

Comparison of Coal Combustion Products to Other Common Materials

Chemical Characteristics

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REPORT SUMMARY

The chemical characteristics of coal combustion products (CCPs) are often discussed with reference to geologic materials and other industrial by-products; however, there are no systematic comparisons of these materials in the literature. This report compares the ranges in chemical characteristics of fly ash, bottom ash, and flue gas desulfurization (FGD) gypsum to the ranges observed for soil and rock, as well as other common products and by-products.

Background

At scientific conferences and in trade journals and the popular media, CCPs are sometimes described as being similar in composition to soils; at other times they are referred to as toxic or hazardous substances. Often, general statements are made with little or no data given to support these characterizations. Such statements can be misleading and have led to confusion, especially among the general public. To provide a more technical basis for characterizing CCP composition, this project collected representative data from the literature and used it as a basis for comparing a number of common materials to each of the types of coal combustion products.

Objectives

- To collect representative data on the chemical characteristics of soil, rock, and selected products and by-products from the literature
- To present a graphic comparison of these data to data on the chemical characteristics of fly ash, bottom ash, and FGD gypsum

Approach

The basic approach was to compare CCPs to other materials using bar charts showing concentration ranges for a number of major and trace constituents. Major element composition of coal fly ash, bottom ash, and FGD gypsum was compared to that of soils and rocks. Trace element concentrations for the CCPs were compared to those for soils, rocks, fertilizers, metal slags, spent foundry sands, and biosolids. Where data were readily available, ranges in leachate concentrations were also compared. Trace element concentrations and leachate concentrations were also compared to regulatory levels. CCP data were derived largely from the Electric Power Research Institute (EPRI) databases containing total composition and leaching characteristics. For the other materials, a literature review was performed to identify data that are current and representative.

Results

- The major chemical composition of both bottom ash and fly ash is similar to that of siliceous rocks, particularly shale. Oxides of silicon, aluminum, iron, and calcium make up more than 90% of most siliceous rocks, soils, fly ash, and bottom ash. Trace elements account for less than 1% of all these materials.
- FGD gypsum is very similar chemically to mined rock gypsum. Both are composed primarily of hydrated calcium sulfate. FGD gypsum is typically more than 90%–95% pure, whereas the purity of mined gypsum is more variable.
- Trace element ranges for fly ash were typically higher than the ranges for soil, rock, and foundry sand and were comparable to or sometimes higher than the ranges for fertilizer, metal slags, and biosolids.
- Trace element ranges for bottom ash were typically higher than the ranges for soil and foundry sands; comparable to or sometimes higher than the ranges for rocks, fertilizers, and biosolids; and comparable to the ranges for metal slags.
- With a few exceptions, trace element ranges for FGD gypsum were generally comparable to or lower than the ranges for rocks and fertilizers and lower than the ranges for soils, metal slags, foundry sands, and biosolids.
- Concentration ranges of trace constituents in fly ash, bottom ash, and FGD gypsum typically fall below the Environmental Protection Agency (EPA) residential soil screening levels and industrial soil screening levels for ingestion and dermal exposure, with the exception of arsenic. Many other materials, including uncontaminated soils and other beneficially used materials, also commonly exceed these screening levels for arsenic.
- CCPs did not exceed any hazardous waste limits in the toxicity characteristic leaching procedure test data from EPRI studies that included 64 samples from 50 power plant sites.

EPRI Perspective

EPRI research on CCPs over the last 30 years has included a variety of laboratory and field studies; one result of this research is a comprehensive database of CCP characteristics under a variety of environmental conditions. Topics of current research include changes in CCP characteristics resulting from new air emissions controls and methods to reduce leaching of trace constituents in certain construction applications.

Keywords

Flue gas desulfurization gypsum

Foundry sand

Fly ash

Metal slag

Rocks

Soils

CONTENTS

1 INTRODUCTION	1-1
Background	1-1
Report Organization	1-1
2 DATA AND METHODS	2-1
3 ROCKS	3-1
Information Sources	3-1
Bulk Chemical Composition	3-1
Trace Element Concentration Ranges	3-2
Data Source Considerations.....	3-2
Trace Element Comparisons to Fly Ash, Bottom Ash, and FGD Gypsum.....	3-3
4 SOILS	4-1
Information Sources	4-1
Comparison of Soil Data Sources	4-1
Trace Element Concentration Ranges	4-6
5 FERTILIZERS	5-1
Information Sources	5-1
Trace Element Concentration Ranges	5-1
6 METAL SLAGS	6-1
Information Sources	6-1
Trace Element Concentration Ranges	6-1
7 SPENT FOUNDRY SANDS.....	7-1
Information Sources	7-1
Trace Element Concentration Ranges	7-1

8 BIOSOLIDS	8-1
Information Sources	8-1
Trace Element Concentration Ranges	8-1
9 REGULATORY LEVELS	9-1
Toxicity Characteristic Leaching Procedure	9-1
EPA Residential and Industrial Soil Screening Levels	9-2
10 SUMMARY	10-1
11 REFERENCES	11-1

LIST OF FIGURES

Figure 3-1 Bulk chemical composition of volcanic ash, shale, and coal ash.....	3-2
Figure 3-2 Trace element concentration ranges in rocks and fly ash	3-4
Figure 3-3 Trace element concentration ranges in rocks and bottom ash	3-4
Figure 3-4 Trace element concentration ranges in rocks and FGD gypsum	3-5
Figure 4-1 Sample locations in USGS (1984) (shown as circles) and USGS (2005) (shown as solid line transects). Figure modified after USGS (2001). Different-color circles represent separate sample collection efforts that are summarized in USGS (1984).....	4-2
Figure 4-2 Distribution of prairie and volcanic soils in the United States (USDA, 2009).....	4-2
Figure 4-3 Comparison of minimum, maximum, 10 th percentile, and 90 th percentile concentration values in the USGS (1984) and USGS (2005) datasets (see Table 4-1).....	4-4
Figure 4-4 Comparison of mean and median concentration values in the USGS (1984) and USGS (2005) datasets	4-4
Figure 4-5 Trace element concentration ranges in U.S. soils and fly ash.....	4-6
Figure 4-6 Trace element concentration ranges in U.S. soils and bottom ash	4-7
Figure 4-7 Trace element concentration ranges in U.S. soils and FGD gypsum	4-7
Figure 5-1 Trace element concentration ranges in fly ash and fertilizers compared as minima and maxima	5-2
Figure 5-2 Trace element concentration ranges in bottom ash and fertilizer compared as minima and maxima	5-2
Figure 5-3 Trace element concentration ranges in FGD gypsum and fertilizer compared as minima and maxima	5-3
Figure 6-1 Trace element concentration ranges in metal slags and fly ash compared as minima and maxima	6-2
Figure 6-2 Trace element concentration ranges in metal slags and bottom ash compared as minima and maxima	6-3
Figure 6-3 Trace element concentration ranges in metal slags and FGD gypsum compared as minima and maxima	6-4
Figure 6-4 TCLP leachate concentration ranges for metal slags and fly ash	6-6
Figure 7-1 Trace element concentration ranges for spent foundry sand and fly ash.....	7-2
Figure 7-2 Trace element concentration ranges for spent foundry sand and bottom ash.....	7-3
Figure 7-3 Trace element concentration ranges for spent foundry sand and FGD gypsum	7-4
Figure 7-4 TCLP leachate concentration ranges for spent foundry sand and fly ash	7-6

Figure 7-5 SPLP leachate concentration ranges for spent foundry sand and fly ash	7-6
Figure 8-1 Trace element concentration ranges for biosolids and fly ash	8-2
Figure 8-2 Trace element concentration ranges for biosolids and bottom ash	8-2
Figure 8-3 Trace element concentration ranges for biosolids and FGD gypsum.....	8-3
Figure 9-1 Coal ash TCLP leachate concentration ranges compared to regulatory limits	9-1
Figure 9-2 Trace element concentration ranges in fly ash compared to EPA residential soil screening levels	9-2
Figure 9-3 Trace element concentration ranges in bottom ash compared to EPA residential soil screening levels.....	9-3
Figure 9-4 Trace element concentration ranges in FGD gypsum compared to EPA residential soil screening levels.....	9-4
Figure 9-5 Comparison of CCP, soil, fertilizer, spent foundry sand, metal slag, and biosolid arsenic concentrations to EPA residential and industrial soil screening levels	9-5

LIST OF TABLES

Table 2-1 Statistical summary of the concentrations of various elements in coal combustion products (all concentrations in mg/kg)	2-3
Table 2-2 Statistical summary of the concentrations of various elements in other materials (all concentrations in mg/kg)	2-4
Table 3-1 Concentration comparisons summary for CCPs and rocks (10 th to 90 th percentile ranges)	3-6
Table 4-1 Summary statistics for soil trace element concentrations reported in USGS (1984) and USGS (2005) (data in mg/kg)	4-5
Table 4-2 Concentration comparisons summary for CCPs and soils.....	4-8
Table 5-1 Concentration comparisons summary for CCPs and fertilizers	5-4
Table 6-1 Concentration comparisons summary for CCPs and metal slags.....	6-5
Table 7-1 Concentration comparisons summary for CCPs and spent foundry sands	7-5
Table 8-1 Concentration comparisons summary for CCPs and biosolids.....	8-4

1

INTRODUCTION

Background

Coal combustion products (CCPs)—fly ash, bottom ash, slag, and flue gas desulfurization (FGD) solids—are produced when coal, a sedimentary rock, is burned to generate electricity. Coal, the parent material of fly ash and bottom ash, contains primarily organic matter along with smaller amounts of inorganic rock fragments and mineral matter. When the organic matter is released from coal during combustion, most of the inorganic matter either drops to the bottom of the boiler as bottom ash, or is captured from the flue gas as fly ash. As a result, fly ash and bottom ash are composed of the same elements as rocks and soils, although the trace elements are enriched relative to the parent coal.

FGD solids are produced when an alkaline material, usually limestone or lime, is added to the flue gas to react with sulfur dioxide. The reaction produces calcium-sulfur compounds that are then removed from the flue gas. The most common FGD process is one using limestone and forced oxidation to form FGD gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). FGD gypsum and mined gypsum are chemically similar and find many of the same uses in products. Both also contain some trace constituents.

This report compares the chemical characteristics of coal combustion products to the chemical characteristics of natural materials and selected manufacturing by-products. Chemical characteristics of coal fly ash, bottom ash, and FGD gypsum are compared to those of materials such as soils, rocks, fertilizers, metal slags, biosolids, and spent foundry sands. Materials were chosen on the basis that they were either naturally occurring or were beneficially reused by-products or products. The basic approach was to provide a graphic comparison of the trace element concentration ranges of CCPs to those of other materials. Data used to produce the graphics are also provided.

Report Organization

Each section of this report compares CCPs with a particular solid material. Section 2 describes the source of all CCP data that are used throughout the report. Sections 3 and 4 present data for rocks and soils, respectively. Extended discussion is provided regarding selection of a data source for soil concentrations. Section 5 compares trace constituents in CCPs and fertilizers. Sections 6, 7, and 8 compare trace constituents in CCPs and beneficially used materials—metal slags, biosolids, and spent foundry sands, respectively. Section 9 presents chemical

Introduction

characteristics of CCPs in the context of regulatory thresholds such as EPA soil screening levels and Toxicity Characteristic Leaching Procedure analyses. Section 10 concludes the report with a brief summary of important findings.

2

DATA AND METHODS

Summaries of all concentrations used for comparison in this study are listed in Tables 2-1 and 2-2. Data sources for materials other than CCPs are discussed in sections of the report where data are compared.

Coal combustion product data were obtained primarily from the CP-Info database (EPRI, 2009a). Where data were not available in CP-Info, data were obtained from the EPRI PISCES database (EPRI, 2009b). The CP-Info and PISCES databases contain results generated during 30 years of EPRI research and represent a broad range of CCP materials. Reports used to compile data for CP-Info include:

- EPRI, 1986. *Mobilization and Attenuation of Trace Elements in an Artificially Weathered Fly Ash*. EPRI, Palo Alto, CA. EA-4747.
- EPRI, 1987. *Matrix Isolation Spectroscopy and the Stability of Polycyclic Aromatics in Coal Ash: Final Report*. EPRI, Palo Alto, CA. EA-5148.
- EPRI, 1987. *Chemical Characterization of Fossil Fuel Combustion Wastes*. EPRI, Palo Alto, CA. EA-5321.
- EPRI, 1994. *A Field and Laboratory Study of Solute Release from Sluiced Fly Ash*. EPRI, Palo Alto, CA. TR-104585.
- EPRI, 1995. *Effects of Flue Gas Desulfurization (FGD) System Additives on Solid By-Products*. EPRI, Palo Alto, CA. TR-102367.
- EPRI, 1996. *Mixtures of a Coal Combustion By-Product and Composted Yard Wastes for Use as Soil Substitutes and Amendments*. EPRI, Palo Alto, CA. TR-106682.
- EPRI, 1999. *Utilization of Coal Combustion By-Products in Agriculture and Land Reclamation*. EPRI, Palo Alto, CA. TR-112746.
- EPRI, 2002. *Mercury Releases from Coal Fly Ash*. EPRI, Palo Alto, CA. 1005259.
- Gustin, M. and Ladwig, K., 2004. *An assessment of the significance of mercury release from coal ash*. *Journal of the Air and Waste Management Association* 54(320-330).
- EPRI, in preparation. *FGD Gypsum Characterization Data*. EPRI, Palo Alto, CA. Scheduled for publication in 2010.

In many studies, multiple CCP sample analyses originate from a single power plant. This created the potential for biasing the dataset, overweighting results produced from a single plant. In the current investigation, results known to originate from a single plant were averaged to produce a single concentration for that plant site. This concentration was then used in

subsequent statistical calculations. Although this approach limited the number of data points available for analysis, it achieved a more representative sampling across the electric utility industry without biasing results from one plant.

In this report, the following statistical values are used: median, minimum, maximum, 10th percentile, and 90th percentile. Median values are also known as the 50th percentile, or data point at which half the values fall below and half fall above. Minima and maxima are the smallest and largest data points in the dataset, respectively. Where possible, the 10th and 90th percentile values were used as better representations of data ranges, due to the possibility of outlier data. In some cases, percentile values were not calculated, due either to lack of data or to the high potential for bias in the dataset. In the case of metal slags, there were not enough data reported to calculate percentages. In the case of fertilizers, the very large variability in reported fertilizer type and manufacturers made percentile calculations less reliable than a comparison of minima and maxima.

In many cases, some or all statistical values were less than method detection limits. In these cases, the detection limit was substituted as the value for that statistic. Ranges are non-existent for the cases where all values are less than detection limits, and are represented graphically as single points or bars. In the case of cadmium in fly ash, the dataset contained a few detection limits higher than most of the detected values. In this case, all non-detects higher than the median of detects were excluded.

Data are presented using bars representing the concentration range of the CCP plotted against the concentration range of the material being compared. Graphically, using a log scale allows plotting of multiple elements on one graph, maintaining the ability to visually compare concentration ranges. The bars are bounded by 10th and 90th percentiles, or by minima and maxima. Elements are then qualitatively grouped into one of seven categories, depending upon how the CCP concentration range compares graphically to the selected material.

