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ABSTRACT

This report evaluates changes in composition and constituent release by leaching that may occur to fly ash and other coal combustion residues (CCRs) in response to changes in air pollution control technology at coal-fired power plants. The addition of flue-gas desulfurization (FGD) systems, selective catalytic reduction, and activated carbon injection to capture mercury and other pollutants will shift mercury and other pollutants from the stack gas to fly ash, FGD gypsum, and other air pollution control residues. The objective is to understand the fate of mercury and other constituents of potential concern (COPC) in air pollution control residues and support EPA's broader goal of ensuring that emissions being controlled in the flue gas at power plants are not later being released to other environmental media.

This report includes data on 73 CCRs [34 fly ashes, 20 flue gas desulfurization (FGD) gypsum, 7 "other" FGD residues (e.g., scrubbers without oxidation or with inhibited oxidation), and 8 blended CCRs "as managed" (e.g., scrubber sludge mixed with fly ash and lime prior to disposal)]. Each of the CCRs sampled has been analyzed for a range of physical properties, total elemental content, and leaching characteristics for mercury, aluminum, antimony, arsenic, barium, boron, cadmium, chromium, cobalt, lead, molybdenum, selenium and thallium.

The leach testing methods that were used in this research consider the impact on leaching of management conditions. These methods are intended to address concerns raised by the National Academy of Science and the EPA's Science Advisory Board with the use of single-point pH tests. Because of the range of field conditions that CCRs are managed during disposal or use as secondary (or alternative) materials, it is important to understand the leaching behavior of materials over the range of plausible field conditions that can include acid mine drainage and co-disposal of fly ash and other CCRs with pyrites or high-sulfur coal rejects. The methods have also been developed into draft protocols for inclusion in EPA's waste testing guidance document, SW-846, which would make them available for more routine use. (http://www.epa.gov/osw/hazard/testmethods/sw846/index.htm)

The major conclusions from this research include:

- There is great variability in both the range of total constituent concentration values and in leaching values (orders of magnitude). In comparing there results to health indicator values such as the maximum concentration limit or toxicity characteristic, there are multiple COPCs of potential concern.
- Distinctive patterns in leaching behavior have been identified over a range of pH values that would plausibly be encountered for CCR management.
- Total constituent content is not a good indicator of leaching which has been found to be a function of the characteristics of the material (pH) and field conditions in which the material is managed.
- The maximum eluate concentration from leaching test results varies over a wide range in pH and is different for different CCR types and elements. This indicates that there is not a single pH for which testing is likely to provide confidence in release estimates over a wide range of disposal and beneficial use options, emphasizing the benefit of multi-pH testing. Furthermore, for CCRs, the rate of constituent release to the environment is affected by leaching conditions (in some cases dramatically so), and that leaching

evaluation under a single set of conditions will, in many cases, lead to inaccurate conclusions about expected leaching in the field.

The intended use for the data in this report is to support future risk and environmental assessments of the CCRs studied. A follow-up report is planned which will use these data in conducting a probabilistic assessment of mercury and other COPCs release rates based on the range of plausible management scenarios for these materials in either disposal or beneficial use situations. The data summarized in this report will also be made available electronically through a leaching assessment tool (LeachXS Lite®) that can be used to develop source-term inputs needed for using groundwater transport and fate models. The leaching assessment tool will also provide means for data management in viewing data resulting from the of the improved leaching test methods.

GLOSSARY OF TERMS

ACI	Activated Carbon Injection
Al	Aluminum
AL	Action Level
APC	Air Pollution Control
APPCD	Air Pollution Prevention and Control Division
As	Arsenic
ASTM	American Society for Testing and Materials
B	Boron
Ba	Barium
BDL	Below Detection Limit
BET	Brunauer, Emmett and Teller (method for estimating surface area)
CAIR	Clean Air Interstate Rule
CAMR	Clean Air Mercury Rule
Cd	Cadmium
CCRs	Coal Combustion Residues
CCV	Continuing Calibration Verification
Co	Cobalt
COPCs	Constituents of Potential Concern
Cr	Chromium
CV	Coefficient of Variation
CVAA	Cold Vapor Atomic Adsorption
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
DOE	United States Department of Energy
DI	Deionized (i.e., deionized water)
DRC	Dynamic Reaction Chamber
dw	dry weight basis
DWEL	Drinking Water Equivalent Level
EPA	United States Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic Precipitator

GLOSSARY OF TERMS - CONTINUED

ESP-CS	Cold-side Electrostatic Precipitator
ESP-HS	Hot-side Electrostatic Precipitator
FF	Fabric Filter (baghouse)
FGD	Flue Gas Desulfurization
FID	Flame Ionization Detector
FO	Forced Oxidation
FSS	Fixated Scrubber Sludge
FSSL	Fixated Scrubber Sludge with Lime
Gyp-U	Unwashed Gypsum
Gyp-W	Washed Gypsum
Hg	Mercury
HHV	Higher Heating Value
Ho	Holmium
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICV	Initial Calibration Verification
In	Indium
IO	Inhibited Oxidation
IOx	Inhibited Oxidation (this abbreviation used in some figures to improve clarity)
LF	Landfill
LOI	Loss On Ignition
LS	Liquid-to-Solid Ratio (LS ratio)
M	Molar
Max	Maximum
MCL	Maximum Contaminant Level (for drinking water)
MDL	Method Detection Limit
Mg Lime	Magnesium Enriched Lime (often also referred to as “mag-lime”)
Min	Minimum
ML	Minimum Level of Quantification
Mo	Molybdenum

GLOSSARY OF TERMS - CONTINUED

NETL	National Energy Technology Laboratory (DOE)
NIOSH	National Institute of Occupational Safety and Health
NO	Natural Oxidation
NO_x	Nitrogen Oxides
NSPS	New Source Performance Standards
OC/EC	Organic Carbon/Elemental Carbon
ORD	Office of Research and Development (EPA)
OSWER	Office of Solid Waste and Emergency Response (EPA)
PAC	Powdered Activated Carbon
Pb	Lead
PJFF	Pulse-Jet Fabric Filter
PM	Particulate Matter
PRB	Sub-bituminous coal mined in Wyoming’s Powder River Basin
PS	Particulate Scrubber
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
RFA	Reference Fly Ash
SAB	EPA Science Advisory Board
SCA	Specific Collection Area
Sb	Antimony
ScS	Scrubber Sludge
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SDA	Spray Dryer Absorber
Se	Selenium
SI	Surface Impoundment
SO_2	Sulfur Dioxide
SOFA	Separated Overfire Air
SPLP	Synthetic Precipitation Leaching Procedure
SRM	Standard Reference Material
S/S	Stabilization/Solidification

GLOSSARY OF TERMS - CONTINUED

SWDA	Solid Waste Disposal Act
TC	Toxicity Characteristic
TCLP	Toxicity Characteristic Leaching Procedure
Tl	Thallium
XAFS	X-Ray Absorption Fine Structure
XRF	X-Ray Fluorescence

EXECUTIVE SUMMARY

This report is the third in a series to evaluate changes in composition and constituent release by leaching that may occur to fly ash and other coal combustion residues (CCRs) in response to changes in air pollution control technology at coal-fired power plants. The addition of flue-gas desulfurization (FGD) systems, selective catalytic reduction, and activated carbon injection to capture mercury and other pollutants will shift mercury and other pollutants from the stack gas to fly ash, FGD gypsum, and other air pollution control residues. The Air Pollution Prevention and Control Division (APPCD) of EPA's Office of Research and Development (ORD) is conducting research to evaluate potential leaching and other cross media transfers of mercury and other constituents of potential concern (COPCs) resulting from the management of CCRs resulting from wider use of state-of-the art air pollution control technology. This research was cited as a priority in EPA's Mercury Roadmap[1] to ensure that one environmental problem is not being traded for another. The objective is to understand the fate of mercury and other COPCs in air pollution control residues and support EPA's broader goal of ensuring that emissions being controlled in the flue gas at power plants are not later being released to other environmental media.

