability calculations (Mach *et al.*, 1996; Zhang, Xianoquan and Li, 1998; Basta and Gradwohl, 2000). However, numerous researchers have noted deficiencies such as artifacts, non-selectivity, and redistribution in sequential soil extractions (Tipping *et al.*, 1985; Rapin *et al.*, 1986; Kersten and Förstner, 1989; Sholkovitz, 1989; Piper and Wandless, 1992; Fiedler *et al.*, 1994; Yarlagadda, Matsumoto and Kathuria, 1995; Raksasataya, Langdon and Kim, 1996; Lo and Yang, 1998).

Evaluation of mining wastes is commonly done by sequential extraction (Clevenger, 1990) and speciation of industrial (brownfield) soils or residues by standard sequential extraction procedures has also become a relatively common practice (Bergers and Harris, 1995; Burckhard, Schwab and Banks, 1995; Bódog *et al.*, 1996; Prudent, Domeizel and Massiani, 1996; Zhixun, 1996; Davidson *et al.*, 1998; Barona *et al.*, 1999). Research has also been done into applying selective extraction to remediate contaminated Superfund soils (Steele and Pichtel, 1998). Work employing parallel sequential extraction and SEM methods has been rare. Baffi *et al.* (1995) did a parallel study on metals in marine sediments. Adamo *et al.* (1996) did a comparative study using SEM on copper and nickel ore and smelter residue, and work is currently in progress on soils from brownfield sites in the United Kingdom (Parrish *et al.*, 2001).

Materials and Methods

Description of samples

National lead samples. The NL site in Pedricktown, NJ, is a 46-acre Superfund site where a secondary-lead (Pb) smelter operated from 1972 until 1984. During its years of operation, the company recycled Pb from spent automotive batteries and separated the plastic from the rubber casings. Two soil samples for this investigation were collected from two surface areas (top 2 to 3 in.), ~500 ft apart, along the perimeter of the plant building. The target-metal contaminant studied in the NL samples is Pb.

Roebling steel samples. The Roebling Steel, Inc. site in Florence, NJ (Roebling, NJ), is a 200-acre inactive facility that was used primarily for the production of steel products from 1906 until 1982. In recent years, parts of the site have been used for various industrial operations, and numerous potential sources of contamination exist at the site. Two Roebling (R) soil samples for this study were collected at a depth of 2 ft from a north-central area of the site. Target-metal contaminants studied in these samples are Pb, arsenic (As), and chromium (Cr).

Methodology and instrumentation

Descriptions of the following methodology and instrumentation are detailed in an attempt to emphasize the importance of recognizing each analytical tool or procedure's site-specific capabilities and limitations.

Macroscopic examination determined that the NL samples contained large, irregular pieces of Pb metal, plastic, concrete, rocks, and plant materials that could not be effectively divided into representative sample splits. These materials were analyzed separately to lessen the "nugget effect"[†]. In addition, many of these items (for example, a 25-mm by 100-mm by 6-mm (1-in. by 4-in. by 1/4-in.) Pb bar) (1) need to be characterized "as is" to give results of value for planning remediation efforts: results may be drastically skewed if the particles are ground and distributed or artificially combined with other and, (2) can break or jam the crushing and pulverizing equipment used to prepare samples for chemical analyses and sequential extractions. Pb materials in this sample subset were identified by species, weighed, noted as a percentage of the whole sample, and factored into concentration percentages of the plus 6·3-mm fraction analyses and overall sample analyses. These materials were not included in the analyses of the sequential extraction samples.

The R samples did not contain any oversized pieces.

A split of each sample was wet-screened to produce four size fractions: plus 6·3 mm (1/4 in.), 6·3 mm by 300 μm (48 mesh), 300 μm by 75 μm (200 mesh), and minus 75 μm. The sized fractions were dried at 105°C, and a representative split of each was ground to minus 180 μm (80 mesh) for chemical analysis of Pb (NL) and Pb, As, and Cr (R).

Comprehensive characterization methodology. Samples of each sized fraction and selected individual representative grains were mounted in epoxy resin, polished, and studied by optical reflected- and transmitted-light microscopy (OM), XRD, and SEM.

The scanning-electron microscope used in this research is equipped with an EDX unit that has a light-element detector to detect elements as light as beryllium (Be, atomic number 4), and a WDX unit that can detect elements as light as boron (B, atomic number 5). Hydrogen (H) cannot be detected by SEM/EDX/WDX which makes this method ineffective for identification of hydroxide species. All the SEM imaging (Figures 1–12) was done in the backscattered-electron mode in which higher average-atomic-number compounds appear brighter than those with lower average atomic numbers. Thus, Pb metal appears brighter than Pb oxide, and heavy-metal compounds appear much brighter than matrix minerals, glasses, and common soil materials. Consequently, the investigator may easily detect and analyze very small (1–5 μm) particles that contain heavy-metal contaminants. The analysis programs include background subtraction, overlap, and matrix corrections for ZAF corrections (average atomic number, mass absorption, and fluorescence) for semi-quantitative analyses. The electron beam of the SEM is ~1–2 μm in diameter and penetrates the first few microns below the polished surface. Therefore, analyses of near-micrometer sized particles may generate X-rays from surrounding

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[†] Samples containing, by chance, one or more of scarce and irregularly distributed Pb nuggets may give an exaggerated impression of the average grade of a deposit or site as a whole.