Table 2-1
Statistical summary of the concentrations of various elements in coal combustion products (all concentrations in mg/kg)

Fly Ash		As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
# Sites		59	39	28	59	58	19	59	36	38	229
Max		1385	10850	17	651	2120	1.3	47	13	131	826
90th Perc.		261	5064	6.2	298	143	0.5146	18	7.6	16	26
50th Perc.		71	923	1.07	133	49	0.1075	11	<4.9	<7.2	10.6
10th Perc.		22	381	0.36	27	21	0.0104	1.8	<4.9	<7.2	2.2
Min		8.1	239	<0.11	11	13	<0.0025	<1.4	<4.9	<7.2	<0.4
		B	Co	Cu	Mn	Ni	Tl	V	Zn	Fe	Mo
# Sites		26	3	57	49	57	59	39	59	66	57
Max		2500	124	1452	1332	353	85	652	2880	175550	236
90th Perc.		1018	101	216	700	231	45	364	683	128838	60
50th Perc.		322	7.9	140	189	102	2.4	254	152	69100	19
10th Perc.		118	7.4	62	91	47	<0.17	59	63	33575	9.0
Min		55	7.3	45	44	23	<0.17	<43.5	25	17000	4
Bottom Ash		As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
# Sites		37	37	37	37	37	160	37	37	37	152
Max		56	9360	<5.5	4710	843	1.3	8.2	7.5	8.4	568
90th Perc.		21	3604	<5.5	1132	53	0.080	4.2	<5.5	<7	14
50th Perc.		7.2	768	<5.5	191	20	0.018	<1.25	<5.5	<7	5.8
10th Perc.		2.6	378	<5.5	51	8.1	0.004	<1.25	<5.5	<7	0.208
Min		<1.3	<61	<5.5	<24	<2.1	<0.002	<1.25	<5.5	<7	<0.064
		B	Co	Cu	Mn	Ni	Tl	V	Zn	Fe	Mo
# Sites		76	NA	37	37	37	21	37	37	37	37
Max		990	NA	146	1940	1267	59	275	717	199500	46
90th Perc.		335	NA	118	892	445	0.88	250	367	158850	27
50th Perc.		82	NA	73	262	123	<0.5	161	59	101200	11
10th Perc.		2.7	NA	39	85	39	<0.5	<50	16	40339	3.9
Min		<2.04	NA	20	73	<12	<0.5	<50	3.8	21600	<1.4
FGD Gypsum		As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
# Sites		27	27	26	27	27	27	27	1	26	27
Max		11	55	0.37	24	2.0	1.5	32	<4.9	2.0	<0.1
90th Perc.		5.9	22	0.21	6.7	<1	0.801	24	<4.9	<0.4	<0.1
50th Perc.		2.9	6.1	0.07	2.4	<1	0.200	4.2	<4.9	<0.4	<0.1
10th Perc.		2.1	2.6	<0.02	0.83	<1	0.035	<2.5	<4.9	<0.4	<0.1
Min		<1.9	0.91	<0.02	0.60	<1	0.0075	<2.5	<4.9	<0.4	<0.1
		B	Co	Cu	Mn	Ni	Tl	V	Zn	Fe	Mo
# Sites		26	26	26	27	26	26	26	26	26	26
Max		387	<1	3.2	129	2.4	<0.05	8.6	23	1823	3.1
90th Perc.		93	<1	2.2	47	2.1	<0.05	4.1	14	1611	1.7
50th Perc.		<25	<1	1.1	8.8	1.1	<0.05	<1	5.4	800	0.53
10th Perc.		<25	<1	<0.4	<1	0.6	<0.05	<1	<1.25	296	0.17
Min		<25	<1	<0.4	<1	<0.2	<0.05	<1	<1.25	130	<0.02

NA – Data Not Available

Table 2-2
Statistical summary of the concentrations of various elements in other materials (all concentrations in mg/kg)

Rock	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
# Samples	18149	31706	27	31384	4257	120	167	1200	30134	1175
Max	138000	537000	5.8	37000	63000	10	20	770	44200	48
90th Perc.	14	1390	3.6	309	44	2	4.9	3	1.8	4.4
50th Perc.	1.6	420	<2	28	15	0.7	1.9	0.90	0.30	1.3
10th Perc.	0.5	67	<2	1.9	3.8	0.1	0.60	0.03	0.08	0.10
Min	<0.0087	0.13	<2	0.14	<0.1	0.03	<0.13	<0.01	<0.0019	<0.008
	B	Co	Cu	Mn	Ni	Tl	V	Zn	Fe	Mo
# Samples	3126	31504	26873	1714	22875	1177	4376	29636	NA	4263
Max	78000	29100	104000	610000	88300	24.8	2730	354000	NA	640
90th Perc.	220	53	122	1740	220	1.8	232	138	NA	18
50th Perc.	0.33	16	30	430	18	0.50	52	72	NA	1.6
10th Perc.	<0.2	0.86	10	49	2.0	0.10	2.6	25	NA	0.24
Min	<0.2	0.02	<0.5	0.09	0.09	<0.003	<0.1	0.11	NA	<0.05
Soil	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
# Samples	1258	1320	830	1320	1320	1268	1268	830	355	1304
Max	97	5000	8.2	2000	700	4.6	4.32	<1	8.78	15
90th Perc.	12	1000	0.5	100	30	0.19	0.8	<1	1.3	2
50th Perc.	5.8	500	0.2	50	15	0.05	0.3	<1	<1	<1
10th Perc.	2.0	200	<0.1	15	<10	0.02	<0.1	<1	<1	<1
Min	<0.1	10	<0.1	<1	<10	<0.02	<0.1	<1	<1	<1
	B	Co	Cu	Mn	Ni	Tl	V	Zn	Fe	Mo
# Samples	1320	1324	1312	1318	1319	830	1320	1249	NA	1299
Max	300	70	700	7000	700	1.8	500	2890	NA	15
90th Perc.	70	15	50	1000	30	0.7	150	99	NA	<3
50th Perc.	30	7	20	300	15	0.5	70	50	NA	<3
10th Perc.	<20	<3	5	100	5	0.2	20	22	NA	<3
Min	<20	<3	<1	<2	<3	<0.1	<7	<5	NA	<3
Foundry Sand	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
# Samples	43	43	43	43	43	43	43	43	43	43
Max	4.8	151	<5.9	149	26	NA	NA	<17.6	<4.5	3.1
90th Perc.	1.98	35	<5.9	35	<7.7	NA	NA	<17.6	<4.5	1.24
50th Perc.	0.83	15	<5.9	2.8	<7.7	NA	NA	<17.6	<4.5	<1.2
10th Perc.	0.14	4.35	<5.9	1.5	<7.7	NA	NA	<17.6	<4.5	<1.2
Min	0.04	<8.7	<5.9	<1	<7.7	NA	NA	<17.6	<4.5	<1.2
	B	Co	Cu	Mn	Ni	Tl	V	Zn	Fe	Mo
# Samples	43	43	43	43	43	43	43	43	43	43
Max	<19.2	95	3318	671	2328	NA	9.1	1640	NA	NA
90th Perc.	<19.2	1.66	62	194	28	NA	<7.4	<33.4	NA	NA
50th Perc.	<19.2	<0.84	<23.1	<45	2.8	NA	<7.4	<33.4	NA	NA
10th Perc.	<19.2	<0.84	<23.1	<45	1.5	NA	<7.4	<33.4	NA	NA
Min	<19.2	<0.84	<23.1	<45	<1.2	NA	<7.4	<33.4	NA	NA
Biosolids	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
# Samples	84	84	84	84	84	84	84	84	84	84
Max	49.2	3460	11.8	1160	450	8.26	24.7	856	27	2.34
90th Perc.	13	1183	6.96	213	171	2.58	13	39	4.02	0.86
50th Perc.	5.08	431	1.75	35	49	0.85	6.2	14	1.62	0.28
10th Perc.	2.61	200	0.97	14.4	21	0.33	3	3.54	0.05	0.10
Min	1.18	75	0.21	6.74	5.81	0.17	1.1	1.94	<0.04	0.04
	B	Co	Cu	Mn	Ni	Tl	V	Zn	Fe	Mo
# Samples	84	84	84	84	84	84	84	84	84	84
Max	204	290	2580	14900	526	1.68	617	8550	NA	132
90th Perc.	106	15.99	955	2945	117	0.37	98	1561	NA	36
50th Perc.	33	4.63	468	433	24	0.13	14	803	NA	11
10th Perc.	9.49	1.79	167	152	11	0.05	6.84	379	NA	4.05
Min	5.7	0.87	115	35	7.44	0.02	2.04	216	NA	2.51
Fertilizers	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
Min	<2	<2	<0.02	<0.5	<1.5	<0.003	<1	<0.01	<0.1	<0.011
Max	4600	704	201	840	1480	2.91	44	6.32	12.2	4.66
	B	Cu	Mn	Co	Ni	Tl	V	Zn	Fe	Mo
Min	<15	<1.5	<2.5	0.25	<0.15	<0.15	<1	<5	NA	<0.04
Max	123644	3620	9641	62	517	3.9	949	460564	NA	39
Metal slags	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Sb	Be
# Samples	73	73	73	73	73	73	73	73	73	73
Min	0.5	24	0.1	10	1.4	0.1	2.2	1.3	1.1	0.6
Max	5.8	1800	19	6200	330	0.1	36	100	18	11
	B	Co	Cu	Mn	Ni	Tl	V	Zn	Fe	Mo
# Samples	73	73	73	73	73	73	73	73	73	73
Min	NA	0.9	1.7	100	2.1	11	170	3.5	NA	0.8
Max	NA	13	540	65700	310	11	1700	690	NA	81

NA – Data Not Available

3

ROCKS

Information Sources

Trace element concentration data for rocks are provided in many different sources, including, but not limited to:

- United States Geological Survey, 2009. *Geochemistry of rock samples from the National Geochemical Database*. U.S. Geological Survey, Reston, VA.
- Blatt and Tracy (eds), 1996. *Petrology: Igneous, Sedimentary and Metamorphic*, 2nd Ed. W.H. Freeman and Company, 529 pp.
- Horn, M.K. and Adams, J.A.S., 1966. *Computer-derived geochemical balances and elemental abundances*. *Geochimica et Cosmochimica Acta*, Vol. 30, pp. 279-297. In Hem, J.D., 1992. *Study and Interpretation of the Chemical Characteristics of Natural Water*. U.S. Geological Survey Professional Paper 2254.
- Taylor, H.E., and F.E. Lichte, 1980. *Chemical composition of Mount St. Helens volcanic ash*. *Geophysical Research Letters*, Vol. 7, No. 11, pp. 949-952.
- Cannon, H.L., 1978. *Report of the workshop at South Seas Plantation Captiva Island, Florida*, *Geochemistry and the Environment* 3 (1978), pp. 17–31. In Adriano, D.C. (ed), 2001. *Trace Elements in the Terrestrial Environment*, Springer-Verlag, New York.

In the current evaluation, the major chemical compositions of CCPs and rocks are compared using data from Blatt and Tracy (1996) and Horn and Adams (1966). Trace element concentrations in CCPs are compared to those in “rocks,” a collective term for all rock types, including igneous, metamorphic, and sedimentary, using data from USGS (2009). CCPs are compared separately to volcanic ash using data reported by Taylor and Lichte (1980).

Bulk Chemical Composition

Fly ash and bottom ash are most similar in bulk chemical composition to siliceous rocks, and the greatest similarity is observed between fly ash and bottom ash and rocks such as volcanic ash and shale (Figure 3-1). The overall chemical composition of coal ash resembles that of siliceous rocks from which it was derived, particularly shale. Oxides of silicon, aluminum, iron, and calcium make up more than 90% of most siliceous rocks, soils, fly ash, and bottom ash. Other major and minor elements (sulfur, sodium, potassium, magnesium, titanium) make up an additional 8%, while trace constituents account for less than 1%.

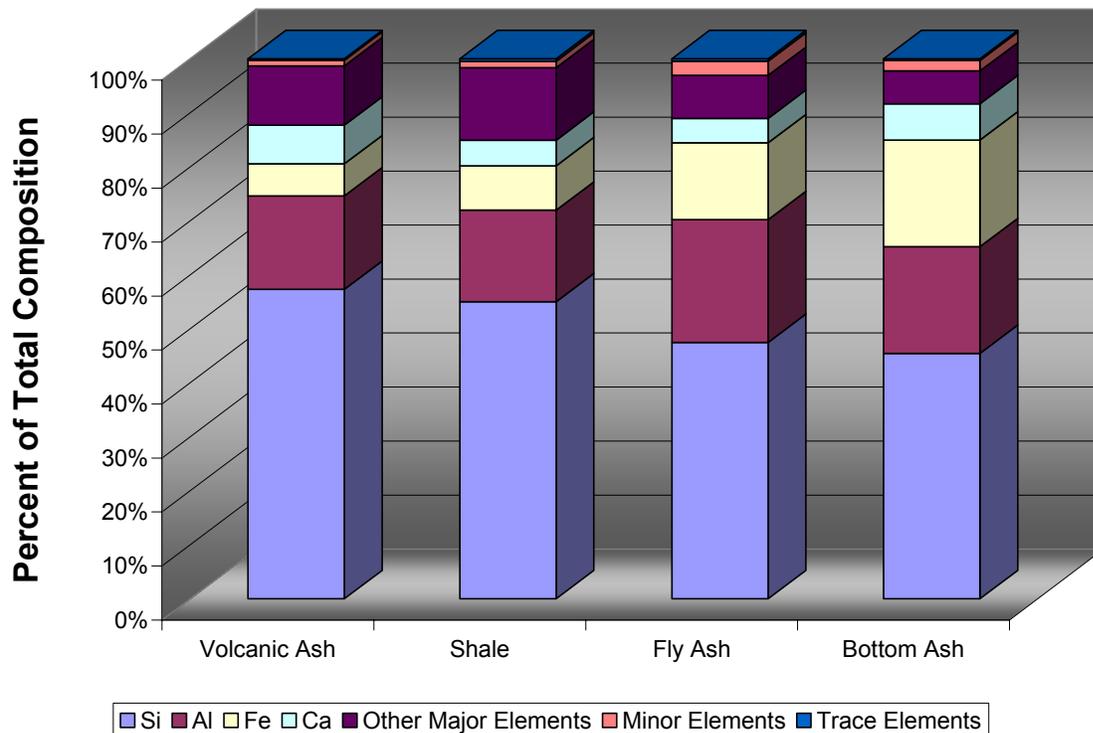


Figure 3-1
Bulk chemical composition of volcanic ash, shale, and coal ash

Trace Element Concentration Ranges

Data Source Considerations

USGS (2009) data are available from a comprehensive dataset referred to as the “National Geochemical Database: Rocks,” containing 414,321 records. The reliability of the data source and the wealth of data contained in the database make this source preferable to others for the current study. Downloadable data are distributed in files unique to the analytical method used to produce the data. For example, the x-ray fluorescence (XRF), instrumental neutron activation analysis (INAA), inductively coupled plasma–atomic emission spectrometry (ICP-AES), or inductively coupled plasma–mass spectrometry (ICP-MS) spreadsheets may be downloaded separately. The data query by method allows the user to choose the analytical method best suited for the element of concern. The USGS web page directs the user toward the most appropriate dataset for a particular element with the following statement, where arsenic is an example:

“Analytical methods for arsenic are listed in a general order of preference based on method consistency, reliability, and detection limits. All total digestion methods are listed before any partial digestion methods.”

The user then downloads the most appropriate dataset for the element of concern, based upon the attributes described above. By doing so, the user possesses a reliable dataset that is also amenable to data analysis.

In this study, trace element concentration ranges as percentiles were calculated based upon the analytical method dataset most appropriate for that element (i.e., listed first in order of preference by the USGS). For example, the arsenic 10th and 90th percentiles are based only on data contained in the INAA dataset, whereas manganese data are evaluated from the ICP-AES dataset.

Trace Element Comparisons to Fly Ash, Bottom Ash, and FGD Gypsum

Trace element concentration ranges of CCPs are compared to those of rocks in Figures 3-2 to 3-4. All comparisons are summarized in Table 3-1. Trace element concentrations in fly ash are generally higher than in rocks, concentrations in bottom ash are comparable to or higher than in rocks, and concentrations in FGD gypsum are generally comparable to or less than in rocks.