Approximately 40% of the 126 million tons of CCRs produced in the U.S. as of 2006 were utilized in agricultural, commercial, and engineering applications. The remainder (i.e., 75 million tons) was managed in either landfills or impoundments. The physical and chemical characteristics of CCRs make them potentially suitable as replacements for materials used in a wide range of products including cement, concrete, road base, and wallboard. Use of CCRs as an alternative to virgin materials helps conserve natural resources and energy, as well as decrease the amount of CCRs being land disposed.

In developing data to characterize the leaching potential of COPCs from the range of likely CCRs resulting from use of state-of-the-art air pollution control technology, improved leaching test methods have been used[2]. The principle advantage of these methods is that they consider the impact on leaching of management conditions. These methods address concerns raised by National Academy of Science and EPA's Science Advisory Board with the use of single-point pH tests. Because of the range of field conditions that CCRs are managed during disposal or use as secondary (or alternative) materials, it is important to understand the leaching behavior of materials over the range of plausible field conditions that can include acid mine drainage and co-disposal of fly ash and other CCRs with pyrites or high-sulfur coal rejects[3, 4]. The methods have

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[1] EPA (2006). EPA's Roadmap for Mercury, EPA-HQ-OPPT-2005-0013. U.S. Environmental Protection Agency, http://www.epa.gov/mercury/pdfs/FINAL-Mercury-Roadmap-6-29.pdf (accessed August 21, 2009).

[2] Improved leaching test methods described in (Kosson et al., 2002) have been developed as draft SW-846 protocols. These methods consider the effect of varying environmental conditions on waste constituent leaching.

[3] National Academy of Sciences (2006). Managing Coal Combustion Residues in Mines, Washington, D.C.

[4] Sanchez, F.; Keeney, R.; Kosson, D., and Delapp, R. Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb. 2006; http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf.

also been developed into draft protocols for inclusion in EPA's waste testing guidance document, SW-846, which would make them available for more routine use. (http://www.epa.gov/osw/hazard/testmethods/sw846/index.htm).

The selected testing approach was chosen for use because it evaluates leaching over a range of values for two key variables [pH and liquid-to-solid ratio (LS)] that both vary in the environment and affect the rate of constituent release from waste. The range of values used in the laboratory testing encompasses the range of values expected to be found in the environment for these parameters. Because the effect of these variables on leaching is evaluated in the laboratory, prediction of leaching from the waste in the field is expected to be done with much greater reliability.

The categories into which samples have been grouped are fly ash, flue gas desulfurization (FGD) gypsum, "other" FGD residues (such as from spray drier absorbers), blended CCRs "as managed" (mixtures of fly ash and scrubber residues with and without added lime or mixture of fly ash and gypsum), and wastewater filter cake. In the first report from this research[5], results of leaching from fly ash were reported for mercury, arsenic, and selenium. Report 2 provided leaching results for an expanded list of materials and COPCs to include mercury, aluminum, antimony, arsenic, barium, boron, cadmium, chromium, cobalt, lead, molybdenum, selenium and thallium[6]. In the current report (Report 3), analyses of eluates from CCR samples presented in Report 1 have been included for the expanded list of COPCs. Report 3 also includes the data previously reported in Report 2, and leach test results for an additional 38 CCRs. A total of 73 samples were evaluated, and all results are presented in the current report to facilitate comparisons (Table ES-1).

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[5] Sanchez, F.; Keeney, R.; Kosson, D., and Delapp, R. Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb. 2006; http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf.

[6] Sanchez, F.; Kosson, D.; Keeney, R.; Delapp, R.; Turner, L.; Kariher, P.; Thorneloe, S. Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control; EPA-600/R-08/077, July 2008; http://www.epa.gov/nrmrl/pubs/600r08077/600r08077.pdf.

Table ES-1. Identification of CCRs evaluated and included in this Report.

Samples Evaluated	Report 1*	Report 2**	Additional Samples Collected	Total in Report 3
Fly Ash	12	5	17	34
FGD Gypsum	-	6	14	20
“Other” FGD Residues	-	5	2	7
Blended CCRs “as managed”	-	7	1	8
Wastewater Treatment Filter Cake	-		4	4

* Sanchez, F.; Keeney, R.; Kosson, D., and Delapp, R. Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb. 2006; http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf.

**Sanchez, F.; Kosson, D.; Keeney, R.; Delapp, R.; Turner, L.; Kariher, P.; Thorneloe, S. Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control; EPA-600/R-08/077, July 2008; http://www.epa.gov/nrmrl/pubs/600r08077/600r08077.pdf.

Each of the CCRs sampled has been analyzed for a range of physical properties, total elemental content, and leaching characteristics. Laboratory leach data are compared to field observations from industry and EPA data from sampling of impoundments and landfills. The laboratory leach results are also compared to reference indicators to provide context for the data including:

- The toxicity characteristic (TC), which is a threshold for hazardous waste determinations;
- The maximum concentration limit (MCL), which is used for protecting drinking water; and,
- The drinking water equivalent level (DWEL), which is used to be protective for non carcinogenic endpoints of toxicity over a lifetime of exposure[7].

These comparisons to reference indicators do not consider dilution and attenuation factors (collectively referred to in this report as attenuation factors) that arise as a consequence of disposal or beneficial use designs and transport from the point of release to the potential receptor. Minimum attenuation factors needed to reduce maximum leach concentrations (based on laboratory test results) to less than MCL or DWEL values are provided to illustrate the importance of consideration of attenuation factors during evaluation of management options.

The intended use for the data in this report is to support future risk and environmental assessments of the CCRs. A follow-up report is planned which will use these data in conducting a probabilistic assessment of mercury and other COPCs release rates based on the range of plausible management scenarios for these materials in either disposal or beneficial use situations.

The data summarized in this report will be made available electronically through a leaching assessment tool that can be used to develop source-term inputs needed for using groundwater

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[7] DWEL was developed for chemicals that have a significant carcinogenic potential and provides risk managers with evaluation on non-cancer endpoints, but infers that carcinogenicity should be considered the toxic effect of greatest concern (http://www.epa.gov/safewater/pubs/gloss2.html#D).

transport and fate models[8]. The leaching assessment tool will provide easier access to the leach data for a range of CCRs and potential field conditions. The tool can be used to develop more detailed leach data as input to more refined assessments of CCRs and support environmental decision-making that will ensure protection of human health and the environment.

Summary of Conclusions

In Table ES-2 and Table ES-3, the total metals content of the fly ash and FGD gypsum samples evaluated is provided along with the leach test results. Reference indicators (i.e., TC, MCL, and DWEL) are also provided to provide some context in understanding the leach results. It is critical to bear in mind that the leach test results represent a distribution of potential constituent release concentrations from the material as disposed or used on the land. The data presented do not include any attempt to estimate the amount of constituent that may reach an aquifer or drinking water well. Leachate leaving a landfill is invariably diluted in ground water to some degree when it reaches the water table, or constituent concentrations are attenuated by sorption and other chemical reactions in groundwater and sediment. Also, groundwater pH may be different from the pH at the site of contaminant release, and so the solubility and mobility of leached contaminants may change when they reach groundwater. None of these dilution or attenuation processes is incorporated into the leaching values presented. Thus, comparisons with regulatory health values, particularly drinking water values, must be done with caution. Groundwater transport and fate modeling would be needed to generate an assessment of the likely risk that may result from the CCRs represented by these data.