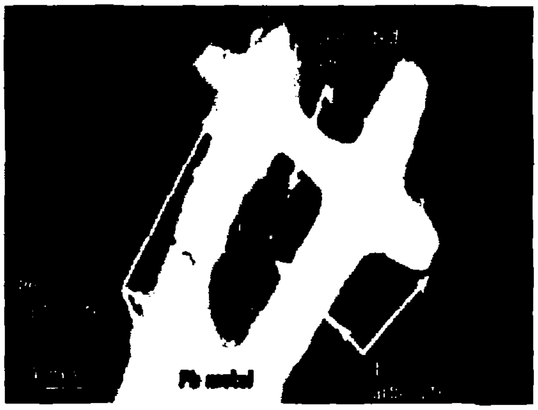

Figure 1. NL sample typical branching Pb metal has altered to Pb carbonates.

Figure 2. NL sample Pb metal with primary Si/C inclusions has altered to various Pb carbonates, Pb oxides, and silicates.

Figure 3. NL sample Pb carbonate lined pores in oversized sandstone rock

materials, making definitive identification of these materials difficult.

EDX and WDX, the two analytical methods used with the SEM, use two different methods to analyze characteristic X-rays given off during electron-beam bombardment. Each method has some individual elemental signals that overlap and interfere with accurate quantification of other elements, but careful comparison of analyses from both methods can produce excellent data for the identification of most chemical phases.

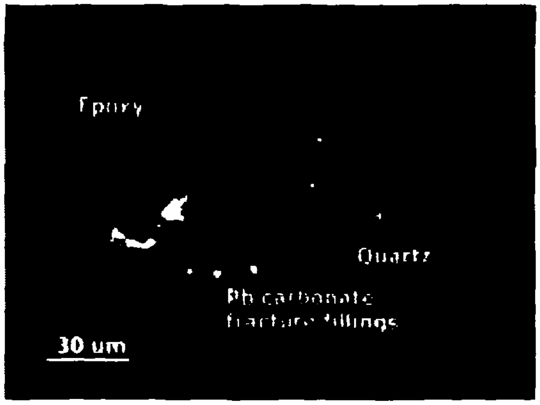

Figure 4. NL sample Pb carbonate filled fractures in quartz particles.

Figure 5. NL sample eroded Pb sulfide crystals intermixed with Pb metal, Pb carbonates, Pb oxides, and Pb–Sb oxides.

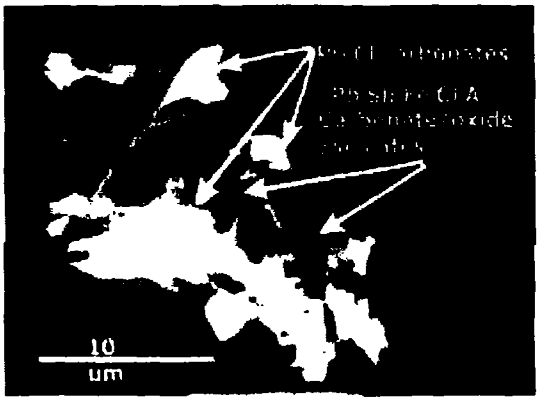

Figure 6. NL-1 leach residue Pb chlorides, Pb carbonates, Pb chlorocarbonates intermixed with Pb–Sb–Fe–Al chlorides/carbonates/oxides/silicates.

XRD analyses were performed on a computer-automated powder diffractometer. Phase analysis was done by the standard Hamawalt search/match tech-

Figure 7. R-1 leach residue Fe–Ca–K silicate slag has Pb oxide inclusions.

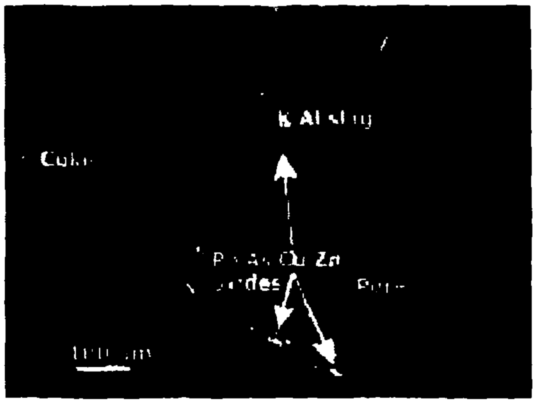

Figure 8. R sample Pb–As–Cu–Zn oxide pore linings in K–Al slag.

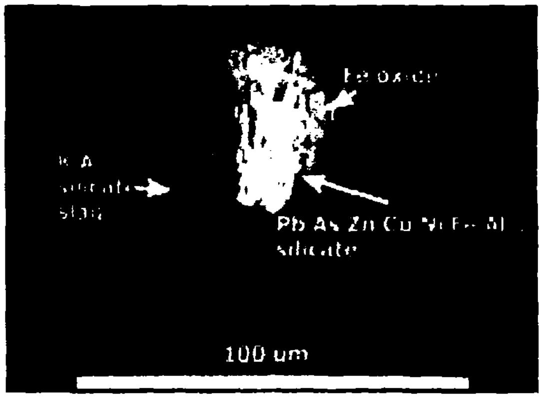

Figure 9. R sample Fe oxide with inclusions and veins of Pb–As–Zn–Cu–Ni–Fe–Al silicate.