When minima and maxima data are used, trace element concentration ranges in fly ash plot within the concentration ranges of rock, with the exceptions of cadmium, selenium, beryllium, and thallium. However, the use of minima and maxima is not recommended in this case. For example, in the case of arsenic in rocks, the maximum for rocks is 138,000 mg/kg, but the 99th percentile is 323 mg/kg—a difference of three orders of magnitude that biases the comparison. Therefore, the use of the 10th and 90th percentiles is more appropriate.

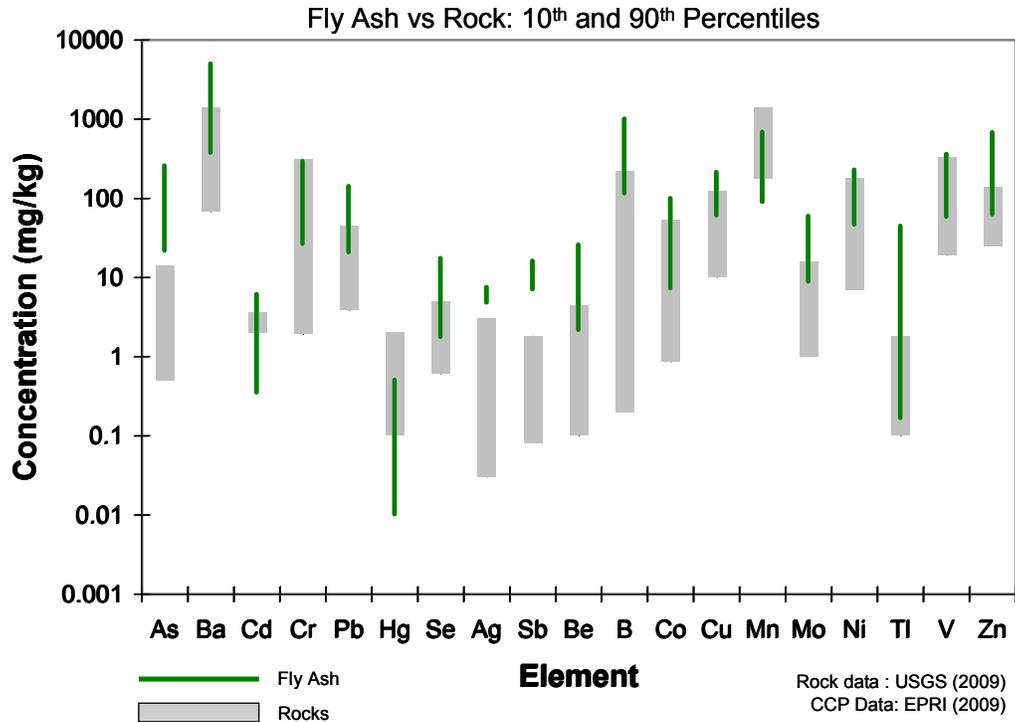


Figure 3-2
Trace element concentration ranges in rocks and fly ash

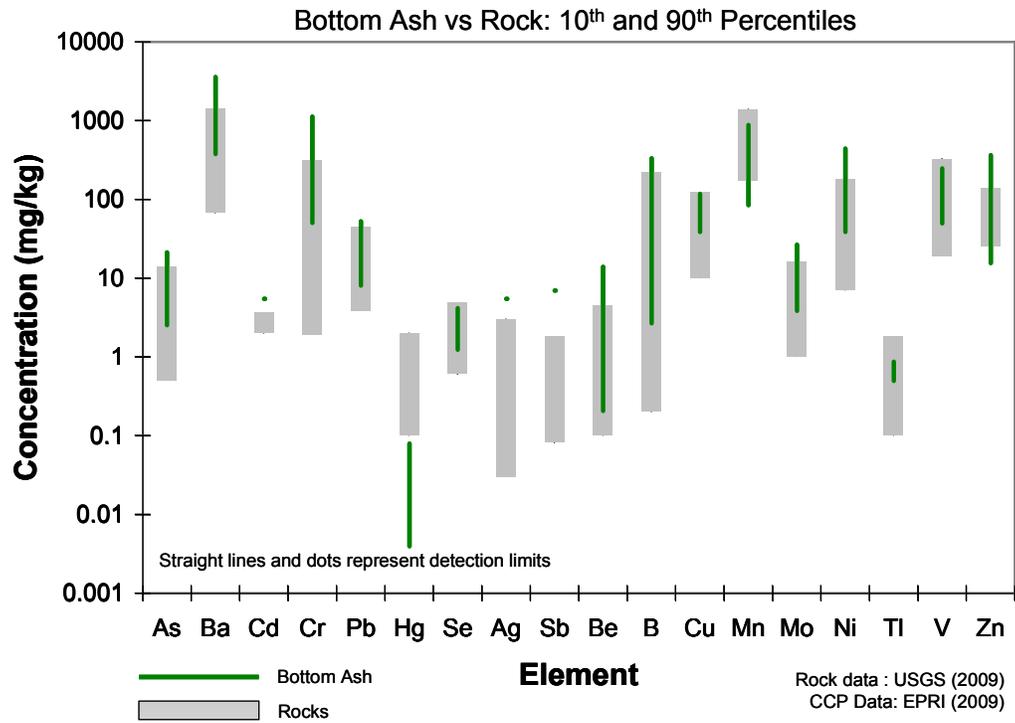


Figure 3-3
Trace element concentration ranges in rocks and bottom ash

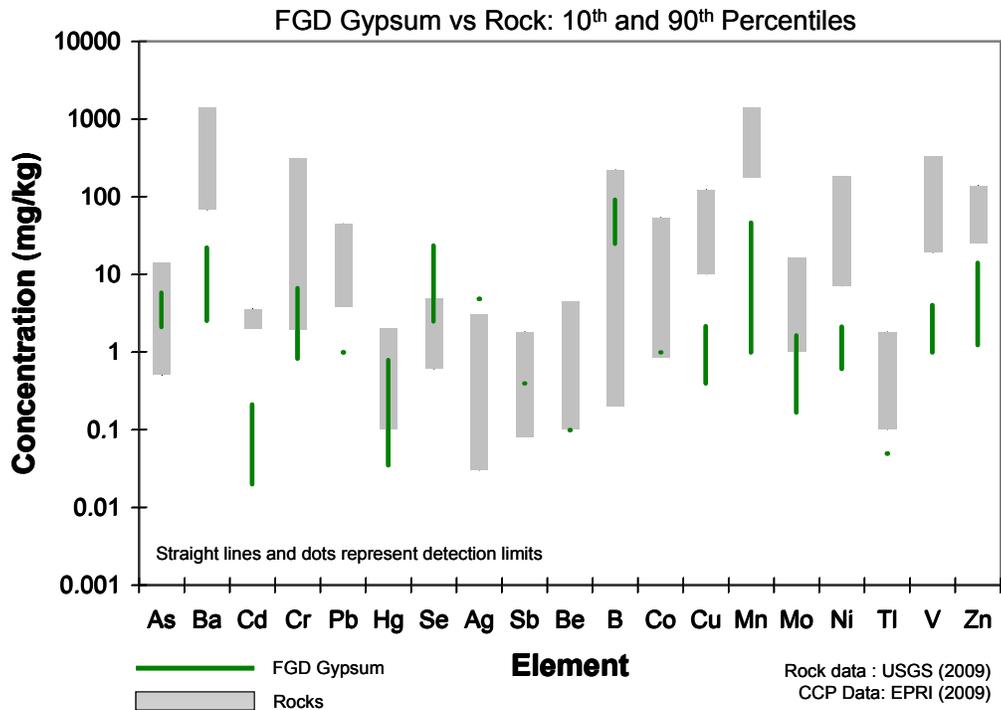


Figure 3-4
Trace element concentration ranges in rocks and FGD gypsum

Table 3-1
Concentration comparisons summary for CCPs and rocks (10th to 90th percentile ranges)

Graphical Comparison	Fly Ash	Bottom Ash	FGD Gypsum
Above range 	As, Ag, Sb		
Overlapping higher 	Ba, Pb, Se, Be, B, Co, Cu, Mo, Ni, Ti, V, Zn	As, Ba, Cr, Pb, Be, B, Mo, Ni	Se
Overlapping 	Cd	Zn	
Within 	Cr	Se, Cu, Ti, V	As, B
Overlapping lower 	Hg, Mn	Mn	Cr, Hg, Co, Mo
Below range 		Hg	Ba, Cd, Pb, Be, Cu, Mn, Ni, Ti, V, Zn
Unable to compare due to all non-detects		Cd, Ag, Sb	Ag, Sb

Key:

 CCPs

 Rocks

4

SOILS

Information Sources

Two primary sources of soil composition data exist for the United States:

- United States Geological Survey (Shacklette and Boerngen), 1984. *Element concentrations in soils and other surficial materials of the coterminous United States: An account of the concentrations of 50 chemical elements in samples of soils and other regoliths*. U.S. Geological Survey Professional Paper 1270.
- United States Geological Survey (Smith et al.), 2005. *Major- and trace-element concentrations in soils from two continental scale transects of the United States and Canada*. U.S. Geological Survey Open-File Report 2005-1253.

The choice of dataset used for comparison is discussed in detail below.

Comparison of Soil Data Sources

Each study proposed to establish “baseline” soil concentrations across the United States. USGS (1984) accomplished this by sampling surface soils across the entire coterminous United States, but at a relatively low sampling density (shown as circles in Figure 4-1). USGS (2005) sampled soils along two transects (North-South and East-West), but at a higher sampling density (shown as solid line transects in Figure 4-1). The following discussion describes advantages and disadvantages to using either study as a primary data source, without rigorous statistical analysis of the data.

The benefits of using USGS (1984) as the primary dataset are:

- The study sampled more total sites (1,323) than USGS (2005) (265). More data provide greater confidence for calculations, and it is more likely that the dataset will capture the total concentration range for a particular element. For example, the highest arsenic concentration in the USGS (2005) dataset is 23 mg/kg, compared to 97 mg/kg in the USGS (1984) study;
- The study included more elements (50) than the USGS (2005) study (42);
- Sample locations were spread across the entire coterminous United States, providing more coverage of factors that influence soil development and chemistry—specifically time, climate, topography, and parent materials (rocks). For example, USGS (2005) appears to entirely neglect volcanic soils, and may focus too heavily on prairie soils (Figure 4-2);
- The study included boron, a commonly found element in CCPs, but USGS (2005) did not;

- The study made a deliberate attempt to avoid sampling disturbed agricultural soils in an effort to present only data that may be considered “pristine.” This is beneficial because the goal of this study is not to compare CCPs to soils affected by anthropogenic sources, but to naturally occurring soils; and
- Detection limits for arsenic, manganese, and selenium are lower than in the USGS (2005) study. These elements are commonly found in CCPs, and can be the focus of regulatory concerns.

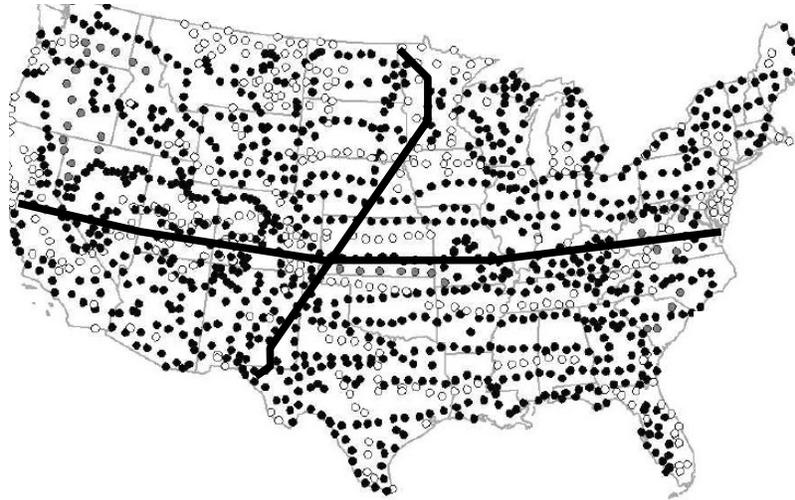


Figure 4-1
 Sample locations in USGS (1984) (shown as circles) and USGS (2005) (shown as solid line transects). Figure modified after USGS (2001). Different-color circles represent separate sample collection efforts that are summarized in USGS (1984).

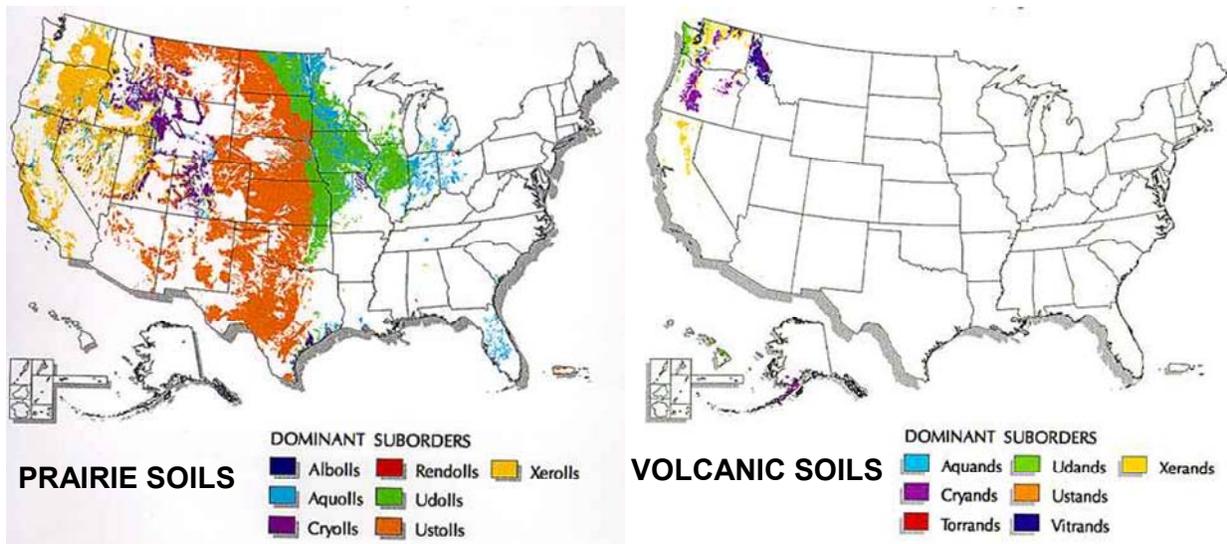


Figure 4-2
 Distribution of prairie and volcanic soils in the United States (USDA, 2009)

The benefits of using USGS (2005) as the primary dataset are:

- The study included thallium, silver, and cadmium, but USGS (1984) did not;
- The study has been used in recent risk assessment activities, such as that performed by the U.S. Department of Agriculture for spent foundry sands;
- Detection limits for cobalt, molybdenum, nickel, lead, antimony, vanadium, and zinc are lower—in some cases substantially lower—than in the USGS (1984) study; and
- The sample density is higher than in USGS (1984). For this study, increased sample density may not play an important role if the overall number of samples is lower, and many geographic areas of the United States were excluded. However, if the study is amended with future attempts to increase areal sample coverage, then increased sample density would be beneficial.

Despite their differences, using one dataset and not the other may not produce significantly different results. For example, the 10th and 90th percentile values of multiple elements are similar, suggesting that an increased total number of samples did not produce significant changes in an element's concentration range when viewed as percentile values (Figure 4-3). The minimum and maximum values show less agreement, suggesting that either detection limit differences or differences in total sample numbers produce less comparability at concentration range extremes (potential outliers). Furthermore, mean and median values from each dataset show generally good agreement and closeness to the 1:1 line (Figure 4-4).