In reviewing the data and keeping these caveats in mind, conclusions to date from the research include:

1. Review of the fly ash and FGD gypsum (Table ES-2 and Table ES-3) show a range of total constituent concentration values, but a much broader range (by orders of magnitude) of leaching values, in nearly all cases. This much greater range of leaching values only partially illustrates what more detailed review of the data shows: that for CCRs, the rate of constituent release to the environment is affected by leaching conditions (in some cases dramatically so), and that leaching evaluation under a single set of conditions may, to the degree that single point leach tests fail to consider actual management conditions, lead to inaccurate conclusions about expected leaching in the field.
2. Comparison of the ranges of totals values and leachate data from the complete data set supports earlier conclusions[9, 10, 11] that the rate of constituent leaching cannot be reliably estimated based on total constituent concentration.

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[8] The leaching assessment tool, LeachXS Lite®, will be available for inclusion in the CCR docket (December 2009).

[9] Senior, C; Thorneloe, S.; Khan, B.; Goss, D. Fate of Mercury Collected from Air Pollution Control Devices; Environmental Management, July 2009, 15-21.

[10] U.S. EPA, Characterization of Mercury-Enriched Coal Combustion Residuals from Electric Utilities Using Enhanced Sorbents for Mercury Control, EPA-600/R-06/008, Feb. 2006; http://www.epa.gov/ORD/NRMRL/pubs/600r06008/600r06008.pdf.

3. The maximum eluate concentration from leaching test results varies over a wide range in pH and is different for different CCR types and elements. This indicates that there is not a single pH for which testing is likely to provide confidence in release estimates over a wide range of disposal and beneficial use options, emphasizing the benefit of multi-pH testing.
4. From the more complete data in this report, distinctive patterns in leaching behavior have been identified over the range of pH values that would plausibly be encountered for CCR disposal, depending on the type of material sampled and the element. This reinforces the above conclusions based on the summary data.
5. Summary data in Table ES-2 on the leach results from evaluation of 34 fly ash samples across the plausible management pH domain of 5.4 to 12.4, indicates leaching concentration ranges over several orders of magnitude as a function of pH and ash source:
    - the leach results at the upper end of the concentration ranges exceeded the TC values for As, Ba, Cd, Cr, and Se.
    - the leach results at the upper end of the concentration ranges exceeded the MCL or DWEL for Sb, As, Ba, B, Cd, Cr, Pb, Mo, Se, and Tl.
6. Summary data in Table ES-3 on the leach results from evaluation of 20 FGD gypsum samples across the plausible management pH domain of 5.4 to 12.4, indicates leaching concentration ranges over several orders of magnitude as a function of pH and FGD gypsum source:
    - the leach results at the upper end of the concentration ranges exceeded the TC values for Cd and Se.
    - the leach results at the upper end of the concentration ranges exceeded the MCL or DWEL for Sb, As, B, Cd, Cr, Mo, Se, and Tl.
7. The variability in total content and the leaching of constituents within a material type (e.g., fly ash, gypsum) is such that, while leaching of many samples exceeds one or more of the available reference indicators, many of the other samples within the material type may be lower than the available regulatory or reference indicators. Additional or more refined assessment of the dataset may allow some distinctions regarding release potential to be made among particular sources of some CCRs, which may be particularly useful in evaluating CCRs in reuse applications.

Work is underway to develop a fourth report that presents such additional analysis of the leaching data to provide more insight into constituent release potential for a wider range of scenarios, including beneficial use applications. This will include calculating potential release

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[11] U.S. EPA, Characterization of Coal Combustion Residuals from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control; EPA-600/R-08/077, July 2008; http://www.epa.gov/nrmrl/pubs/600r08077/600r08077.pdf.

rates over a specified time for a range of management scenarios including use in engineering and commercial applications using probabilistic assessment modeling[12].

In interpreting the results provided in this report, please note that the CCRs analyzed in this report are not considered to be a representative sample of all CCRs produced in the U.S. For many of the observations, only a few data points were available. It is hoped that through broader use of the improved leach test methods (as used in this report), that additional data from CCR characterization will become available. That will help better define trends associated with changes in air pollution control at coal-fired power plants.

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[12] Sanchez, F. and D. S. Kosson, 2005. Probabilistic approach for estimating the release of contaminants under field management scenarios. *Waste Management* 25(5), 643-472 (2005).

Table ES-2. Leach results for 5.4 ≤ pH ≤ 12.4 and at “own pH[13]” from evaluation of thirty-four fly ashes.

	Hg	**Sb**	**As**	**Ba**	**B**	**Cd**	**Cr**	**Co**	**Pb**	**Mo**	**Se**	**TI**
Total in Material (mg/kg)	0.01 – 1.5	3 – 14	17 – 510	590 – 7,000	NA	0.3 – 1.8	66 – 210	16 – 66	24 – 120	6.9 – 77	1.1 – 210	0.72 – 13
Leach results (µg/L)	<0.01 – 0.50	<0.3 – 11,000	0.32 – 18,000	50 – 670,000	210 – 270,000	<0.1 – 320	<0.3 – 7,300	<0.3 – 500	<0.2 – 35	<0.5 – 130,000	5.7 – 29,000	<0.3 – 790
TC (µg/L)	200	-	5,000	100,000	-	1,000	5,000	-	5,000	-	1,000	-
MCL (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2

Note: The shade is used to indicate where there could be a potential concern for a metal when comparing the leach results to the MCL, DWEL, or TC. Note that MCL and DWEL values represent well concentrations; leachate dilution and attenuation processes that would occur in groundwater before leachate reaches a well are not accounted for, and so MCL and DWEL values are compared to leaching concentrations here to provide context for the test results and initial screening.

Table ES-3. Leach results for 5.4 ≤ pH ≤ 12.4 and at “own pH” from evaluation of twenty FGD gypsums.

	Hg	**Sb**	**As**	**Ba**	**B**	**Cd**	**Cr**	**Co**	**Pb**	**Mo**	**Se**	**TI**
Total in Material (mg/kg)	0.01 – 3.1	0.14 – 8.2	0.95 – 10	2.4 – 67	NA	0.11 – 0.61	1.2 – 20	0.77 – 4.4	0.51 – 12	1.1 – 12	2.3 – 46	0.24 – 2.3
Leach results (µg/L)	<0.01– 0.66	<0.3 – 330	0.32 – 1,200	30 – 560	12 – 270,000	<0.2 – 370	<0.3 – 240	<0.2 – 1,100	<0.2 – 12	0.36 – 1,900	3.6 – 16,000	<0.3 – 1,100
TC (µg/L)	200	-	5,000	100,000	-	1,000	5,000	-	5,000	-	1,000	-
MCL (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2

Note: The shade is used to indicate where there could be a potential concern for a metal when comparing the leach results to the MCL, DWEL, or TC. Note that MCL and DWEL values represent well concentrations; leachate dilution and attenuation processes that would occur in groundwater before leachate reaches a well are not accounted for, and so MCL and DWEL values are compared to leaching concentrations here to provide context for the test results and initial screening.

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[13] “Own pH” is defined as the end-point (equilibrium) eluate pH when a CCR is extracted with DI water at liquid to solid ratio of 10 mL/g, and is measured as part of leach testing as a function of pH.