Figure 10. R-4 leach residue Pb–Fe–Zn–Al silicate locked with Fe–Ti–Zn–Ni oxides.

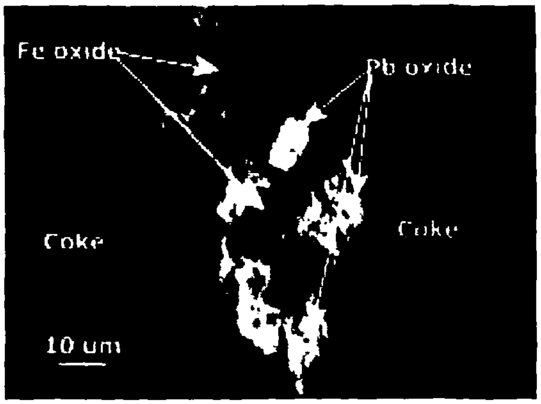

Figure 11. R sample Pb oxide locked with Fe oxide in coke.

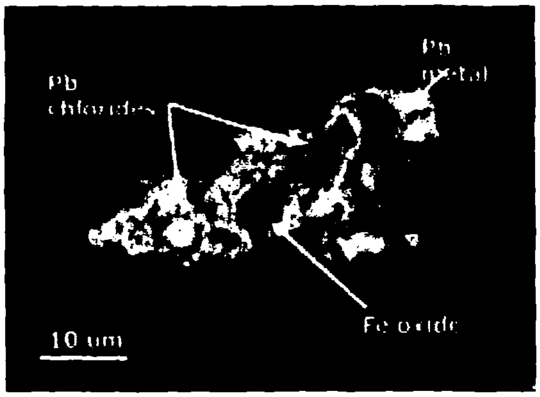

Figure 12. R-1 leach residue Pb chlorides intermixed with Pb metal and Fe oxide.

nique. XRD is qualitative and is functional only when more than 1 wt% (%: percentages in this report are based on weight unless otherwise noted) of a crystalline material is present. Quantities of crystalline phases may be estimated by relative peak heights. XRD identifies crystalline solids by comparison of an X-ray diffraction pattern with thousands of known patterns, but it has a relatively high limit of detection, and overlapping patterns may lead to misidentified species in multicomponent materials. Non-crystalline materials such as glass slags are undetectable by this method. Metal "crystallites", such as the metallic Pb and steel found in these samples, tend to be present in samples as relatively fewer, larger pieces compared to the typically more numerous, smaller particles of oxides, silicates, or carbonates. The chance that a few large metal particles are oriented so that they will diffract X-rays into the detection tube is much less than for the more numerous smaller particles. For example, 0·1 g of Pb may be present in a total of only 50 pieces, and there is only a very small chance that any of these pieces will be oriented such that they will diffract X-rays into the detector. The same weight of Pb carbonate ($PbCO_3$) may be present in millions of crystallites that orient in the right direction. Metals may, therefore, be grossly underestimated or be undetected in XRD data.

Size classification was performed by wet-screening and chemical analysis of the sized fractions. It is a tool used to determine if contaminants are concentrated in particular sizes. This type of information can be used in volume-reduction remediation schemes, in which the clean size fractions are separated from the contaminated size fractions. Wet-screening can wash away water-soluble species. Analysis of splits of the study samples that were stirred and soaked for 12 h produced negligible leached contaminants.

Complete wet chemical analyses were performed on all samples. Wet chemical analyses provide quantitative elemental compositions but not species, and may encounter problems with interference, detection levels, the nugget effect, and variances in "representative" samples.

An understanding of the strengths and weaknesses of these analytical tools and procedures, along with adequate quality-assurance and operational procedures, keeps problems to a minimum. The result is a comprehensive and accurate method of examination that provides needed identification and quantification information about targeted species.

Sequential extraction methodology. The sequential extraction procedure followed is the classic method developed by Tessier, Campbell and Bission (1979). Tessier's method employs four leaching steps for the speciation of the metals of interest: exchangeable metals, metals bound to carbonates, metals bound to iron (Fe) and manganese (Mn) oxides, metals bound to organic matter, and residual metal species. Splits of each of the soil samples used in the sequential extractions were ground to minus 75 μm (200 mesh). All extraction leaches were chemically analyzed and residues were analyzed by chemical analysis, XRD, and SEM/EDX/WDX.

National Lead Samples

Comprehensive characterization results and discussion

Head chemical analyses for the two NL samples are shown in Table 1. The analyses were done on splits after oversized pieces of Pb metal, plastic, rocks, etc., had been hand-picked from the sample (see sample preparation section).

*Table 1 Head analyses for contaminant elements (ppm)**

Element	NL-1[†]	NL-2[†]	NL-1[‡]	NL-2[‡]	R-1	R-2
Pb	68,000	12,400	103,500	13,600	8600	756
As					20	29
Cr					45	23

[*] Analyses rounded to whole numbers

[†] Excludes hand-picked oversized pieces

[‡] Includes hand-picked oversized pieces.

The oversized, hand-picked materials found in NL-1 consisted of bars, chunks, and branching pieces of Pb metal, carbon (C)-enriched slag, plant material, and plastic. A single oversized chunk of Pb metal and a few large pieces of concrete and sandstone were in the oversized materials in NL-2. When the amount of Pb metal in the hand-picked oversize fractions is factored into the head analyses, the total Pb content is calculated to be about 20% higher for NL-1 and 5% higher for NL-2. These higher values were used as a basis for the percentages listed in Tables 2 and 3 and discussed below.