The USGS (1984) study was chosen as the primary dataset for comparisons, substituting USGS (2005) data for thallium, silver, and cadmium. The reasoning is as follows:

- USGS (1984) offers a more thorough analysis of the entire coterminous United States, including more major soil types, climatic zones, and parent materials (rocks);
- USGS (1984) attempted to exclude potentially contaminated soils in an effort to describe “baseline” concentrations. Although this may not have been totally achievable, it helps to ensure that CCPs are compared to naturally occurring concentrations in soils;
- Arsenic and selenium detection limits in USGS (1984) were lower, providing a more conservative comparison to CCPs;
- Higher sample density is not believed to improve the dataset quality for comparisons to CCPs; and
- Both datasets produce similar summary statistics, including 10th and 90th percentile, median, and mean values.

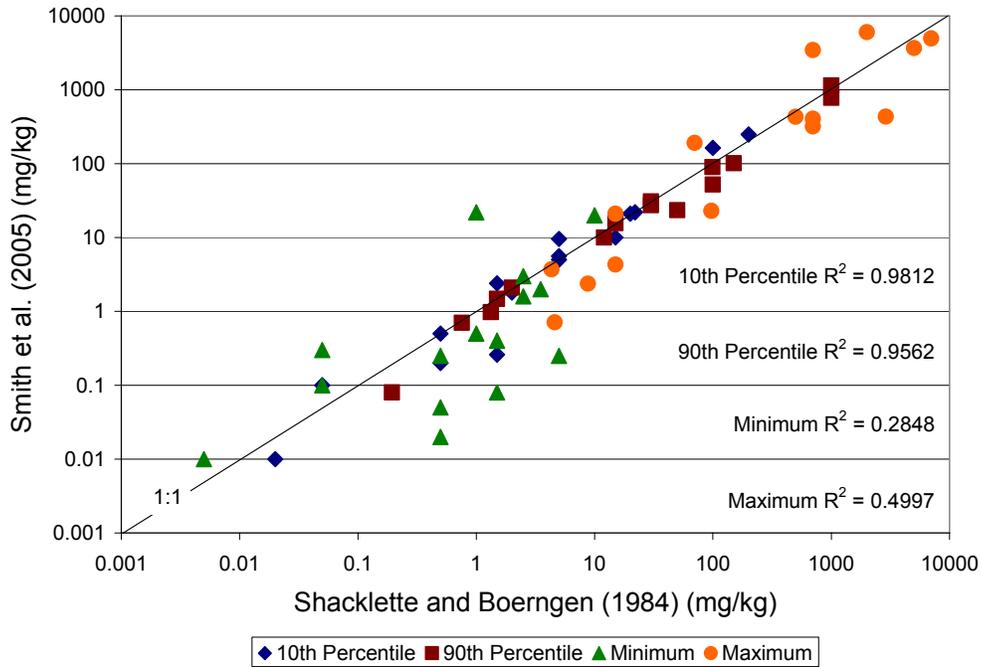


Figure 4-3
Comparison of minimum, maximum, 10th percentile, and 90th percentile concentration values in the USGS (1984) and USGS (2005) datasets (see Table 4-1)

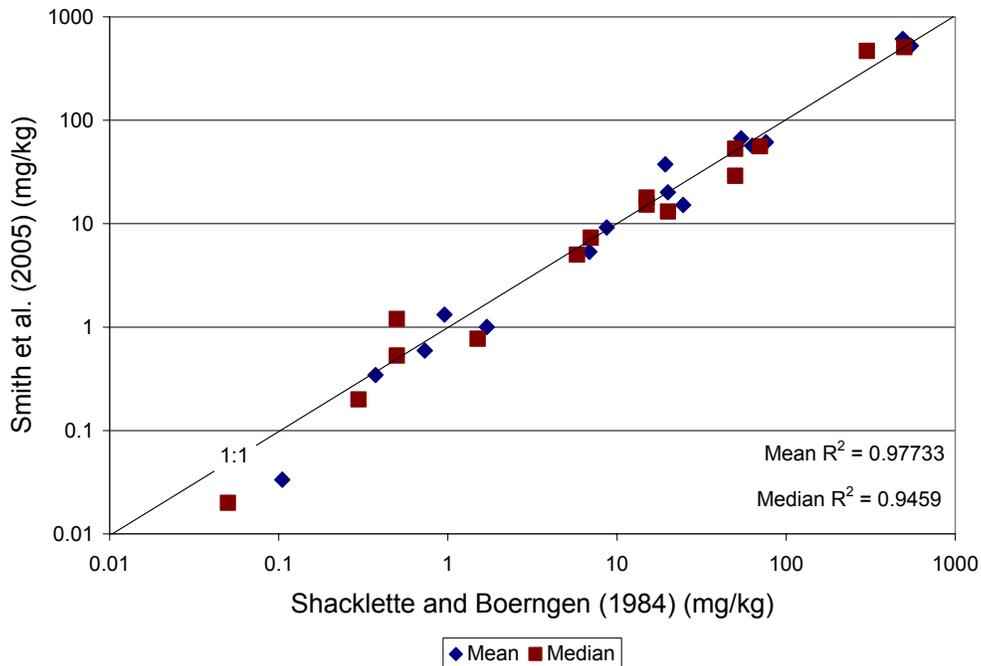


Figure 4-4
Comparison of mean and median concentration values in the USGS (1984) and USGS (2005) datasets

Table 4-1

Summary statistics for soil trace element concentrations reported in USGS (1984) and USGS (2005) (data in mg/kg)

Element	Mean		Median		Min		Max		10th Percentile		90th Percentile		Detection Limits	
	S&B	Smith	S&B	Smith	S&B	Smith	S&B	Smith	S&B	Smith	S&B	Smith	S&B	Smith
Ag		<1		<1		<1		<1		<1		<1	1	1
As	6.9	5.3	5.8	5.0	<0.1	0.3	97	23	2.0	1.8	12	10	0.1	1
B	32		30		<20		300		<20		70		20	
Ba	546	526	500	508	10	20	5000	3670	200	249	1000	777		
Be	1.0	1.3	0.5	1.2	0.5	<0.1	15	4.3	0.5	0.5	2.0	2.1	0.1	0.1
Cd		0.28		0.20		0.04		8.2		<0.1		0.50		0.1
Co	8.7	9.2	7.0	7.3	<3	0.4	70	191	<3	2.4	15	16	3	0.1
Cr	54	67	50	29	1	<1	2000	6030	15	10	100	52		1
Cu	25	15	20	13	<1	<0.5	700	404	5.0	5.0	50	23	1	0.5
Hg	0.10	0.03	0.05	0.02	<0.02	<0.02	4.6	0.71	0.02	<0.02	0.19	0.08	0.02	0.02
Mn	489	611	300	468	1	22	7000	4966	100	163	1000	1140	2	5
Mo	<3	1.0	<3	0.77	1.5	0.08	15	21	<3	0.26	1.5	1.48	3	0.05
Ni	19	37	15	15	<3	1.6	700	3447	5.0	5.6	30	31	3	0.5
Pb	20	20	15	18	5.0	<0.5	700	319	<10	9.6	30	27	10	0.5
Sb	<1	0.6	<1	0.53	<1	<0.05	8.8	2.4	<1	0.20	1.3	0.98	1	0.05
Se	0.37	0.34	0.30	0.20	<0.1	<0.2	4.3	3.7	<0.1	<0.2	0.75	0.70	0.1	0.2
Tl		0.45		0.47		<0.1		1.8		0.20		0.70		0.1
V	76	61	70	56	3.5	2	500	430	20	21	150	101	7	1
Zn	63	57	50	53	2.5	3	2890	433	22	22	99	90	5	1

"S&B" refers to Shacklette and Boerngen (1984) and "Smith" refers to Smith et al. (2005).

Blank cells indicate that data were not reported.

Data plotted in Figures 4-3 and 4-4 as 1/2 DL if value is less than DL.

Trace Element Concentration Ranges

Trace element concentration ranges of CCPs are compared to those of soil in Figures 4-5 to 4-7. All comparisons are summarized in Table 4-2. Most elements exhibit higher concentration ranges in fly ash and bottom ash compared to soils. Concentrations in FGD gypsum are generally less than in soils, except for selenium and mercury.

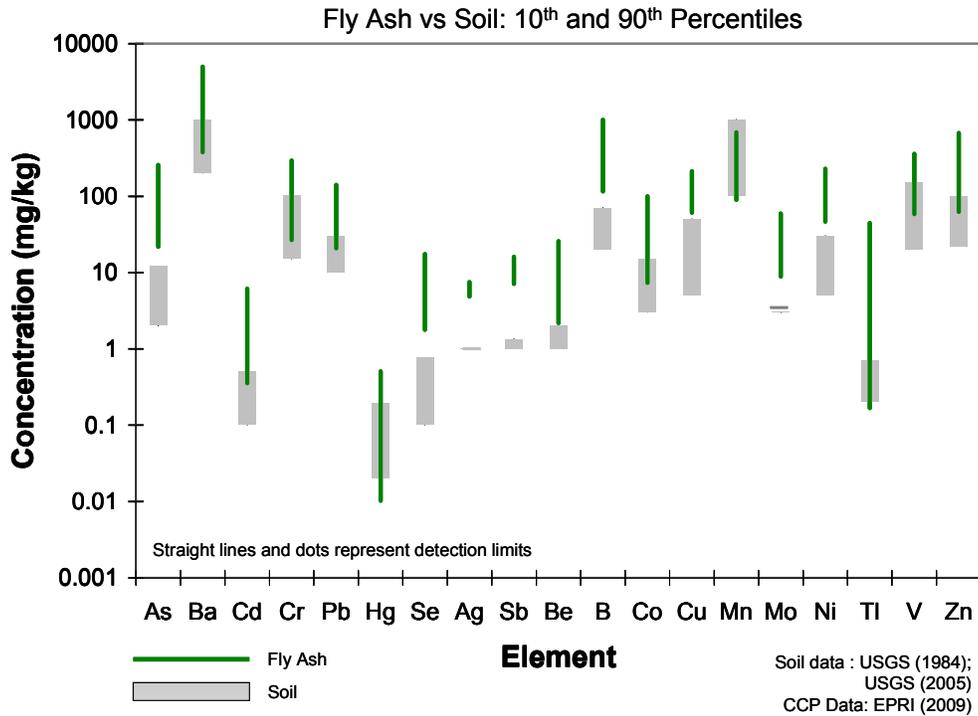


Figure 4-5
Trace element concentration ranges in U.S. soils and fly ash

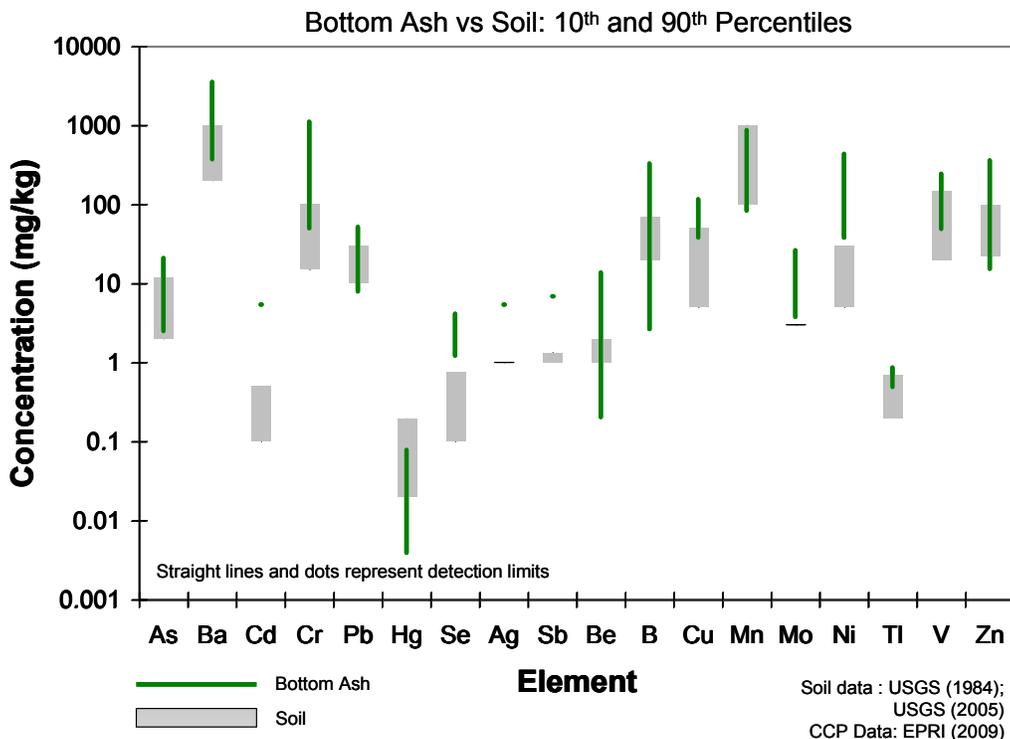


Figure 4-6
Trace element concentration ranges in U.S. soils and bottom ash

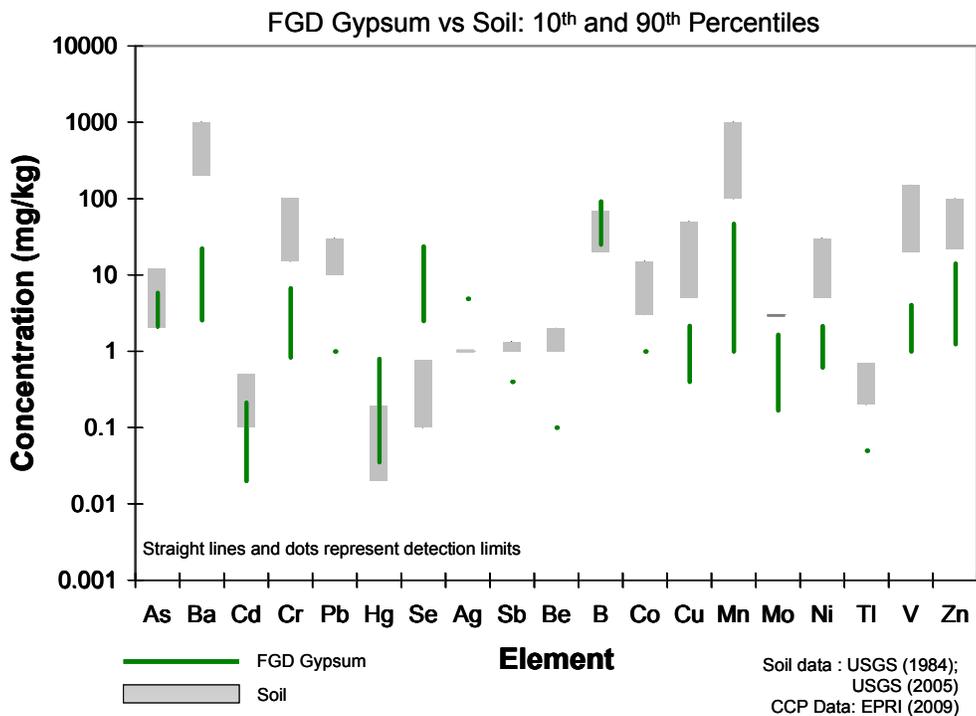


Figure 4-7
Trace element concentration ranges in U.S. soils and FGD gypsum

Table 4-2
Concentration comparisons summary for CCPs and soils

Comparison	Fly Ash	Bottom Ash	FGD Gypsum
Above range 	As, Se, Ag, Sb, Be, B, Cu, Ni, Mo	Se, Mo, Ni	Se
Overlapping higher 	Ba, Cd, Cr, Pb, Co, V, Zn	As, Ba, Cr, Cu, Tl, V	Hg, B
Overlapping 	Hg, Tl	Pb, Be, B, Zn	
Within 			As
Overlapping lower 	Mn	Hg, Mn	Cd
Below range 			Ba, Cr, Pb, Sb, Be, Co, Cu, Mn, Ni, Tl, V, Zn
Unable to compare due to all non-detects		Cd, Ag, Sb	Ag, Mo

<u>Key:</u>	
	CCPs
	Soils

5

FERTILIZERS

Information Sources

No single data source provided all necessary information to compare fertilizers and CCPs. The following data sources contain information relevant to the current study:

- U.S. Environmental Protection Agency, January 1999. *Background Report on Fertilizer Use, Contaminants and Regulations*. Office of Pollution Prevention and Toxics. EPA 747-R-98-003.
- Shaffer, M., 2001. *Waste Lands: The Threat of Toxic Fertilizer*. California Public Interest Research Group Charitable Trust.
- U.S. Environmental Protection Agency, August 1999. *Estimating Risk from Contaminants Contained in Agricultural Fertilizers*. Office of Solid Waste. EPA 68-W-98-0085.
- Washington State Department of Ecology, 1997. *Screening survey for metals in fertilizers and industrial by-product fertilizers in Washington State*. Ecology Publication #97-341. December 1997.
- Washington State Department of Agriculture, 2009. *Metals analysis conducted by WSDA*. Accessed online 9/16/09 at <http://agr.wa.gov/PestFert/Fertilizers/Metals.aspx>.
- Minnesota Department of Agriculture, 2009. *MDA fertilizer heavy metal analysis reports*. Accessed online 9/16/09 at <http://www.mda.state.mn.us/chemicals/fertilizers/heavymetals.htm>.
- Minnesota Department of Health, 2009. *Heavy metals in fertilizers*. Accessed online 9/16/09 at <http://www.health.state.mn.us/divs/eh/risk/studies/metals.html>.