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1. INTRODUCTION

More wide-spread implementation of multi-pollutant controls is occurring at U.S. coal-fired power plants. Although much research has occurred to characterize high-volume coal combustion residues [i.e., fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) solids] extending back to the 1970s, previous research has not considered the wide range of field conditions that occur for coal combustion residues (CCRs) during land disposal and use in agricultural, commercial, and engineering applications. The objective of this research is to characterize the changes in total composition and constituent release potential occurring to CCRs resulting from wider use of multi-pollutant controls at U.S. coal-fired power plants. This characterization includes detailed analysis of the fly ash and other air pollution control residues in relationship to differences in air pollution control configurations and coal rank. The characterization also includes evaluating the leaching potential of constituents of potential concern (COPCs) across the range of plausible management conditions that CCRs are likely to encounter during land disposal or use in agricultural, commercial, and engineering applications. This research was cited as a priority in EPA's Mercury Roadmap (EPA, 2006b) to evaluate the potential for any cross-media transfers from the management of CCRs resulting from more stringent air pollution control at coal fired power plants. This report is part of a series of reports helping to document the findings of this research to provide more credible, up-to-date data on CCRs to identify any potential cross-media transfers.

The focus of this report is to present an evaluation of air pollution control residues that may result from the use of SO_2 scrubbers and other air pollution control technologies being used to control multiple pollutants at coal-fired power plants. The pathway of concern addressed in this report is the potential for transfer of pollutants to water resources or other environmental systems (e.g., soils, sediments). The residues studied for this report were fly ashes, unwashed and washed flue gas desulfurization (FGD) gypsum, scrubber sludge, blended CCR residues "as managed" (mixtures of fly ash and scrubber residues with and without added lime or mixture of fly ash and gypsum), and wastewater filter cake generated from power plants with a range of air pollution control configurations.

In particular, this report focuses on the potential for leaching of mercury and other COPCs during land disposal or beneficial use of the CCRs is the focus of this report. This research is part of an on-going effort by EPA to use an integrated, comprehensive approach to account for the fate of mercury and other metals in coal throughout the life-cycle stages of CCR management (Sanchez et al., 2006; Thorneloe et al., 2009; Thorneloe et al., 2008). Related research and assessment on environmental fate of constituents during CCR management includes conducting thermal stability studies, leach testing, and probabilistic assessment modeling to determine the fate of mercury and other metals that are in coal combustion residues resulting from implementation of multi-pollutant control technology (EPA, 2002; Kilgroe et al., 2001).

CCRs include bottom ash, boiler slag, fly ash, scrubber residues and other miscellaneous solids generated during the combustion of coal. Air pollution control can concentrate or partition metals to fly ash and scrubber residues. The boiler slag and bottom ash are not of interest in this study because air emission controls are not expected to change their composition. Use of multi-pollutant controls minimizes air emissions of mercury and other metals by the transfer of the metals to the fly ash and other CCRs. This research will help determine the fate of mercury and other COPCs from the management of CCRs through either disposal or reuse. Fly ash may include unburned carbonaceous materials and inorganic materials in coal that do not burn, such as oxides of silicon, aluminum, iron, and calcium. Fly ash is light enough to be entrained in the flue gas stream and captured in the air pollution control equipment.

The type and characteristics of FGD scrubber residue produced is primarily a function of (i) the scrubber sorbent used (i.e., limestone, lime, magnesium enriched lime referred to as Mg lime, or alkaline fly ash), (ii) the extent of oxidation during scrubbing (i.e., forced oxidation, natural oxidation, or inhibited oxidation), (iii) post-scrubber processing, including possibly dewatering or thickening, drying, water rinsing, or blending with other materials, and (iv) coal rank combusted. The presence and leaching characteristics of the COPCs in air pollution control residues is a consequence of the coal combusted, process sequence employed, process conditions, process additives and use or disposal scenario.

Figure 1 illustrates the processes used in the production of materials that were sampled for this study, sample nomenclature, and the typical management pathways for each material. FGD gypsum is defined here as the by-product of the SO_2 wet scrubbing process when the scrubber residue is subjected to forced oxidation. In forced oxidation systems, nearly all of the by-product is calcium sulfate dihydrate ($CaSO_4•H_2O$). The resulting wet gypsum is partially dewatered and then either disposed in a landfill (unwashed gypsum; Gyp-U) or water rinsed (in some cases) and dried to produce washed gypsum (washed gypsum; Gyp-W) that then potentially can be used in wallboard manufacturing or agricultural applications. Scrubber sludge (ScS) is the by-product of the SO_2 wet scrubbing process resulting from neutralization of acid gases at facilities that use either inhibited oxidation or natural oxidation of scrubber residue. In inhibited oxidation systems, nearly all of the by-product is calcium sulfite hemihydrates ($CaSO_3•½H_2O$). In natural oxidation systems, the by-product is a mixture of $CaSO_3•½H_2O$ and $CaSO_4•H_2O$. Scrubber sludge typically will be either partially dewatered in a thickener and then disposed in a surface impoundment, or after thickening, further dewatered and mixed with fly ash to form blended CCRs "as managed[14]." In most cases, additional lime is also blended with the scrubber sludge and fly ash. The blend of fly ash and scrubber sludge is typically between 0.5 to 1.5 parts fly ash to 1 part scrubber sludge on a dry weight basis, with 0 or 2-4% additional lime added. Blended CCRs typically are either disposed in a landfill or supplied to a beneficial use (e.g., fill in mining applications). Facilities that have spray dryer absorbers (SDA) collect fly ash and FGD residues simultaneously as a sample residue stream.

This report evaluates the characteristics of fly ash, FGD gypsum, SDA, scrubber sludge, and blended CCRs "as managed" from thirty one (31) coal combustion facilities. In addition filter cake from waste water treatment was evaluated from four facilities.

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[14] As managed is defined as how the material is managed by the coal-fired power plant either through disposal or reuse.

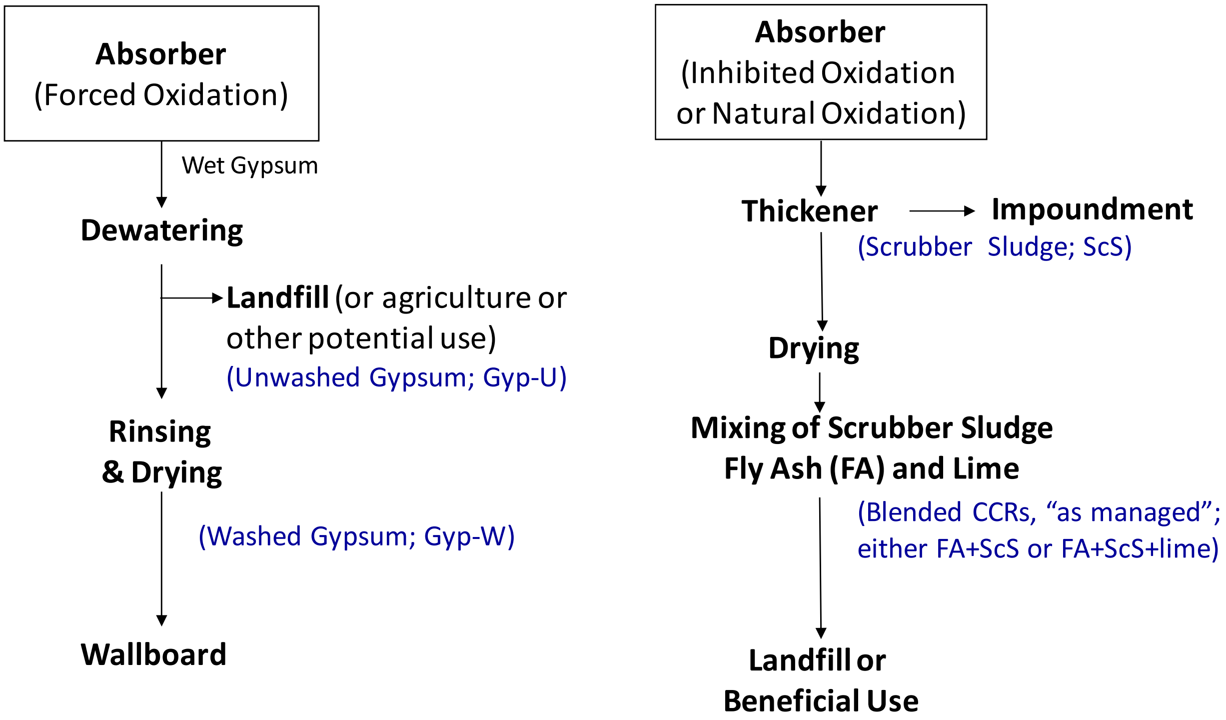

Figure 1. Flow diagram describing processing and nomenclature of FGD scrubber residues and samples included in this study.