The NL-sample data illustrate the difficulty of sampling inhomogeneous materials and dealing with the nugget effect. Representative samples were difficult to split from the samples supplied for this study, and percentages of Pb-bearing materials reported here for the NL samples may be misleading as representative Pb values for the overall site.

Size-distribution data for the NL samples are shown in Table 3. The data are adjusted to include the hand-picked oversize pieces of Pb metal that were removed prior to the head analyses. The Pb in the two samples is distributed differently, which indicates inhomogeneity in the soils. The plus 6·3-mm fraction of sample NL-1 represents only about 5% of the sample weight, but it contains nearly 40% of the Pb in the sample, the bulk of which is metallic Pb or its alteration products $PbCO_3$, Pb oxides, and mixed Pb oxide/carbonates. Sample NL-2 contains considerably less Pb, which concentrated in both the plus 6·3-mm fraction and the minus 75-μm fraction. No size fraction in either sample is without some percentage of Pb-bearing particles.

The Pb in the NL samples is contained in multiple species, modes, and occurrences. Most particles are intimate mixes of two to three species. The largest proportion is oversize elemental Pb, estimated visually by point and weight counts (Table 2). Pieces range from a bar, 25-mm by 100-mm by 13-mm (1-in. by 4-in. by 1/2-in.), down to sub-micron inclusions of metallic Pb mixed with other Pb and non-Pb species. The metallic Pb has ubiquitous small inclusions of silicon (Si) and C and is often permeated and coated with $PbCO_3$ and Pb oxides.

*Table 2. Pb species estimated percent distributions in NL samples**[†]

Pb species	NL-1	NL-2
Pb metal	70	20
Pb carbonates	20	60
Pb oxides	5	10
Pb oxycarbonates	5	10
Pb silicates & sulfides	< 1	< 1

[*] Extrapolated from wet chemical analyses of residues and SEM EDX WDX data from head samples

[†] Includes hand-picked oversized pieces

$PbCO_3$ is found in most of the Pb-bearing particles as discrete pieces from 100 μm to sub-micron in size. The Pb carbonates are commonly intermixed with Pb oxides, antimony (Sb) oxides, tin (Sn) oxides, Pb

*Table 3. Size-distribution data for NL samples**

	Size	Weight (%)	Pb analysis (ppm)	Pb distribution (%)
NL-1	Plus 6·3 mm	4·9	743,000·0	38·0
	6·3 mm by 300 μm	37·7	79,500·0	31·4
	300 μm by 75 μm	32·7	24,700·0	8·5
	Minus 75 μm	24·7	85,400·0	22·1
	Total	100·0	95,500·0	100·0
NL-2	Plus 6·3 mm	4·9	28,800·0	10·8
	6·3 mm by 300 μm	45·0	9440·0	32·6
	300 μm by 75 μm	28·3	6350·0	13·8
	Minus 75 μm	21·8	25,600·0	42·8
	Total	100·0	13,000·0	100·0

*Weights of all size fractions and the Pb analyses of the plus 6·3-mm fraction were adjusted to account for the hand-picked oversize pieces.

sulfides and sulfates, silicates, and non-Pb-bearing species of Fe oxides, C, and silicates in particles of mixed slag.

Pb oxides are usually associated with Pb metal, Sb oxides, Sn oxides, and $PbCO_3$. A Pb oxide/carbonate ($PbO{\cdot}PbCO_3$) was identified. Traces of Pb-sulfide-bearing slag, Pb sulfates, and Pb silicates occur in the samples and a trace of As occurs in association with Ni, Sb, and Sn.

The Pb metal contains Sb and silicon carbide (SiC) inclusions from the smelting process (Figures 1 and 2). All other Pb species are apparently derived from alteration of the Pb metal. The metal is oxidized and forms at least three distinct Pb-carbonate species (Figure 2). A Pb carbonate that is relatively high in Pb and C and low in oxygen (O) forms the first alteration layer nearest edges of Pb-metal pieces. This carbonate also permeates the interior of the metal in pore spaces (Figure 2). As this alteration product is exposed further to weathering, a second type of Pb carbonate results. This carbonate usually forms intermediate layers between the inner, less-oxidized carbonate and the outer, more-oxidized Pb carbonate; its chemistry shows an increase in O. A third carbonate is commonly in outer, heavily oxidized layers of Pb carbonate and may be partially hydrated. This layer becomes more porous with distance from the metal surface, and it is the layer in which soil and sand particles are found cemented to the metal particles (Figure 1).

As the altered Pb metal becomes more degraded, large areas of Pb carbonate surround the metal and cement soil and sand to it. The carbonate solutions migrated through the soil to reprecipitate on sand grains, or to cement sand (usually quartz or Fe oxide) and soil together into new conglomerated particles (Figure 1). These solutions infiltrated minute cracks, even in very competent quartz grains (Figures 3 and 4), and permeated the small percentage of carbon and sandstone particles in the soil. Eventually, the metal particles are reduced to mere remnants, recognizable only by their brightness and distinctive small, dark SiC inclusions in SEM backscattered-electron mode (Figure 2). Sb and Sn form small oxide particles which eventually combine to form larger particles (Figure 2).