Calculations of percentile values were not performed due to the wide variability in reported fertilizer types and manufacturers. Fertilizers are compared to CCPs on the basis of minima and maxima concentrations.

Trace Element Concentration Ranges

Trace element concentration ranges of CCPs are compared to those of fertilizers in Figures 5-1 to 5-3. All comparisons are summarized in Table 5-1. Fly ash and bottom ash concentrations are generally comparable to or slightly higher than those of fertilizers. Concentrations in FGD gypsum are typically comparable to or lower than those of fertilizers.

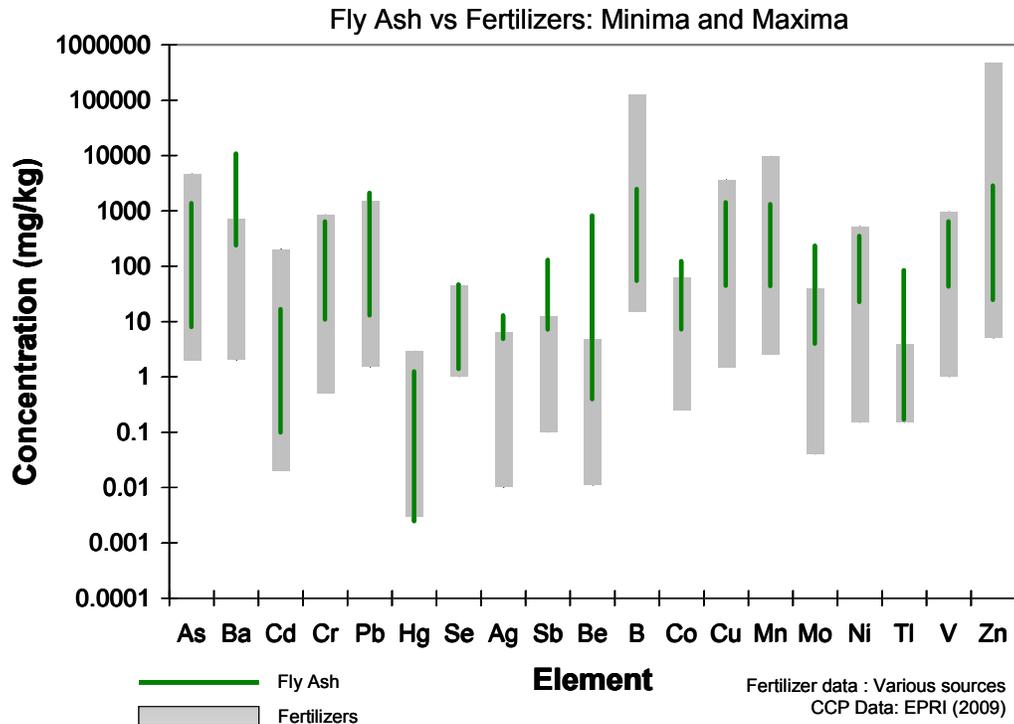


Figure 5-1
Trace element concentration ranges in fly ash and fertilizers compared as minima and maxima

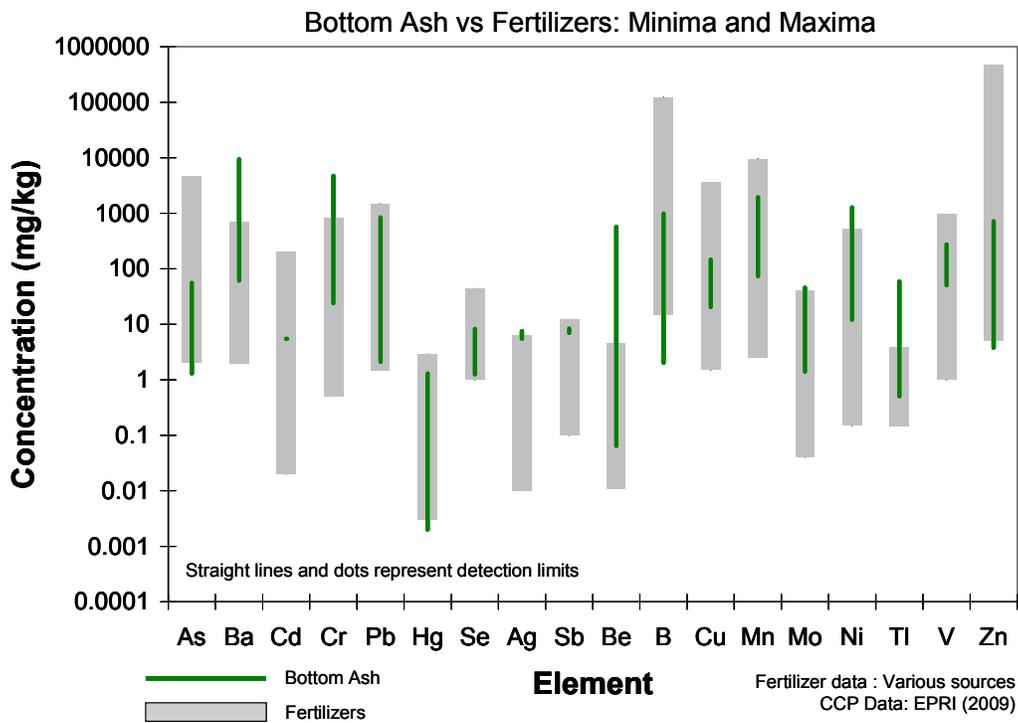


Figure 5-2
Trace element concentration ranges in bottom ash and fertilizer compared as minima and maxima

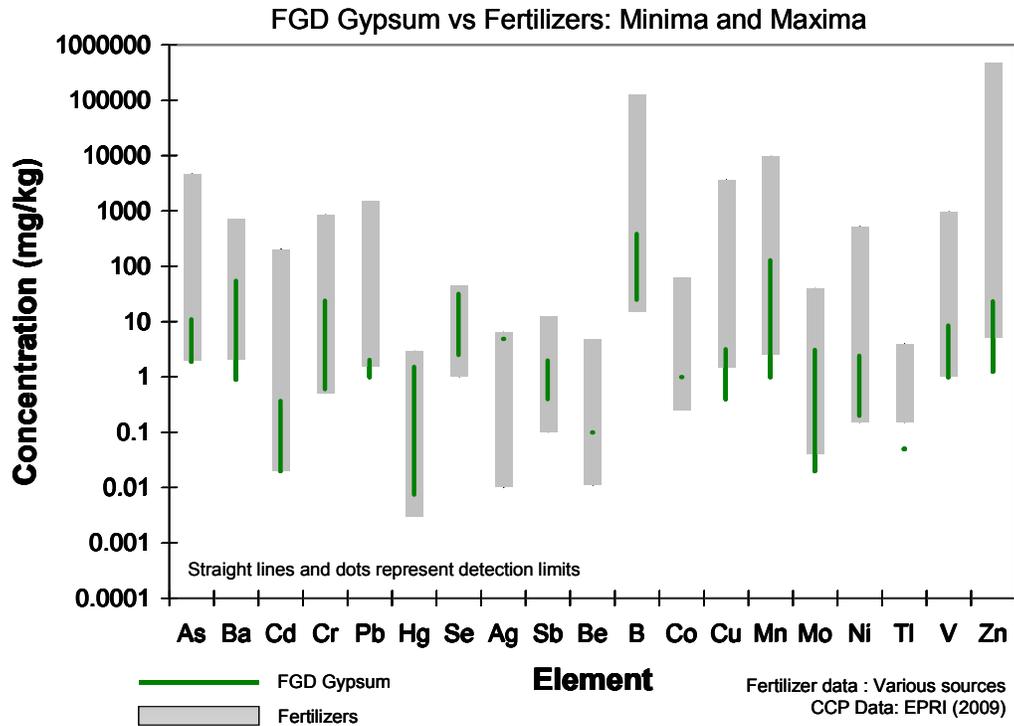


Figure 5-3
 Trace element concentration ranges in FGD gypsum and fertilizer compared as minima and maxima

Table 5-1
Concentration comparisons summary for CCPs and fertilizers

Comparison	Fly Ash	Bottom Ash	FGD Gypsum
Above range 			
Overlapping higher 	Ba, Pb, Se, Ag, Sb, Be, Co, Mo, Tl	Ba, Cr, Ag, Be, Mo, Ni, Tl	
Overlapping 			
Within 	As, Cd, Cr, B, Cu, Mn, Ni, V, Zn	Pb, Se, Cu, Mn, V, Sb	Cr, Hg, Se, Sb, B, Ni
Overlapping lower 	Hg	As, Hg, B, Zn	As, Ba, Cd, Pb, Cu, Mn, Mo, V, Zn
Below range 			Tl
Unable to compare due to all non-detects		Cd	Ag, Be, Co

Key:

 CCPs

 Fertilizers

6

METAL SLAGS

Information Sources

The chemical characteristics of metal slags (blast furnace, basic oxygen furnace, and electric arc furnace) are described in detail in the following study:

- Proctor, D.M., K.A. Fehling, E.C. Shay, J.L. Wittenborn, J.J. Green, C. Avent, R.D. Bigham, M. Connolly, B. Lee, T.O. Shepker, and M.A. Zak, 2000. *Physical and Chemical Characteristics of Blast Furnace, Basic Oxygen Furnace, and Electric Arc Furnace Steel Industry Slags*. Environmental Science & Technology, Volume 34, No. 8, pp. 1576-1582.

Iron and steel slag are produced as the nonmetallic co-product of iron and steel production. The industry produces three main slag types: blast furnace, basic oxygen furnace, and electric arc furnace slag. Each is composed primarily of fluxing agents such as lime, and the molten impurities of iron or steel (Proctor et al., 2000).

The report contains data for slag samples from 58 active mills, including sites that produced approximately 47% of steel industry slag in North America. It provides total metals composition and leachate characteristics, representing the most complete characterization of steel slag produced in North America at the time of its publication. No more current or complete study was found during the literature review for this report.

In the Proctor et al. (2000) report, the individual data were not reported, but were presented in summary form. The current comparison is limited to comparing minima and maxima for concentration range bounds. Also, blast furnace, basic oxygen furnace, and electric arc furnace are all referred to collectively as “metal slags” for comparison.

Trace Element Concentration Ranges

Trace element concentration ranges of CCPs are compared to those of metal slags in Figures 6-1 to 6-3. All comparisons are summarized in Table 6-1. Fly ash concentrations are generally comparable to or slightly higher than metal slag concentrations. Bottom ash concentrations are comparable to metal slag concentrations. Concentrations in FGD gypsum are typically lower than in metal slags.

TCLP leachate concentrations are plotted in Figure 6-4. Coal ash leachate concentrations overlap those of metal slags, although the fly ash ranges are larger for about half of the constituents.

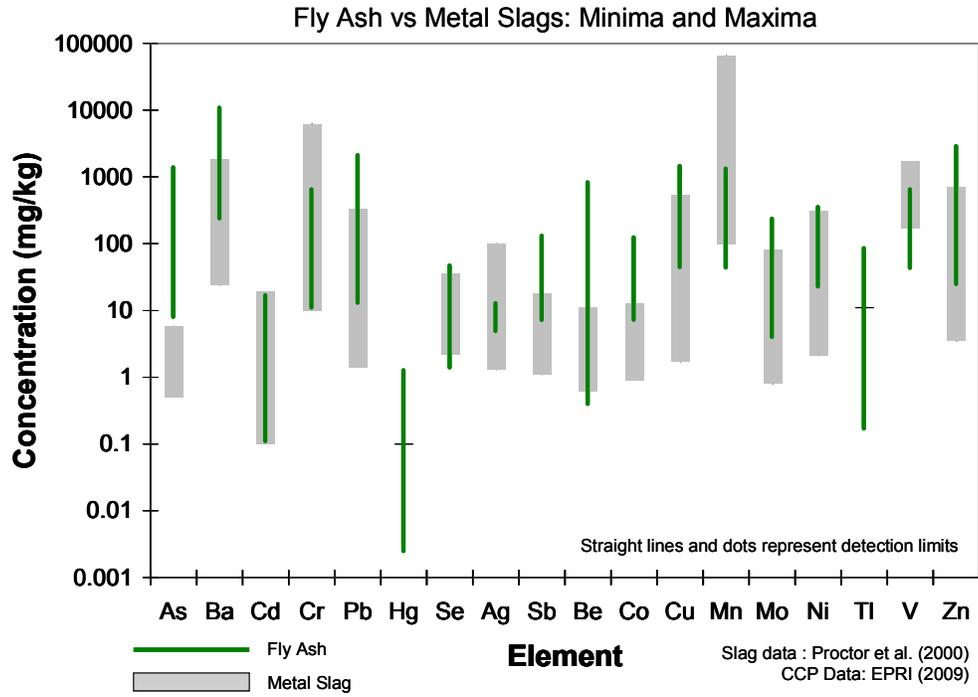


Figure 6-1
Trace element concentration ranges in metal slags and fly ash compared as minima and maxima

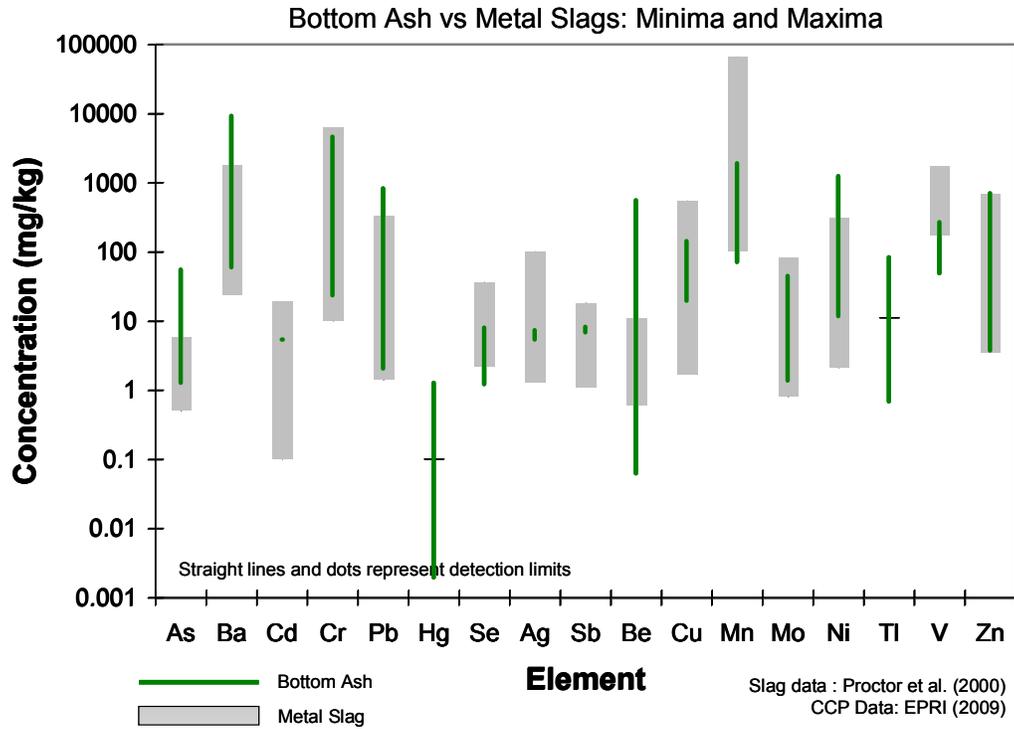


Figure 6-2
 Trace element concentration ranges in metal slags and bottom ash compared as minima and maxima