When coal is burned in an electric utility boiler, the resulting high combustion temperatures vaporize the Hg in the coal to form gaseous elemental mercury (Hg^0). Subsequent cooling of the combustion gases and interaction of the gaseous Hg^0 with other combustion products may result in a portion of the Hg being converted to gaseous oxidized forms of mercury (Hg^{2+}) and particle-bound mercury (Hg_p). The specific chemical form–known as the speciation-as a strong impact on the capture of mercury and other metals by boiler air pollution control (APC) equipment (EPA, 2001).

Mercury and other elements partition between the combustion gas, fly ash and scrubber residues. Depending upon the gas conditioning, presence or absence of post-combustion NO_x control and other air pollution control technology in use, there may be changes occurring to the fly ash that can affect the stability and mobility of mercury and other metals in the CCRs. Similarly, NO_x control and SO_2 scrubber technology may affect the content, stability and mobility of mercury and other metals in scrubber residues.

The specific objectives of the research reported here are to:

1. Conduct analysis on range of air pollution control residues (i.e., fly ash, FGD residues and other CCRs) resulting from differences in coal rank and air pollution control configurations;
2. Evaluate the potential for leaching to groundwater of mercury and other COPCs (i.e., aluminum, antimony, arsenic, barium, boron, cadmium, chromium, cobalt, lead, molybdenum, selenium, and thallium) removed from the flue gas of coal-fired power plants using multi-pollutant controls to reduce air pollution; and

3. Provide the foundation for assessing the impact of enhanced mercury and multi-pollutant control technology on leaching of mercury and other COPCs from CCR management including storage, beneficial use, and disposal.

This is the third of a series of reports that addresses the potential for cross-media transfer of COPCs from CCRs. The first report focused on the use of sorbent injection (activated carbon and brominated activated carbon) for enhanced mercury control (Sanchez et al., 2006). The second report focused on facilities that use wet scrubbers for multi-pollutant control and includes results for 23 CCRs (fly ash, gypsum, scrubber sludge, fixated scrubber sludge) sampled from eight facilities (Sanchez et al., 2008). This report focuses on CCRs from coal-fired power plants that use air pollution control technologies, other than those evaluated in the first two reports, necessary to span the range of anticipated coal-types and air pollution control technology configurations. A subsequent report will address:

- Assessment of leaching of COPCs under additional management scenarios, including impoundments and beneficial use on the land (report 4); and,
- Broader correlation of CCR leaching characteristics to coal rank, combustion facility characteristics and geochemical speciation within CCRs supported by information and analysis on additional trace elements and primary constituents (report 4).

Sampled CCRs were subjected to multiple leaching conditions according to the designated leaching assessment approach, which is designed to examine leaching potential over a range of pH and LS ratios. Leaching conditions included batch equilibrium[15] extractions at acidic, neutral and alkaline conditions at an LS of 10 mL/g, and LS from 0.5 to 10 mL/g using distilled water as the leachant. In this report, the results of this testing are being used to evaluate the likely range of leaching characteristics during land disposal (i.e., landfill or surface impoundment) scenarios. Results of the laboratory leaching tests carried out in this study were compared to the range of observed constituent concentrations in field leachates reported in a U.S. EPA database (EPA, 2007b) and an Electric Power Research Institute (EPRI) database (EPRI, 2006). The testing results presented here will be used for evaluating disposal and beneficial use scenarios in a subsequent report.

The extensive nature of the results reported here necessitates detailed data presentation with only a broad assessment overview. Future reports will provide more detailed data evaluation and application of the data to evaluation of specific CCR management scenarios.

As part of this research program, a quality assurance/quality control (QA/QC) plan consistent with EPA requirements was developed for the leaching assessment approach (see Section 2.4). The QA/QC methodology included initial verification of acceptable mercury retention during laboratory testing through evaluation of a mass balance around testing procedures (Sanchez et al., 2006). Modifications to the QA/QC program to reduce the experimental and analytical burden while maintaining confidence in the resulting data, based on program results to date, are presented in Report 2 (Sanchez et al., 2008); further modifications are identified in this report.

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[15] In the context of leaching tests, the term “equilibrium” is used to indicate that the test method result is a reasonable approximation of chemical equilibrium conditions even though thermodynamic equilibrium may not be approached for all constituents.

Laboratory testing for leaching assessment was carried out at the EPA National Risk Management Research Laboratory (Research Triangle Park, North Carolina).

1.1. REGULATORY CONTEXT

1.1.1. Waste Management

The management of coal combustion residues is subject to the Resource Conservation and Recovery Act (RCRA) which is the federal law regulating both solid and hazardous wastes. Hazardous waste regulations are developed under Subtitle C of RCRA whereas other solid and non-hazardous wastes fall under RCRA Subtitle D. Subtitle C wastes are federally regulated while Subtitle D wastes are regulated primarily at the state level. The original version of RCRA did not specify whether CCRs were Subtitle C or D wastes. In 1980, the Solid Waste Disposal Act (SWDA) amendments to RCRA conditionally excluded CCRs from Subtitle C regulation pending completion of a study of CCR hazards. Since that time, CCRs have been regulated at the state level under Subtitle D.

The SWDA amendments to RCRA required EPA to prepare a Report to Congress identifying CCR hazards and recommending a regulatory approach for CCRs. In this report (EPA, 1988) and the subsequent regulatory determination, EPA recommended that CCRs generated by electric utilities continue to be regulated under RCRA Subtitle D (See 58 FR 42466, August 9, 1993).

Other residues generated at coal-fired electric utilities were not included in this 1993 decision. EPA conducted a follow-up study specifically aimed at low-volume, co-managed wastes[16] and issued another Report to Congress (EPA, 1999) with a similar recommendation. In April 2000, EPA issued a regulatory determination retaining the existing exemption from hazardous waste regulation for these wastes, although national regulation under RCRA Subtitle D were considered to be warranted (see 65 FR 32214, May 22, 2000). Concern also was expressed over the use of CCRs as backfill for mine reclamation operations, and it was determined that this practice should also be regulated under a federal Subtitle D rule. No regulation of other beneficial uses of CCRs was considered necessary at that time. Currently, the agency is in the process of developing these regulations (http://www.epa.gov/osw/nonhaz/industrial/special/index.htm). The results presented in this report, and subsequent reports, will help provide the information needed to identify the release potential of mercury and other metals that have been removed from stack gases into air pollution control residues, over a range of plausible management options. These data will help identify those conditions that will either reduce or enhance releases to the land so that the effects of different management conditions can be factored into any controls developed under the regulations.

1.1.2. Air Pollution Control

Coal-fired power plants are the largest remaining source of anthropogenic mercury emissions in the country. Power plants are also a major source of nitrogen and sulfur oxides, particulate matter, and carbon dioxide. New environmental regulations in the U.S. will result in lower mercury air emissions, but potentially more mercury in CCRs. The Clean Air Mercury Rule (CAMR) would have required the electric utility sector to remove at least 70% of the mercury

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[16] Co-managed wastes are low-volume wastes that are co-managed with the high-volume CCRs.

released from power plant stack emissions by 2018. However, CAMR was vacated by the United States Court of Appeals for the District of Columbia Circuit in 2008. EPA is currently developing regulations under Section 112 of the Clean Air Act to reduce hazardous air pollutants (including mercury) from coal-fired power plants. Twenty states have implemented their own mercury regulations already, according to the National Association of Clean Air Agencies (Senior et al., 2009). Other EPA regulations[17] will necessitate the addition of new air pollution control devices for NO_x and SO_2 at some power plants. This can also affect the fate of mercury and other COPCs.