Occasionally sulfur (S) is present in the metal, and Pb-sulfide crystals form among the contaminant products (Figure 5). Sulfidized layers also form on the outside of Pb-metal particles and combine with other alteration products to form unique patterned alteration rinds.

The following Pb-bearing materials and closely associated metal species were identified in the comprehensive study:

- Large pieces of Pb metal, plastic, slag, concrete, rocks, and plant materials.
- Quartz sand, clay, and, organics.
- Pb metal, carbonates, oxides, sulfides, and sulfates.
- *Mixed slags and oxides of Pb–Sb, Fe, Mn, Si, Zn,* Al, Mg, C, and Sn.
- Mixed Pb oxides and carbonates.
- SB–Ni–Sn arsenides.

Most of the Pb metal fragments are larger and much heavier than the matrix materials (which are mostly quartz). An estimated 85% or more of the Pb-bearing materials could be removed from the soils, particularly those like NL-1, by simple screening and gravity-separation equipment; careful control of these methods could remove most of the Pb-bearing materials, particularly in the coarser size fractions.

Sequential extraction results and discussion

Pb analyses for the products of sequential extractions of NL-1 and NL-2 are summarized in Table 4. The data show distinct differences in the samples taken from the

Table 4. Sequential extraction Pb analyses for the NL samples

Product	NL-1 Pb analysis (ppm)*	NL-2 Pb analysis (ppm)*
Head[†]	68,000	12,400
Calculated average total[‡]	68,200	12,500
1st leach extractant	222 (< 1%)	2020 (16%)
2nd leach extractant	51,500 (76%)	6390 (51%)
3rd leach extractant	12,900 (19%)	3590 (29%)
4th leach extractant	1290 (2%)	131 (1%)
4th leach residue	2330 (3%)	392 (3%)

*Average of replicate analyses. Analyses are rounded to 3 significant figures

[†] Excludes hand-picked oversized Pb pieces and Pb metal pieces that could not be ground to minus 180 μm for analyses and tests

[‡] Sum of averaged replicate analyses of extractants and residue

two areas of the site. NL-1 has more total Pb (by a factor of five) but had a significantly smaller percentage of Pb extracted by the $MgCl_2$ in the first leach than did sample NL-2. Most of the Pb metal in both samples was extracted in the first two extraction steps.

All sequential extraction procedures were performed as described in Tessier, Campbell and Bission (1979) with the following exceptions: The NL samples were ground to minus 75 μm (200 mesh). The residue from the first leach of sample NL-1 (with $MgCl_2$) consistently showed a weight gain for the triplicate analyses and for the portion prepared for XRD. Consequently, the residue was washed with an additional 8 ml of deionized water. After drying and reweighing, the weight gain was persistent. SEM characterization of the first leach residue of N-1 confirmed that the weight gained by the residue in the first leach of NL-1 was caused by addition of chlorine (Cl). Pb (probably metal) was leached and then reprecipitated as Pb chloride ($PbCl_2$) (Figure 6).

SEM/EDX/WDX examination indicates that clusters of fine crystals of Pb compounds occur in the residues from the first leach. Analyses of these crystals show that they are a mixture of compounds containing various amounts of Pb, Sb, Fe, Cl, Si, O, and C. Pb combined with the Cl from the leachant used in the extraction and then precipitated as $PbCl_2$ among the skeletal crystals. In addition, the $MgCl_2$ may have attacked some of the oxides, carbonates, and silica, as well as the metallic Pb, and released additional elements to combine into precipitated compounds. A number of original Pb-bearing particles were not leached in the first extraction.

Skeletal crystals remain in the residues from the second extraction, as do the original grains of various oxides and sulfides.

After leaching most of the metallic Pb and $PbCO_3$, the leach residues from the third and fourth extractions included porous shells and skeletal crystal structures of the remaining Pb oxides, sulfides, and silicates. The fourth (final) leach residue contained numerous Pb-bearing particles including porous and skeletal Pb oxide crystals, a very small amount of the metallic Pb, and resistant Pb silicate, sulfide, and phosphate species.

XRD identified trace amounts of resistant $PbO \cdot PbCO_3$ in all NL-1 leach residues but not in the NL-2 residues. Optical and SEM studies confirmed the presence of this compound, but it is generally found intimately mixed with Pb oxides and individual particles of $PbCO_3$ and is difficult to differentiate.

Table 5. Pb species in sequential extraction residues of NL samples

Pb species	Residue 1	Residue 2	Residue 3	Residue 4
Pb metal	x	x		
Pb chlorides	x			
Pb oxides	x	x	x	x
$PbCO_3$	x			
Mixed $PbO \cdot PbCO_3$	x	x	x	x
Pb–Sb oxides	x	x	x	x
Pb–Fe oxides	x	x	x	x
Pb–Sn oxides	x	x	x	x
Sb oxides	x	x	x	x
Pb sulfides and silicates	x	x	x	x

Although XRD identified only $PbO \cdot PbCO_3$ in the fourth leach residue, SEM/EDX/WDX studies identified other residual Pb-bearing materials as various mixed Pb, Sb, Sn, and Fe oxides. The Pb species found in the sequential extraction residues by XRD and SEM/EDX/WDX are shown in Table 5.