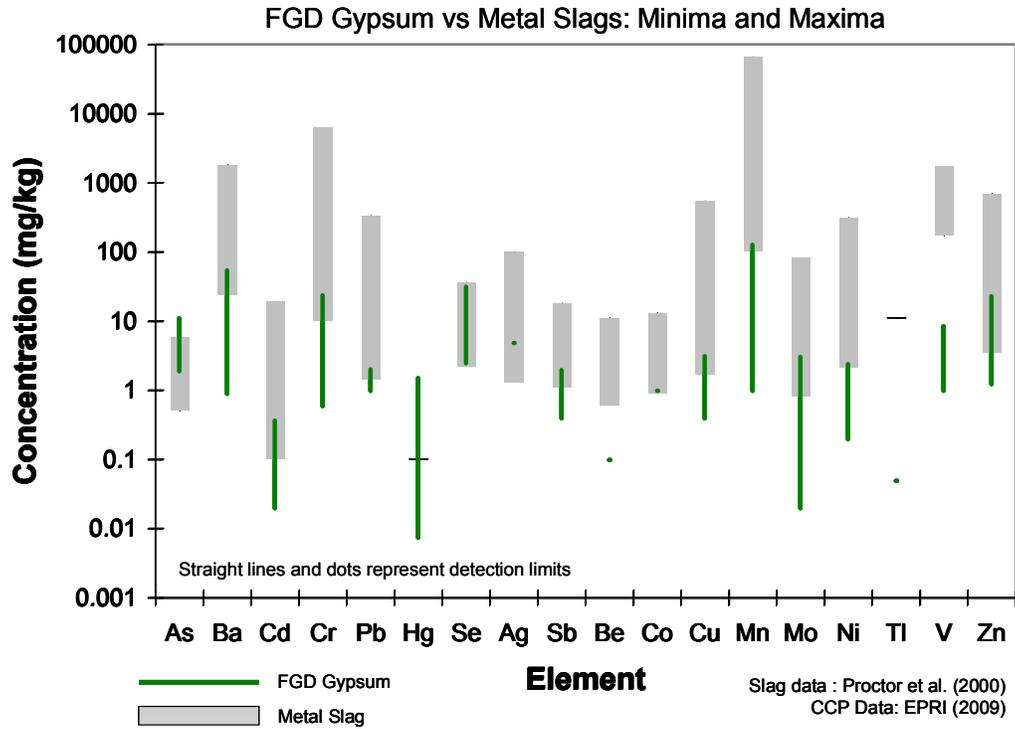


Figure 6-3
 Trace element concentration ranges in metal slags and FGD gypsum compared as minima and maxima

Table 6-1
Concentration comparisons summary for CCPs and metal slags

Comparison	Fly Ash	Bottom Ash	FGD Gypsum
Above range 	As		
Overlapping higher 	Ba, Pb, Sb, Co, Cu, Mo, Ni, Zn	As, Ba, Pb, Ni	As
Overlapping 	Se, Be	Be, Zn	
Within 	Cd, Cr, Ag	Cr, Ag, Sb, Cu, Mo	Se
Overlapping lower 	Mn, V	Se, Mn, V	Ba, Cd, Cr, Pb, Sb, Cu, Mn, Mo, Ni, Zn
Below range 			Be, V
Unable to compare due to all non-detects	Hg, Tl	Hg, Cd, Tl	Hg, Ag, Co, Tl

<u>Key:</u>	
	CCPs
	Metal Slags

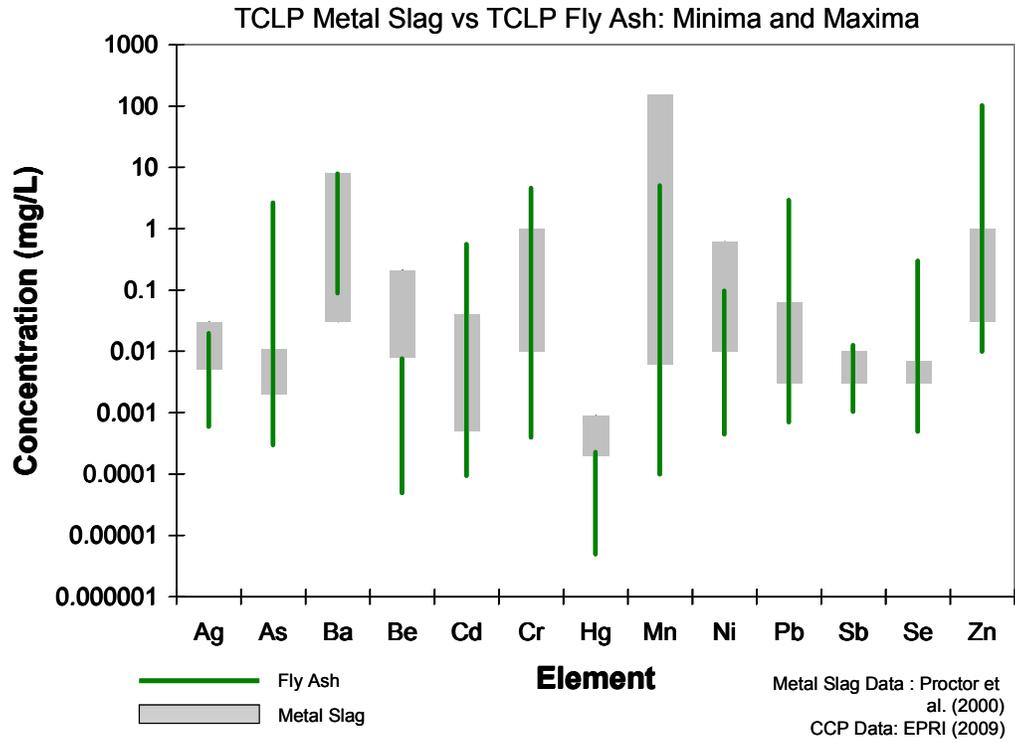


Figure 6-4
TCLP leachate concentration ranges for metal slags and fly ash

7

SPENT FOUNDRY SANDS

Information Sources

Molding sands from ferrous and non-ferrous foundries are produced by mixing silica sand with clay or organic chemical binders, most commonly bentonite clay binders. The chemical characteristics of spent foundry sands are described in great detail in the following study:

- Dungan, Robert S., and Nikki H. Dees, 2008. *The Characterization of Total and Leachable Metals in Foundry Molding Sands*. Journal of Environmental Management, Volume 90 (2009), pp. 539-548.

This study represents the most current and comprehensive review of spent foundry sand total metals concentrations and leachate characteristics, and has been used in recent risk assessments related to spent foundry sands and their potential for beneficial reuse. The study team collected 43 waste molding sands, 74% of which were considered ferrous green sands. This percentage is believed to be representative of the industry as a whole.

Trace Element Concentration Ranges

Trace element concentration ranges of CCPs are compared to those of spent foundry sands in Figures 7-1 to 7-3. All comparisons are summarized in Table 7-1. Concentration ranges for fly ash and bottom ash are typically higher than for spent foundry sands. FGD gypsum concentration ranges are typically lower than spent foundry sand concentration ranges, with the exceptions of arsenic and boron.

TCLP and SPLP leaching data are plotted in Figures 7-4 and 7-5. For TCLP, the ranges for barium, cadmium, chromium, and lead for fly ash overlap those for foundry sand, but the ranges are much larger for fly ash. The fly ash ranges for silver, antimony, beryllium, copper, and nickel are all completely below the ranges for foundry sands. For SPLP, the fly ash ranges are typically comparable to or below ranges for foundry sands, with the exception of arsenic, chromium, and barium.

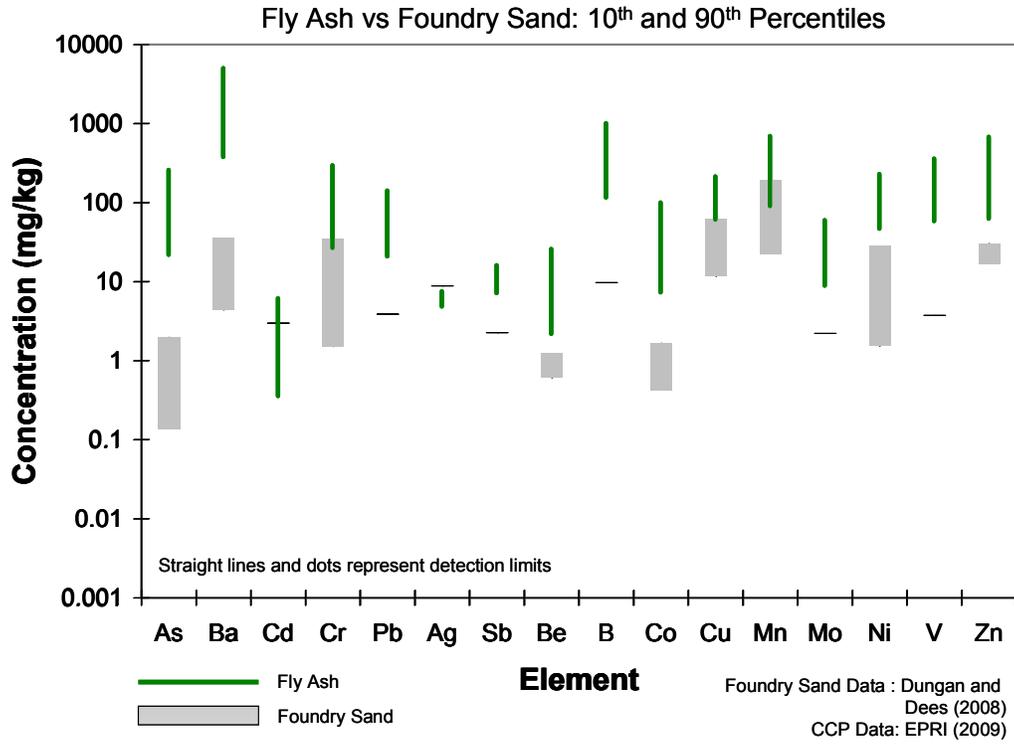


Figure 7-1
 Trace element concentration ranges for spent foundry sand and fly ash

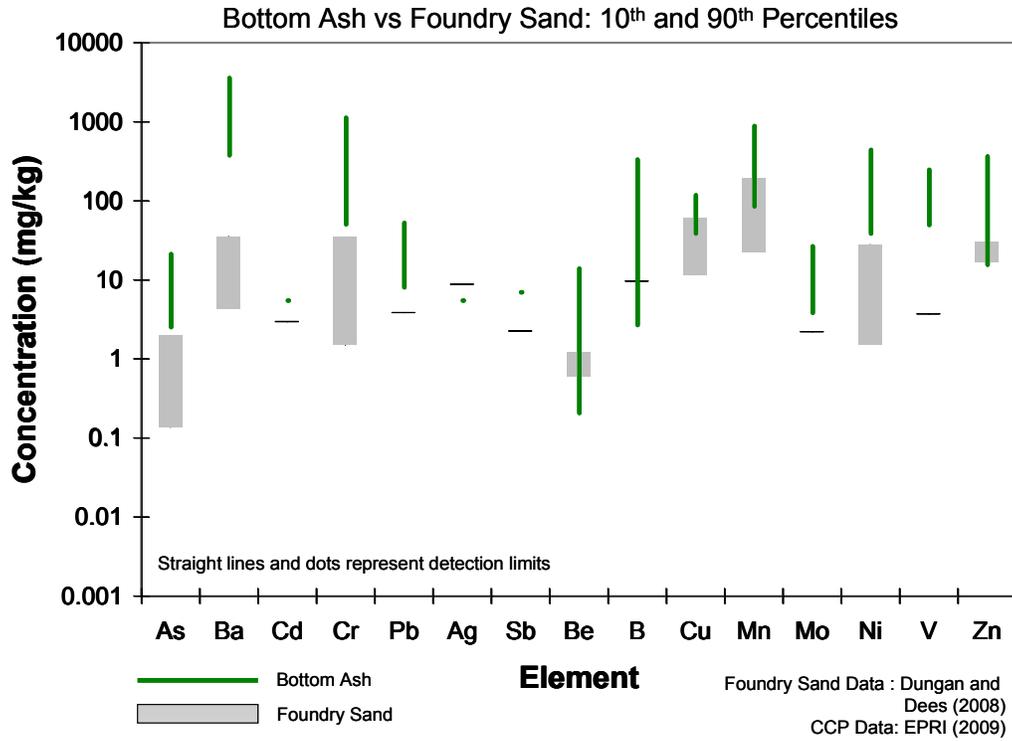


Figure 7-2
 Trace element concentration ranges for spent foundry sand and bottom ash

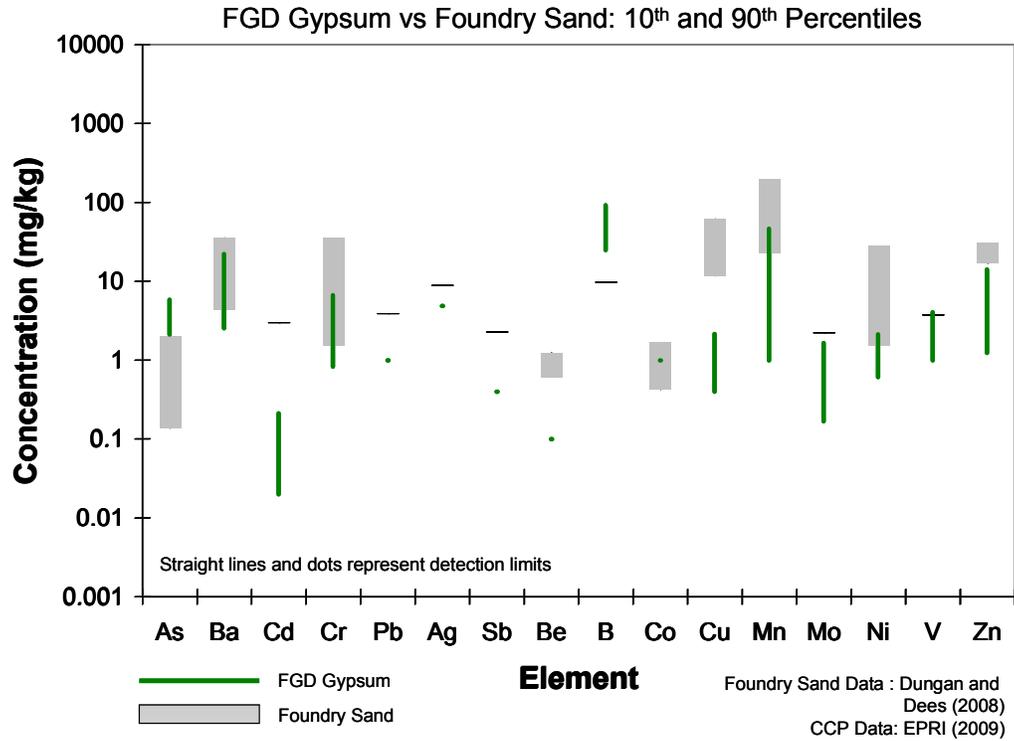


Figure 7-3
Trace element concentration ranges for spent foundry sand and FGD gypsum