1.2. CONFIGURATIONS OF U.S. COAL FIRED POWER PLANTS AND MULTI-POLLUTANT CONTROL TECHNOLOGIES

In the U.S., there are approximately 1,100 units at approximately 500 coal-fired electricity generating facilities. These facilities represent a range of coal ranks, boiler types, and air pollution control technologies. The combined capacity of U.S. coal-fired power plants as of 2007 is 315 GW with a projection to 360 GW by 2030 (DOE-EIA, 2009). The coal rank burned and facility design characteristics affect the effectiveness of multi-pollutant control technologies that are or could be used at these plants. The U.S. coal-fired power plants typically burn one of three types of fuel: (1) bituminous coal (also referred to as “high rank” coal), (2) sub-bituminous coal, and (3) and lignite (sub-bituminous coal and lignite are referred to as “low rank” coals). Some of the characteristics of interest related to the possible environmental impacts of burning these different coal ranks are given in Table 1 (EPA, 2005).

Table 1. General characteristics of coals burned in U. S. power plants (EPA, 2005).

	Mercury ppm (dry)		**Chlorine ppm (dry)**		**Sulfur % (dry)**		**Ash % (dry)**		**HHV[a] BTU/lb (dry)**	
Coal	**Range**	**Avg**	**Range**	**Avg**	**Range**	**Avg**	**Range**	**Avg**	**Range**	**Avg**
Bituminous	0.036 - 0.279	0.113	48 – 2,730	1,033	0.55 - 4.10	1.69	5.4 - 27.3	11.1	8,650–14,000	13,200
Sub-bituminous	0.025 - 0.136	0.071	51 – 1,143	158	0.22 - 1.16	0.50	4.7 - 26.7	8.0	8,610–13,200	12,000
Lignite	0.080 - 0.127	0.107	133 - 233	188	0.8 - 1.42	1.30	12.2 - 24.6	19.4	9,490–10,700	10,000

[a] Higher Heating Value.

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[17] On March 10, 2005, EPA announced the Clean Air Interstate Rule (CAIR) (FR 25612, May 2005) which is expected to increase the use of wet scrubbers and selective catalytic reduction (SCR) units to help reduce sulfur dioxide and nitrogen oxides emissions from coal-fired power plants. On July 11, 2008, United States Court of Appeals for the District of Columbia Circuit remanded CAIR back to EPA for further review and clarification. Thus the rule remains in effect; however, EPA is in the process of developing a replacement rule that will address the Court’s concerns.

1.2.1. Current Air Pollution Control Technologies

A range of pollution control technologies is used to reduce particulate, SO_2, and NO_x and these technologies also impact the emission of mercury and other metals. The pollution control technology type and configurations vary across facilities. [18]

Table 2 shows the current and projected coal-fired capacity by air pollution control technology configuration using data published in a 2005 report (EPA, 2005). Although the projected capacity information is considered dated, the projections for air pollution control appear relevant. The major finding from this report is the projected usage for wet scrubbers which are expected to double or triple in response to implementation of CAIR. Post-combustion particulate matter controls used at coal-fired utility boilers in the United States can include electrostatic precipitators (ESPs), fabric filters (FFs), particulate scrubbers (PSs), or mechanical collectors (MCs). Post-combustion SO_2 controls can consist of a wet scrubber (WS), spray dryer adsorber (SDA), or duct injection. Post-combustion NO_x controls typically involve selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR).

In response to current and proposed NO_x and SO_2 control requirements, additional post-combustion NO_x control and flue gas desulfurization (FGD) systems for SO_2 control are expected to be installed and more widely used in the future. Some estimates project a doubling or tripling of the number of wet scrubbers as a result of CAIR implementation. Over half of the U.S. coal-fired capacity is projected to be equipped with SCR and, or, FGD technology by 2020. Currently, some power plants only use post-combustion NO_x controls during summer months or when tropospheric ozone is more of a concern. However, likely changes will involve using post-combustion NO_x control year-round.

The mercury capture efficiency of existing ESPs and FFs appears to be heavily dependent on the partitioning of mercury between the particulate and vapor phases and the distribution of mercury species (e.g., elemental or oxidized) in the vapor phase. In general, ESPs and FFs which are designed for particulate control are quite efficient at removing mercury in the particulate phase; however, the overall mercury removal efficiency in these devices may be low if most of the mercury entering the device is in the vapor phase (MTI, 2001). Many factors contribute to the observed differences in mercury removal efficiency, such as the mercury oxidation state. Differences in mercury contents of U.S. coals also result in a range of mercury concentrations in the flue gas from the boiler. In general, it is easier to achieve higher mercury percent removal with higher mercury inlet concentrations (MTI, 2001). Further, the chlorine content of the coal may have an impact on mercury removal because the oxidation state of mercury is strongly affected by the presence of halides in the flue gas. In general, the higher the chlorine content of the coal, the more likely the mercury will be present in its oxidized state, enhancing the likelihood of its removal from the gas stream. The addition of post-combustion NO_x controls may improve mercury capture efficiency of particulate collection devices for some cases as a result of the oxidation of elemental mercury (EPA, 2001).

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[18] Concerns regarding carbon dioxide emissions from coal fired power plants are beyond the scope of this report.

Table 2. Projected coal-fired capacity by air pollution control configuration as per data collection in 1999 (EPA, 2005). CCR samples evaluated in this report are from configurations indicated by shaded (light gray) rows. 2005 capacity reflects date of data collection for EPA report (EPA, 2005).

Air Pollution Control Configuration	**2005 Capacity, MW**	**2010 Capacity, MW (projected)**	**2020 Capacity, MW (projected)**
Cold-side ESP	111,616	75,732	48,915
Cold-side ESP + Wet Scrubber	41,745	34,570	33,117
Cold-side ESP + Wet Scrubber + ACI	-	379	379
Cold-side ESP + Dry Scrubber	2,515	3,161	5,403
Cold-side ESP + SCR	45,984	35,312	22,528
Cold-side ESP + SCR + Wet Scrubber	27,775	62,663	98,138
Cold-side ESP + SCR + Dry Scrubber	-	11,979	13,153
Cold-side ESP + SNCR	7,019	4,576	2,534
Cold-side ESP + SNCR + Wet Scrubber	317	2,830	6,088
Fabric Filter	11,969	10,885	7,646
Fabric Filter + Dry Scrubber	8,832	8,037	9,163
Fabric Filter + Wet Scrubber	4,960	4,960	4,960
Fabric Filter + Dry Scrubber + ACI	-	195	195
Fabric Filter + SCR	2,210	2,950	1,330
Fabric Filter + SCR + Dry Scrubber	2,002	2,601	4,422
Fabric Filter + SCR + Wet Scrubber	805	805	2,363
Fabric Filter + SNCR	267	267	345
Fabric Filter + SNCR + Dry Scrubber	559	557	557
Fabric Filter + SNCR + Wet Scrubber	932	932	1,108
Hot-side ESP	18,929	11,763	10,160
Hot-side ESP + Wet Scrubber	8,724	10,509	10,398
Hot-side ESP + Dry Scrubber	-	538	538
Hot-side ESP + SCR	5,952	3,233	1,847
Hot-side ESP + SCR + Wet Scrubber	688	6,864	9,912
Hot-side ESP + SNCR	684	1,490	1,334
Hot-side ESP + SNCR + Wet Scrubber	474	474	627
Existing or Planned Retrofit Units	**~305,000**	**~298,000**	**297,000**
New Builds of Coal Steam Units	**2005 Capacity, MW**	**2010 Capacity, MW**	**2020 Capacity, MW**
Fabric Filter + SCR + Wet Scrubber	-	221	17,292
Total All Units	**~305,000**	**~298,500**	**~314,400**