Quartz was identified as a primary phase in all the residues from both NL-1 and NL-2. Approximately 90% of the sample is composed of quartz. Minor amounts of carbonaceous materials and silicious slags are present. XRD tentatively identified traces of a mica mineral (muscovite or phlogopite) in both NL-1 and NL-2 leach residues; chemical, OM, and SEM analyses confirmed that less than 1% of a micaceous mineral is present in both samples.

Comparison of the two procedures for the national lead samples

The comprehensive characterization procedures and the sequential extraction procedures have both strengths and weaknesses, as is the case for most analytical methods. The sequential extraction of the NL samples extracted much of the targeted species at the theoretically correct step, but the multitude of species and the physical attributes of the contaminants made speciation by this method impractical. However, it produced useful data when combined with the data derived from the comprehensive investigation.

Metallic Pb predominates in the NL soil samples. Most of the elemental Pb leached out in the first two steps of the sequential extractions, masking the possible amount of other exchangeable Pb and $PbCO_3$ in the samples. It is unclear why a greater percentage of Pb was leached from NL-2 (16%) than from NL-1 (< 1%) in the first leach. Evidence from the SEM study of the residues suggests that, in both samples, Pb was first extracted then reprecipitated as $PbCl_2$. Both first and second leaches contain Cl which readily combines with Pb. A total of 77% of the Pb was leached in these first two extractions in NL-1 and 67% of the Pb in NL-2.

The fact that some of the leached Pb reprecipitated as $PbCl_2$ or other precipitates interferes with the determination of the amount of Pb carbonates originally in the sample. Both the Pb carbonates and new precipitates (from the metal) were leached primarily in the second extraction.

None of the leachants completely dissolved the Pb–Sb–Sn–Fe oxides, the mixed Pb oxide/carbonates, the Pb silicates, or the Pb sulfides.

These data indicate that the leachants used by Tessier, Campbell and Bission (1979) are not suitable for remediation strategies on soils such as the NL samples that require complete extraction of all Pb species. Even in finely ground samples (minus 180 μm (80 mesh)), many of the extractable species were not completely leached with the theoretically appropriate extractant, and the resistant species, such as the Pb oxides and Pb oxide/carbonates did not leach with the correct extractants.

The comprehensive characterization procedure for this study, which used a combination of analytical tools, proved to be a more effective means to determine species of contaminants in the NL soil samples. When used in combination, each analytical tool provided valuable data.

For example, the SEM backscatter detector cannot image a contrast of materials with very close (<0·3 difference) average atomic numbers. Thus, $PbCO_3$ mixed with Pb oxides or Sb oxides and a Pb oxide/carbonate appear similar in SEM images, but these four species appear different under polarized transmitted light microscopy. Thus mapping the four species by OM and analyzing the areas by SEM helps to discern the species and their relative abundances.

Roebling Steel Samples

Comprehensive characterization results and discussion

The R samples contain only small amounts of the target contaminants Pb, Cr, and As. These elements were generally found together in 1- to 20-μm particles and occasionally in particles as large as 50 μm. The contaminants occur in Pb metal and Pb, Cu, Zn, Ni, As, Fe, and Cr alloys, oxides, carbonates, and silicates. Head Pb, Cr, and As analyses for the two Roebling samples, R-1 and R-2, are shown in Table 1. Sample R-1 had more than 10 times the amount of Pb of sample R-2. R-2 had 5 times more Cr than R-1, but the As levels were about equal. No oversized pieces needed to be removed from either sample.

Size-distribution data for the R samples are shown in Table 6. The head analyses in this table, calculated from the size analyses, are somewhat different from those shown in Tables 1 and 7. This is because the low levels of these metals are particularly susceptible to the nugget effect.

As was the case with the NL samples, the size distribution of the contaminants was very different in the two R samples, an indication of the inhomogeneity

Table 6. Size-distribution data for Roebling samples

	Size	Weight (%)	Analysis (ppm)			Distribution (%)		
			Pb	As*	Cr	Pb	As	Cr
R-1	Plus 6·3 mm	42·0	303·0	12·0	204·0	2·0	26·9	54·6
	6·3 mm by 300 μm	43·9	11,400·0	14·0	104·0	78·8	32·8	29·1
	300 μm by 75 μm	9·0	8200·0	30·0	186·0	11·6	14·4	10·7
	Minus 75 μm	5·1	9500·0	95·0	171·0	7·6	25·9	5·6
	Totals	100·0	6350·0	19·0	157·0	100·0	100·0	100·0
R-2	Plus 6·3 mm	20·7	861·0	5·0	184·0	19·6	4·4	10·9
	6·3 mm by 300 μm	56·5	359·0	17·0	413·0	22·4	40·6	66·7
	300 μm by 75 μm	14·3	934·0	41·0	363·0	14·7	24·8	14·8
	Minus 75 μm	8·5	4620·0	84·0	311·0	43·3	30·2	7·6
	Totals	100·0	907·0	24·0	350·0	100·0	100·0	100·0

*Analyses rounded to whole numbers.