Table 7-1
Concentration comparisons summary for CCPs and spent foundry sands

Comparison	Fly Ash	Bottom Ash	FGD Gypsum
Above range 	As, Ba, Pb, Sb, Be, B, Co, Mo, Ni, V, Zn	As, Ba, Cr, Pb, Mo, Ni, V	As, B
Overlapping higher 	Cr, Cu, Mn	Cu, Mn	
Overlapping 		Be, Zn	
Within 			
Overlapping lower 			Ba, Cr, Mn, Ni
Below range 			Be, Cu, Zn
Unable to compare due to all non-detects	Cd, Ag	Cd, Ag, Sb, B	Cd, Pb, Ag, Sb, Co, Mo, V

Key:

 CCPs
 Spent Foundry Sands

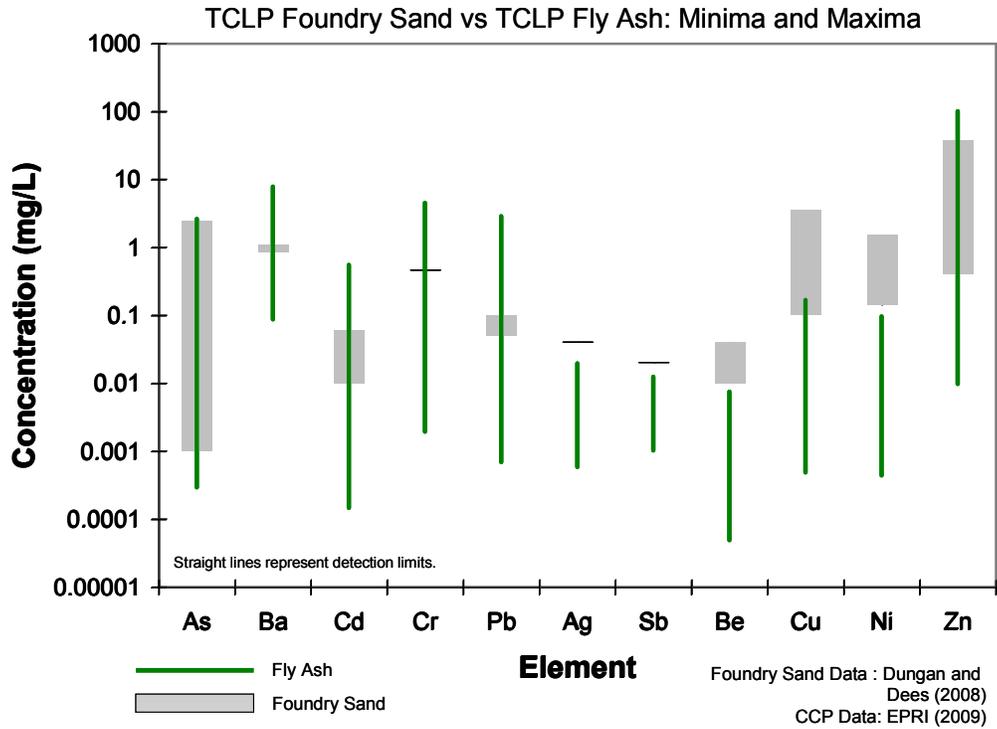


Figure 7-4
TCLP leachate concentration ranges for spent foundry sand and fly ash

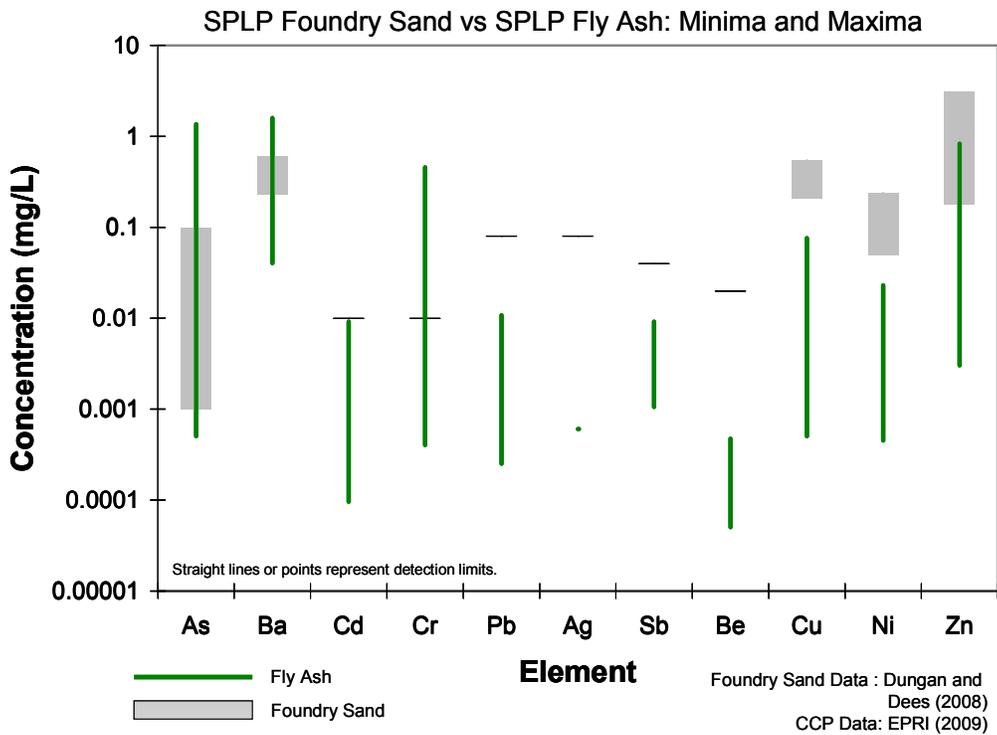


Figure 7-5
SPLP leachate concentration ranges for spent foundry sand and fly ash

8

BIOSOLIDS

Information Sources

Biosolids are the nutrient-rich organic materials resulting from the treatment of sewage sludge, and are often beneficially used as fertilizers and soil amendments. The U.S. Environmental Protection Agency recently completed a review of treated sewage sludge (biosolids) characteristics. The results of the survey are presented in the following report:

- U.S. Environmental Protection Agency, 2009. *Targeted National Sewage Sludge Survey Statistical Analysis Report*. EPA-822-R-08-018.

The survey collected samples from 74 randomly selected publicly owned treatment works in 35 states, analyzing for 145 analytes, including 28 metals. The survey is the most comprehensive and reliable dataset produced to date for use in the current study.

Trace Element Concentration Ranges

Trace element concentration ranges of CCPs are compared to those of biosolids in Figures 8-1 to 8-3. All comparisons are summarized in Table 8-1. Concentration ranges for fly ash and bottom ash are generally comparable to or higher than the ranges for biosolids. FGD gypsum concentration ranges are typically lower than the ranges for biosolids.

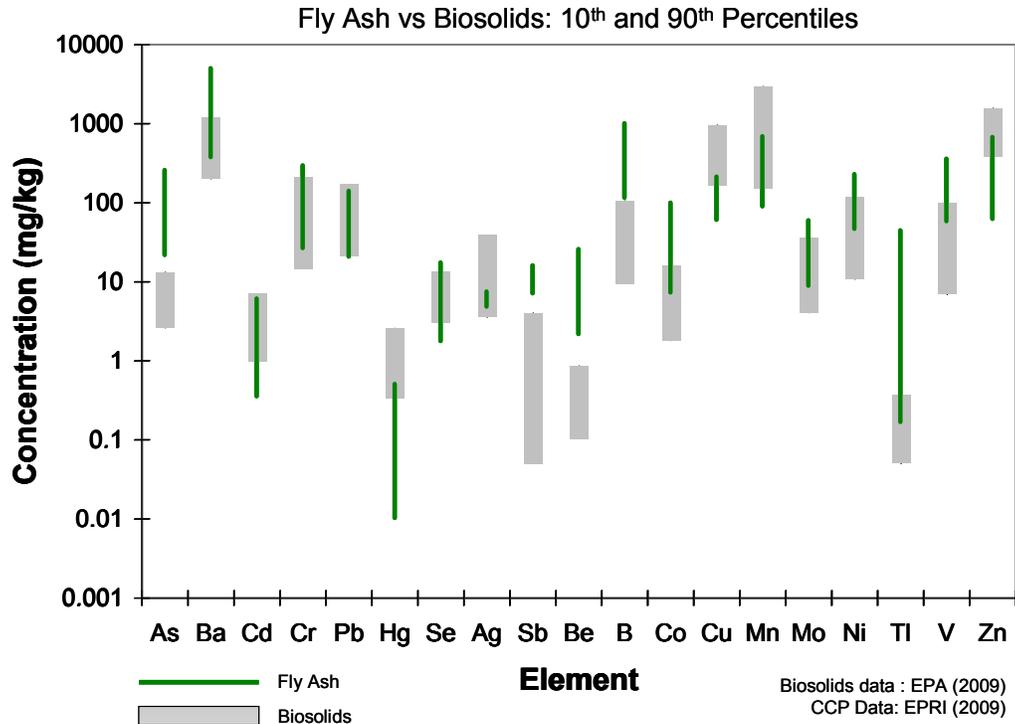


Figure 8-1
Trace element concentration ranges for biosolids and fly ash

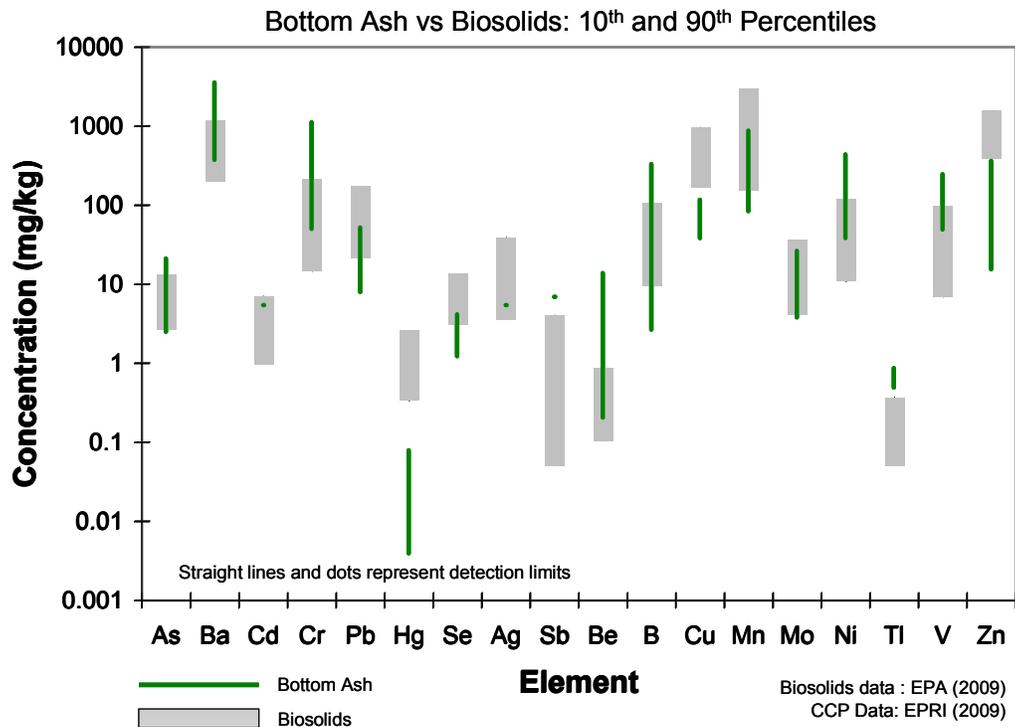


Figure 8-2
Trace element concentration ranges for biosolids and bottom ash

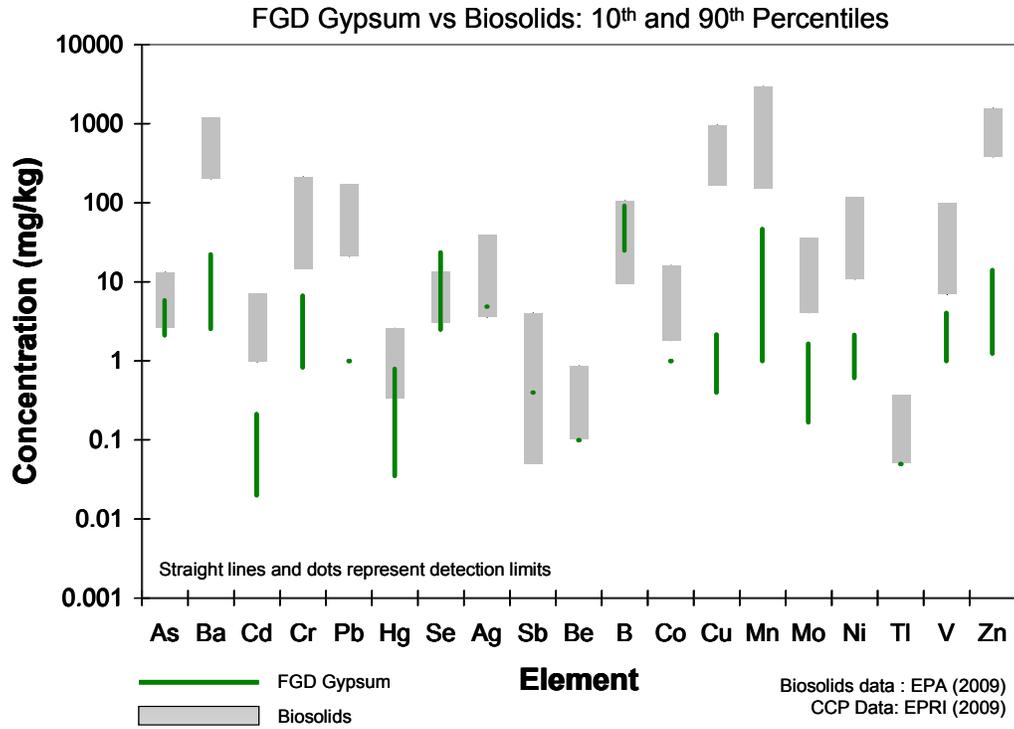


Figure 8-3
Trace element concentration ranges for biosolids and FGD gypsum

Table 8-1
Concentration comparisons summary for CCPs and biosolids

Comparison	Fly Ash	Bottom Ash	FGD Gypsum
Above range 	As, Sb, Be, B	Tl	
Overlapping higher 	Ba, Cr, Co, Mo, Ni, Tl, V	Ba, Cr, Be, Ni, V	
Overlapping 	Se	As, B	Se
Within 	Ag		B
Overlapping lower 	Cd, Pb, Hg, Cu, Mn, Zn	Pb, Se, Mn, Mo	As, Hg
Below range 		Hg, Cu, Zn	Ba, Cd, Cr, Pb, Be, Co, Cu, Mn, Mo, Ni, Tl, V, Zn
Unable to compare due to all non-detects		Cd, Ag, Sb	Ag, Sb

<u>Key:</u>	
	CCPs
	Biosolids

9

REGULATORY LEVELS

Toxicity Characteristic Leaching Procedure

CCPs did not exceed any hazardous limits in TCLP test data from EPRI studies (Figure 9-1). Out of 64 samples from 50 different power plant sites identified in EPRI databases, no TCLP result for CCPs exceeded the TCLP hazardous waste limits. These data are consistent with EPA data from the previous regulatory determinations indicating very few hazardous waste limit exceedances using the RCRA criteria.