Note: IGCC units are not included as part of this list.
Note: Current capacity includes some SCR and FGD projected to be built in 2005 and 2006.
Note: 2010 and 2020 is capacity projected for final CAIR rule.
Note: Integrated Planning Model (IPM) projects some coal retirements and new coal in 2010 and 2020. (http://www.epa.gov/airmarkt/progsregs/epa-ipm/index.html)

1.2.2. Wet Scrubbers, NO_x Controls and Multi-pollutant Controls

Wet FGD scrubbers are the most widely used technology for SO_2 control. Scrubbers are typically installed downstream of particulate control (i.e., ESP or FF). Removal of PM from the flue gas before it enters the wet scrubber reduces solids in the scrubbing solution and minimizes impacts to the fly ash that might affect its beneficial use.

FGD technology uses sorbents and chemical reactants such as limestone (calcium carbonate) or lime (hydrated to form calcium hydroxide) to remove sulfur dioxide from the flue gas created from coal combustion. Limestone is ground into a fine powder and then combined with water to spray the slurry into combustion gases as they pass through a scrubber vessel. The residues are collected primarily as calcium sulfite (a chemically reduced material produced in natural oxidation or inhibited oxidation scrubbers), or can be oxidized to form calcium sulfate or FGD gypsum (using forced oxidation). The most widely used FGD systems use either forced oxidation scrubbers with limestone addition, or natural/inhibited oxidation scrubbers with lime or Mg-lime addition[19]. Wet scrubbers that use forced oxidation produce calcium sulfate (gypsum) and are expected to be the most prevalent technology because of the potential beneficial use of gypsum and easier management and handling of the residues. There are also dry FGD systems that include spray dryer absorbers, usually in combination with a FF (EPA, 2001; Srivastava et al., 2001).

NO_x emissions are controlled through the use of low NO_x producing burners and use of a selective catalytic reduction (SCR) system in the flue gas that is capable of a 90% reduction of flue gas NO_x emissions. SCR is typically installed upstream of the PM control device. Sometimes selective non-catalytic reduction (SNCR) is used for NO_x control, although use of SNCR is less common.

Figure 2 illustrates options for multi-pollutant control at power plants.

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[19] As of 1999: Total FGD units–151; limestone forced oxidation (FO)-38 units (25%); limestone natural/inhibited oxidation - 65 (43%); lime FO (all forms other than Mg-lime) - 1 (<1%); lime natural/inhibited oxidation (all forms other than Mg-lime) - 23 (15%); Mg-lime FO - 0 (0%); Mg-lime natural/inhibited oxidation - 25 (17%). It is estimated that the numbers of natural/inhibited systems has remained nearly the same since 1999, and the limestone FO units have increased significantly. In the future, limestone FO units will increase significantly, and all types of natural/inhibited units will likely decrease (Ladwig, 2007).

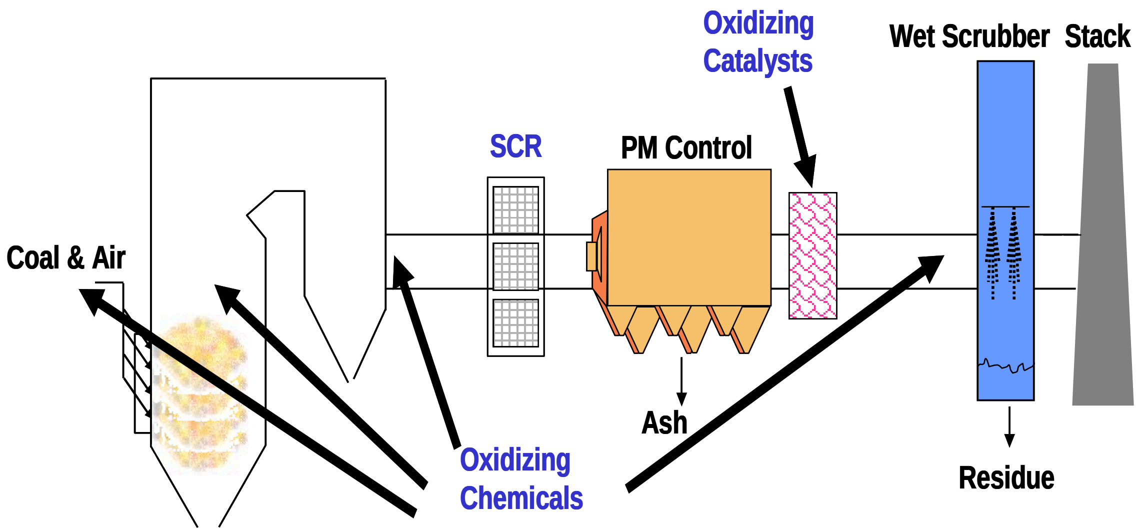

Figure 2. Illustration of available technology for multi-pollutant control at coal-fired power plants.

Improvements in wet scrubber performance to enhance mercury capture depend on oxidizing elemental mercury (Hg^0) to Hg^{2+} by using additives to the flue gas or scrubber. A DOE-funded study found that wet scrubbers can remove as much as 90% of the oxidized gaseous mercury (Hg^{2+}) in the flue gas but none of the elemental mercury (Pavlish et al., 2003). The percentage of total Hg removed by multi-pollutant controls (particulate and scrubber devices) is influenced by coal chlorine content, which determines the Hg oxidation status exiting the particulate control and entering the scrubber. Fuel blending, addition of oxidizing chemicals, controlling unburned carbon content in the fly ash, and addition of a mercury-specific oxidizing catalyst downstream of the particulate matter control can help improve mercury capture (EPA, 2005).

1.2.3. Mercury Control Using Sorbent Injection

Injection of dry sorbents, such as powdered activated carbon (PAC), has been used for control of mercury emissions from waste combustors and has been tested at numerous utility units in the United States. There are different approaches that can be used to increase mercury capture efficiency as illustrated in Figure 3 and Figure 4. Figure 3 presents a coal-fired boiler with sorbent injection and spray cooling. Figure 4 presents a power plant with a hot-side ESP (HS-ESP), carbon injection, and a compact hybrid particle collector (COHPAC^{TM}). Dry sorbent is typically injected into the ductwork upstream of a PM control device – normally either an ESP or FF. Usually the sorbent is pneumatically injected as a powder. The injection location is determined by the existing plant configuration. Another approach, designed to segregate collected fly ash from collected sorbent, would be to retrofit a pulse-jet FF (PJFF) downstream of an existing ESP and inject the sorbent between the ESP and the PJFF. This type includes of COHPAC^{TM} and when combined with sorbent injection is referred to as Toxic Emission Control (TOXECON^{TM}). The TOXECON configuration can be useful because it avoids commingling the larger fly ash stream with mercury recovered on the injected sorbent. Implementation of sorbent injection for mercury control will likely entail either:

- Injection of powdered sorbent upstream of the existing PM control device (ESP or FF); or
- Injection of powdered sorbent downstream of the existing ESP and upstream of a retrofit fabric filter, the TOXECON™ option; or
- Injection of powdered sorbent between ESP fields (TOXECON-II™ approach).