Table 7. Sequential extraction Pb, As, and Cr analyses for the Roebling samples

Product	R-1 analysis (ppm)*			R-2 analysis (ppm)*		
	Pb	As	Cr	Pb	As	Cr
Head	8610	20	45	756	29	234
Calculated average[†]	8360	18	39	785	25	213
1st leach extractant	128 (2%)	ND	ND	15 (2%)	ND	ND
2nd leach extractant	5570 (67%)	<1 (<6%)	6 (15%)	134 (17%)	<1 (<4%)	7 (3%)
3rd leach extractant	2320 (28%)	<1 (<6%)	10 (26%)	411 (52%)	1 (4%)	17 (8%)
4th leach extractant	97 (1%)	ND	5 (13%)	29 (4%)	<1 (<4%)	3 (1%)
4th leach residue	246 (3%)	16 (89%)	18 (46%)	195 (26%)	22 (88%)	185 (88%)

*Average of replicate analyses. Analyses are rounded to nearest ppm.
ND is below the detection limits for the equipment.

Analyses above the detection limit but below 1 ppm are noted as <1 ppm.

[†] *Sum of averaged replicate analyses of extractants and residues*

of the soils at the site. Nearly 80% of the Pb in sample R-1 is in the 6·3-mm by 300-μm fraction, but 43% of the Pb in sample R-2 is in the minus 75-μm fraction that represents only 8·5% of the weight of the sample. Cr is concentrated slightly in the plus 6·3-mm fraction of sample R-1 and in the 6·3-mm by 300-μm fraction in sample R-2. Arsenic is concentrated in the fractions finer than 300 μm of both samples.

No Pb, As, or Cr species were observed by OM or XRD because the contaminant species were below detection levels. However, because the contaminant particles are generally less than 50 μm and most were near 10 μm in diameter, they could be effectively characterized by SEM.

The total number of target particles (containing Pb, As, or Cr) detected in the R samples was relatively small (approximately 100 particles) and, therefore, the sizes noted may not be statistically representative.

The sizes noted should be considered minimum sizes in these samples, because the target particles are generally not elongated nor oriented perpendicular to the surface of the mount. Any error in the determinations would underestimate the sizes of the particles. However, results collected from the 31 mounts of R materials indicate that the target particles fall within a narrow size range, and these size classifications would adequately define the contaminant particles for most practical remediation strategies.

The polished surfaces were studied by SEM in a backscattered electron mode with a combination of EDX and WDX. All of the Pb-, As-, and Cr-species identifications are based on these SEM/EDX/WDX determinations. The following chemical compositions, in approximate order of abundance and with typical particle size in parentheses, were identified:

- No oversize materials.
- Limonite, magnetite, quartz, hematite, mullite, and organics.
- Mixed carbon and silicate slag particles containing Pb–C–Zn–Cr–Ni–As–Cu–Al–Fe oxides, silicates, and carbonates.
- Fe oxides and carbonates containing Pb–Cd–Zn–Cr–Ni–As–Cu–Al–Fe oxides and carbonates.

The particles that contain As and Cr in these samples also contain Pb and usually Zn, Cu, and Ni. These particles are either silicates or are very small oxides or metal–alloy particles encapsulated in silicate slags. A number of the Pb-bearing particles do not contain As and Cr. Many of these particles are oxides or silicates and many are associated with Fe oxides (Figures 7 and 11).

The matrix materials of the R samples are approximately three-quarters C-containing (coke) slags and one-quarter silicate slags. The silicate slags are divided among potassium (K)–Al silicates, calcium (Ca)–Al silicates or Fe–Al silicates (Figures 7 and 8). The silicate slags often have Fe or Fe–Ti intergrowths that sometimes form dendritic patterns in the glass slags; this Fe does not contain Cr. Metallic Fe and Fe-oxide particles also occur as minor matrix constituents. Some of the Fe oxides contain a few percent Pb. Most of the slags are porous to scoriaceous (Figure 8).

Small particles of mixed silicates and oxides of Pb, Zn, Cu, As, Ni, Fe, Al, and, very rarely, Cr and Cd, are found in both coke and silicate slags, Fe oxides, and occasionally with barite. These particles usually occur as inclusions in oxides or silicates and are generally less than 30 μm in diameter. Particles of Pb carbonate and Pb oxide/carbonate appear to be alteration products.

Sequential extraction results and discussion

Analyses for Pb, As, and Cr in R-1 and R-2 extraction products are summarized in Table 7. Chemical analyses of the final residues indicate that a small amount of the Pb and most of the As and Cr resisted all of the leachants used in the extraction procedure.

New splits of the two R samples were ground to 180 μm (80 mesh) for leaching because the finer ground material (minus 75 μm) caused suspension problems due to a high volume of coke.

None of the residues from the sequential extraction steps contained enough Pb, As, or Cr species to be detectable by XRD. FeO, Fe_2O_3, quartz, hematite, and mullite were detected by XRD in all the leach residues, as well as a trace of dolomite in the first leach residue. The non-crystalline silica and coke which make up the bulk of the matrix materials are not detectable by XRD methods, which analyze materials by their crystalline character. Thus, the qualitative amounts reported in XRD studies are relative to the total amount of crystalline species. In the case of the R samples, these amounts are very small compared to the total samples.

The SEM study confirmed that only very minor amounts of these crystalline matrix species exist in the original and leach-residue samples. A trace of $PbCl_2$ was detected in the first leach residue of the R samples (Figure 12).

Due to the small amount of material in the extraction residues, only one mount for each residue was examined by SEM/EDX/WDX. This limitation, added to the low overall number of target-species particles (particularly containing As and/or Cr), rendered the quantities of species in each residue statistically meaningless, although qualitative residue species identifications are valid. Species identified in SEM/EDX/WDX examination of the sequential extraction residues are listed in Table 8.