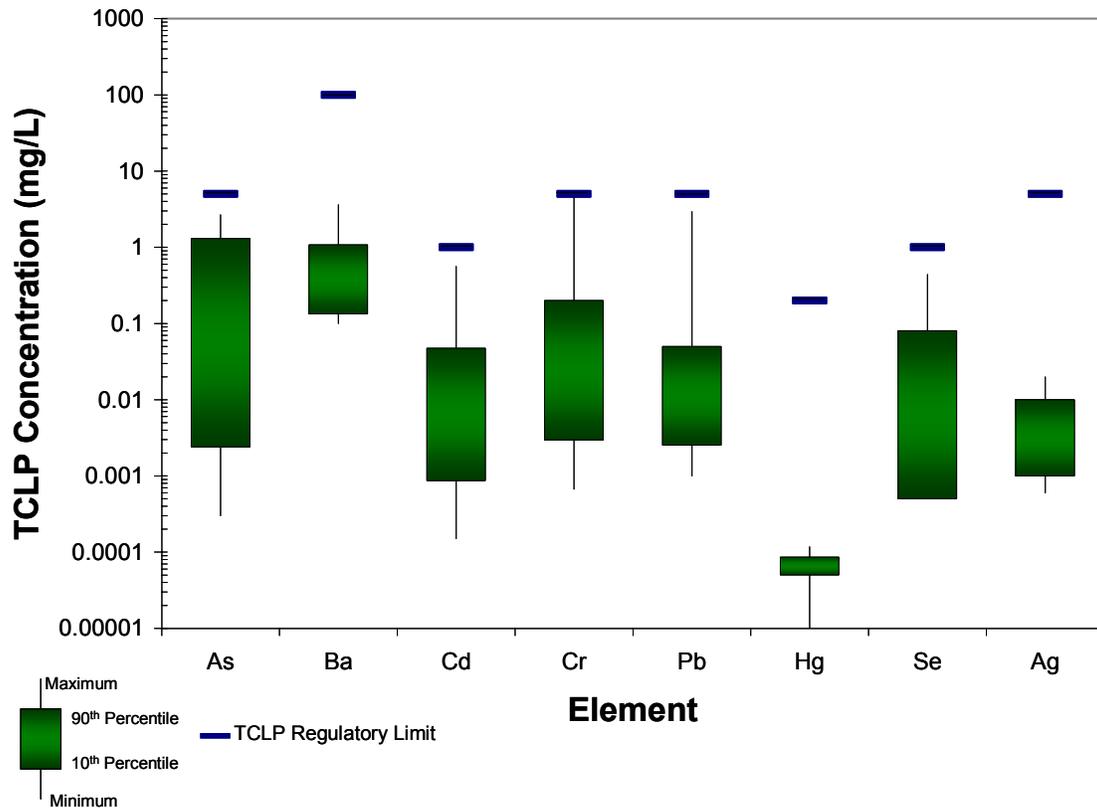


Figure 9-1
Coal ash TCLP leachate concentration ranges compared to regulatory limits

EPA Residential and Industrial Soil Screening Levels

Concentration ranges of fly ash, bottom ash, and FGD gypsum are compared to EPA’s residential soil screening levels (RSLs) for ingestion and dermal exposure in Figures 9-2, 9-3, and 9-4. Most trace element concentration concentrations fall below the RSLs for all three materials, with the exception of arsenic. Materials other than coal ash and gypsum, including uncontaminated soil, also typically exceed the RSL as well as the industrial soil screening level (ISL) for arsenic (Figure 9-5).

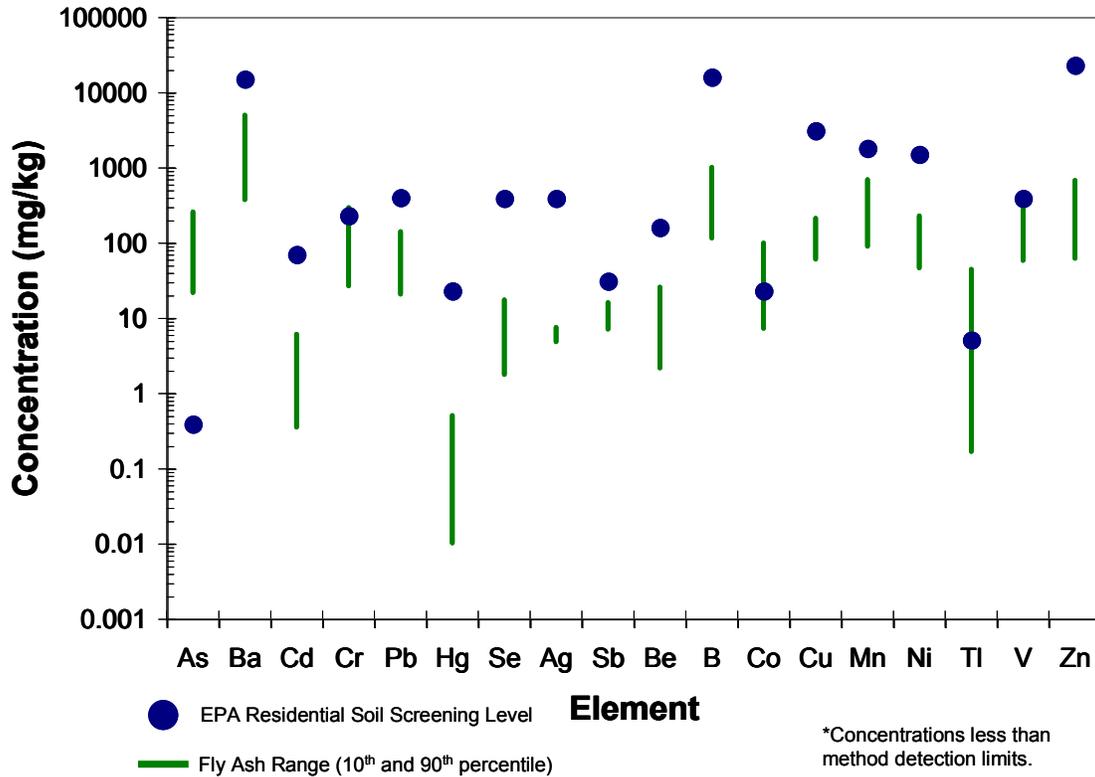


Figure 9-2
Trace element concentration ranges in fly ash compared to EPA residential soil screening levels

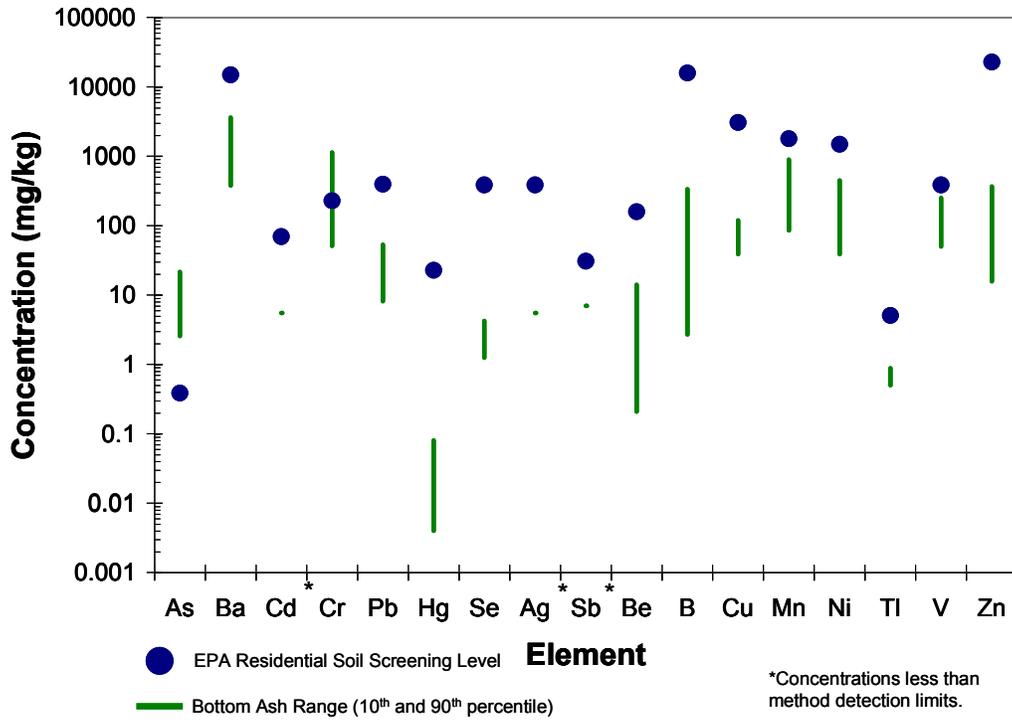


Figure 9-3
 Trace element concentration ranges in bottom ash compared to EPA residential soil screening levels

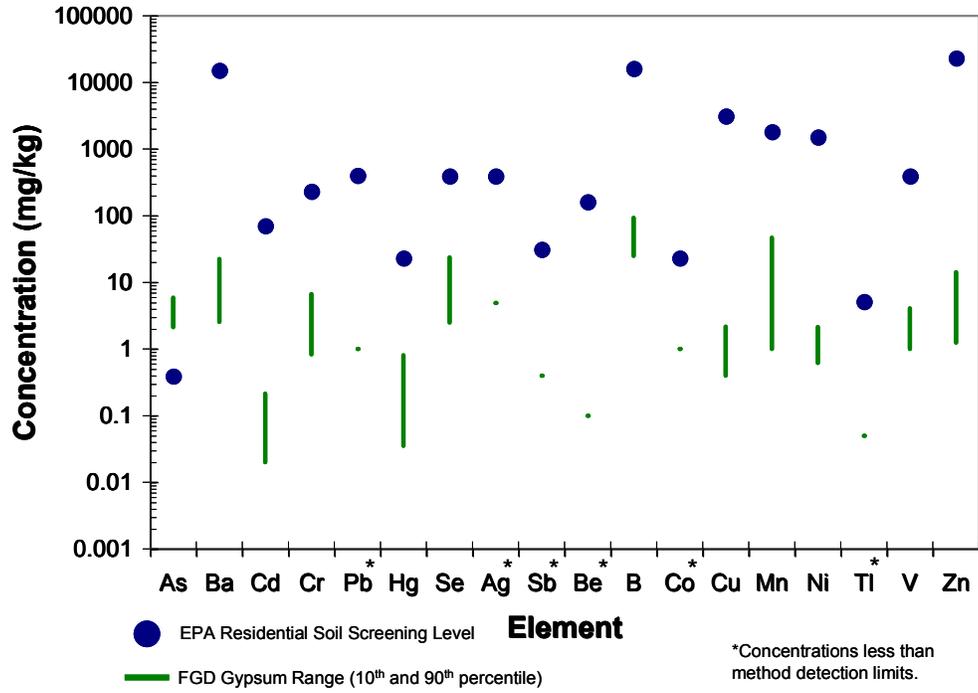


Figure 9-4
Trace element concentration ranges in FGD gypsum compared to EPA residential soil screening levels

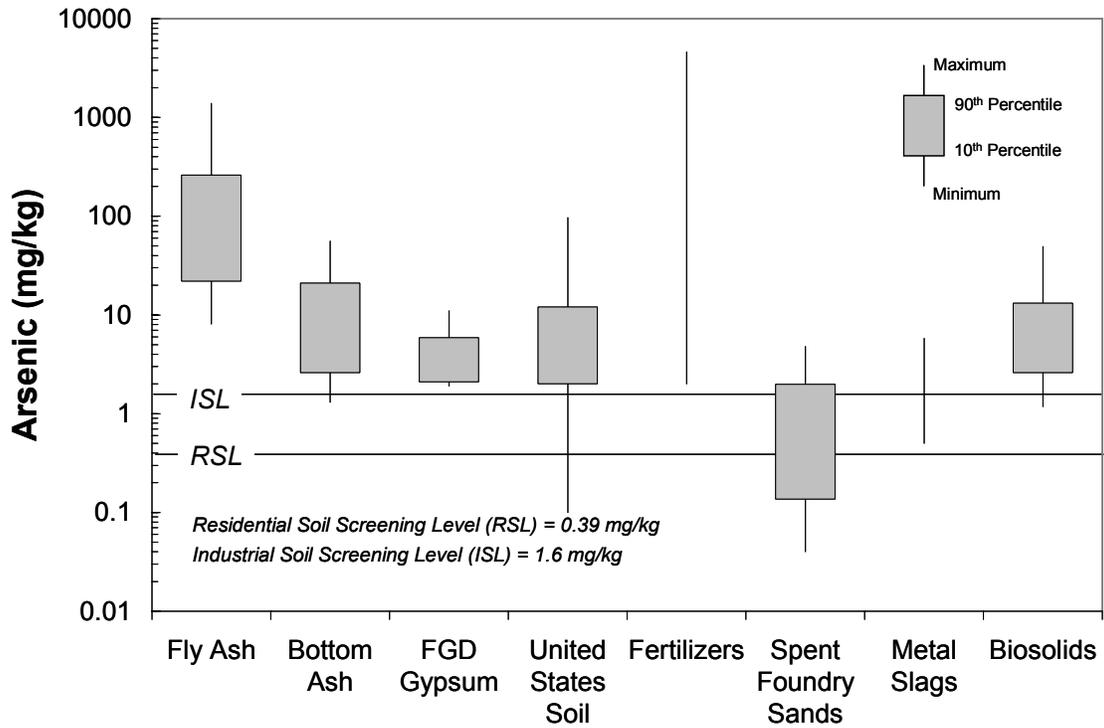


Figure 9-5
Comparison of CCP, soil, fertilizer, spent foundry sand, metal slag, and biosolid arsenic concentrations to EPA residential and industrial soil screening levels

10

SUMMARY

This report compared chemical characteristics of CCPs to chemical characteristics of common natural and manufactured materials, including rock, soil, fertilizer, metal slag, spent foundry sands, and biosolids. A literature review was performed to identify data that were current, representative, and credible. Both major chemistry and trace element chemistry of the CCPs were compared to the chemistry of the six other materials.

- The overall major chemical composition of both bottom ash and fly ash is similar to that of siliceous rocks, particularly shale. Oxides of silicon, aluminum, iron, and calcium make up more than 90% of most siliceous rocks, soils, fly ash, and bottom ash. Trace elements make up less than 1% of all of these materials.
- Trace element ranges for fly ash were typically higher than the ranges for soil, rock, and foundry sand, and comparable to or sometimes higher than the ranges for fertilizer, metal slags, and biosolids.
- Trace element ranges for bottom ash were typically higher than the ranges for soil and foundry sands, comparable to or sometimes higher than the ranges for rocks, fertilizer, and biosolids, and comparable to the ranges for metal slags.
- FGD gypsum is very similar chemically to mined rock gypsum. Both are composed almost exclusively of hydrated calcium sulfate. With a few exceptions, trace element ranges for FGD gypsum were generally comparable to or lower than the ranges for rocks and fertilizers, and lower than the ranges for soils, metal slags, foundry sands, and biosolids.
- Concentration ranges of trace constituents in fly ash, bottom ash, and FGD gypsum typically fall below the EPA residential and industrial soil screening levels for ingestion and dermal exposure, with the exception of arsenic. Many materials, including uncontaminated soils and other beneficially used materials, also commonly exceed the RSL and ISL for arsenic.
- CCPs did not exceed any hazardous limits in TCLP test data from EPRI studies. Out of 64 samples from 50 different power plant sites identified in EPRI databases, no TCLP result for CCPs exceeded the TCLP hazardous waste limits. These data are consistent with EPA data from the previous regulatory determinations, indicating very few hazardous waste limit exceedances using the RCRA criteria.

11

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