Table 8. Pb, Cr, and As species in sequential extraction residues of R samples

Pb species	Residue 1	Residue 2	Residue 3	Residue 4
Pb metal	x			
Pb chlorides	x			
Pb oxides	x	x	x	x
Pb–Fe oxides	x	x	x	x
$PbCO_3$	x			
Mixed PbO/$PbCO_3$	x			
Pb silicates	x	x	x	x
Pb–Al silicates	x	x	x	x
Pb–Fe–Zn–Al silicates	x	x	x	x
Cr–As–Pb–Cd–Zn–Ni silicates*	x	x	x	x

*Extrapolated from wet chemical analyses of residues and SEM/EDX/WDX data from head samples

Comparison of the two procedures for the Roebling steel samples

The R samples presented unique challenges to each of the analytical tools used. Chemical analysis detected the very small amounts of heavy-metal elements in the samples. However, it was unable to identify the species of the heavy-metals or to predict the resistance of the As and Cr species to the extractants. OM was unsuited to the identification and quantification of target species in particles as small as these. Although relatively small particles are not a hindrance to successful identification by XRD, the small quantity of the target species and lack of crystallinity in the matrix materials rendered complete characterization of the samples by XRD impossible. SEM/EDX/WDX was used to identify and qualitatively and semi-quantitatively analyze the target particles. However, the small (under 5 μm) and porous particles made analysis difficult and in some cases possibly suspect, because of the close proximity of the C- and O-bearing epoxy mounting medium. As discussed previously, neither EDX nor WDX is able to distinguish hydroxides. Clearly, several complementary tools are necessary to generate the accurate and useful information gained from a successful comprehensive evaluation.

The sequential extractions revealed both the solubility and the resistance of some of the heavy-metal species to extractants. As with the NL samples, much of the Pb metal leached along with the exchangeable Pb and reprecipitated as $PbCl_2$ or as multi-metallic chlorides in the first residue. These were re-leached along with carbonates and oxides in later extractions.

Knowledge of the characteristics of species facilitates the successful interpretation of sequential extraction data.

Conclusions

As described in the sections on methodologies and on procedure comparisons, none of the analytical tools are capable of adequately defining the speciation of heavy-metals in complex materials such as are found at many industrial sites. The comprehensive evaluation by chemical analysis, size analysis, OM, SEM, and XRD can be enhanced by information derived from sequential extraction. However, the sequential extraction method examined did not provide an adequate evaluation of the species present. This study indicates that a complete analysis of speciation should use information from multiple methods.

The sequential extraction procedures by Tessier, Campbell and Bission 1979 were developed for soils and river or ocean sediments that generally contain low levels of contaminants in relatively small, liberated particles. The procedures have been validated on standard or artificial soils that contained single phases of the target contaminants. Brownfield sites often contain a different and more complex suite of contaminants, and speciation of these soils by any standard sequential extraction alone may not be consistent or complete.

In the case of the NL samples, the sample data demonstrate the difficulty of sampling inhomogeneous materials and dealing with the nugget effect. Diagnostic samples were difficult to split from the representative samples supplied for this study. However, data from this study explain a great deal about the nature of the Pb-bearing materials at the site and suggest promising physical-remediation strategies.

This research illustrates that metals such as Pb may be partially leached during standard sequential extractions and then reprecipitated as new species in the residues to be leached at the next extractive stage (redistribution). Information about species determinations may thus be false or misinterpreted, even if the other species are leached correctly in the series. Thus, with the Tessier, Campbell and Bission (1979) method used on these samples, the metallic Pb was partially leached with exchangeable Pb in the first extraction, then partially reprecipitated as $PbCl_2$ in crystalline masses or as coatings on other materials in the residue. The Pb metal leached incompletely in the first extraction, and it was not possible to determine how much of the leachant Pb was from metallic Pb and how much was from other exchangeable Pb (from clays, hydroxides, humic acids).

The Pb metal that did not leach, or that precipitated, remained in the first residue and leached out with carbonates in the second extraction, and perhaps also with oxides in the third extraction. Thus, the extractions gave unreliable amounts of each of the species identified by these leaches. No metallic Pb, ground to minus 180 μm, survived the fourth extraction for organics. In addition, combination Pb oxide/carbonates were found in all of the residues in one of the NL samples, and it is notable that some oxides and oxide/carbonates persisted past the extraction step meant to determine oxides.

In the case of the R samples, the slag and coke hosts in which the small-particle contaminants were encapsulated were unaffected by the leachants and protected many of the contaminant particles from leaching during sequential extractions. The fact that the contaminants survived all the extraction steps is a valuable information for risk management strategies. Remediation schemes use vitrification to encapsulate contaminants in such glass slags to stabilize them and prevent them from leaching into the environment.

This research raises the question of whether it is possible to develop an effective stand-alone sequential extraction series for species determination in these types of materials. Based on the results of this investigation, an effective generic sequential extraction procedure seems unlikely. The sequential extractions need to be based on, or coupled with, comprehensive species determinations to ascertain what species are actually present. A customized, site-specific, sequential extraction procedure, "calibrated" by comprehensive characterization, might be developed for sites to easily and rapidly determine species distributions after complete speciation has been established.

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