In general, factors that affect the performance of sorbent technology for mercury methods include:

- Injection rate of the sorbent measured in lb/MMacf[20];
- Flue gas conditions, including temperature and concentrations of HCl and sulfur trioxide (SO_3), and oxidation state of the mercury present;
- The air pollution control configuration;
- The characteristics of the sorbent (e.g., conventional or halogenated); and
- The method of injecting the sorbent.

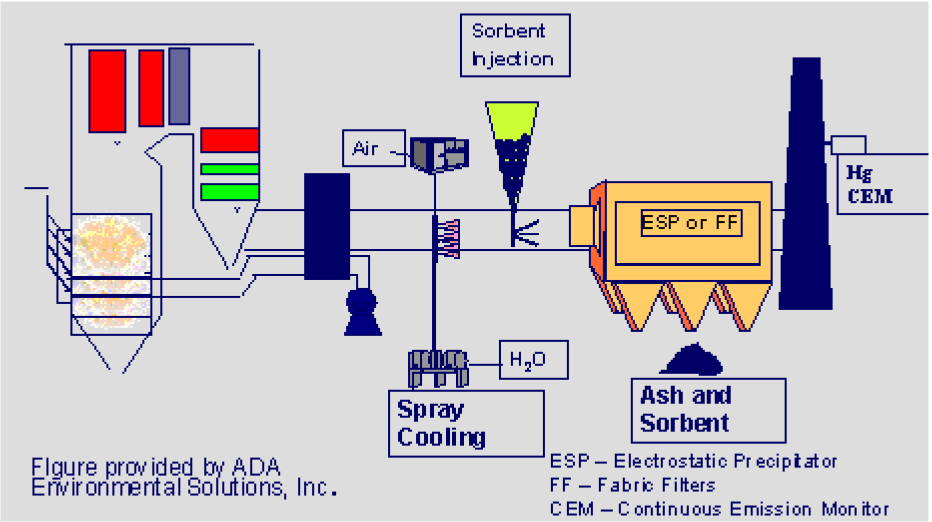

Figure 3. Coal-fired boiler with sorbent injection and spray cooling (Senior et al., 2003).

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[20] Sorbent injection rate is expressed in lb/MMacf, i.e., pounds of sorbent injected for each million actual cubic feet of gas. For a 500 MW boiler, a sorbent rate of 1.0 lb/MMacf will correspond to approximately 120 lb/hour of sorbent.

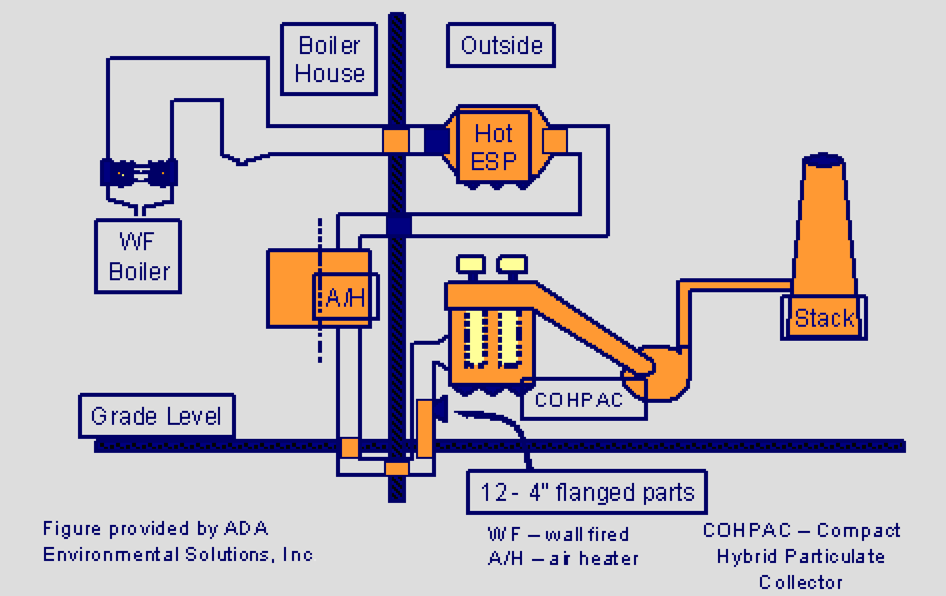

Figure 4. Flow diagram for power plant with a hot ESP, carbon injection, and a compact hybrid particulate collector (Senior et al., 2003).

1.2.4. Mercury Control by Conventional PAC Injection

The most widely tested sorbent for mercury control at utility boilers is PAC.

In general, the efficacy of mercury capture using standard PAC increases with the relative amount of Hg^{2+} (compared with Hg^0) in flue gas[21], the number of active sites[22] in the PAC, and lower temperature. The amount of Hg^{2+} in flue gas is usually directly influenced by the amount of chlorine present in the flue gas, with higher chlorine content enhancing Hg^{2+} formation. Based on these factors, standard PAC injection appears to be generally effective for mercury capture on low-sulfur bituminous coal applications, but less effective for the following applications:

- Low-rank coals with ESP (current capacity of greater than 150 GW; the capacity with this configuration is not expected to increase significantly in the future). Lower chlorine and higher calcium contents in coal lead to lower levels of chlorine in flue gas, which results in reduced oxidation of mercury and, therefore, lower Hg^{2+} in flue gas;
- Low-rank coals with SDA and FF (current capacity of greater than 10 GW; the number of facilities with this configuration is expected to increase significantly in the future). Similar effect as above, except lime reagent from the SDA scavenges even more chlorine from flue gas;

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[21] Standard PAC binds mercury via physical (i.e., weak) bonds, which are formed more easily with Hg^{2+}. There have been results that show a similar removal for both elemental and oxidized mercury. However, the results do not account for surface catalyzed oxidation of Hg^0 followed by sorption on the carbon (EPA, 2005).

[22] These are collection of atoms/radicals such as oxygen, chlorine, hydroxyls, which provide binding sites.

- High-sulfur coal (current capacity with wet FGD of approximately 100 GW; the number of facilities with this configuration is likely to increase to more than 150 GW). Relatively high levels of SO_3 compete for active sites on PAC, which reduces the number of sites available for mercury. Generally, plants will use wet FGD and, in many cases, SCR; PAC injection may be needed to meet mercury reduction limits; and
- Hot-side ESPs (current capacity of approximately 30 GW; the number of facilities with this configuration is not likely to increase). Weak (physical) bonds get ruptured at higher temperatures resulting in lower sorption capacity.

1.2.5. Mercury Control by Halogenated PAC Injection

Some situations, as described above, may not have adequate chlorine present in the flue gas for good mercury capture by standard PAC. Pre-halogenated PAC sorbents have been developed to overcome some of the limitations associated with PAC injection for mercury control in power plant applications (Nelson, 2004; Nelson et al., 2004).

Halogenated PACs offer several potential benefits. Relative to standard PAC, halogenated PAC use:

- may expand the usefulness of sorbent injection to many situations where standard PAC may not be as effective;
- may avoid the need for installation of downstream FF, thereby improving cost-effectiveness of mercury capture;
- would, in general, be at lower injection rates, which potentially will lead to fewer plant impacts and a lower carbon content in the captured fly ash;
- may result in somewhat better performance with low-sulfur (including low-rank) coals because of less competition from SO_3; and,
- may be a relatively inexpensive and attractive control technology option for technology transfer to developing countries as it does not involve the capital intensive FF installation.

Performance of a halogenated sorbent such as brominated PAC appears to be relatively consistent regardless of coal type and appears to be mostly determined by whether or not the capture is in-flight (as in upstream of a CS-ESP) or on a fabric filter.

1.3. COAL COMBUSTION RESIDUES

In 2006, 125 million tons of coal combustion residues were produced with ~54 million tons being used in commercial, engineering, and agricultural applications (ACAA, 2007). CCRs result from unburned carbon and inorganic materials in coals that do not burn, such as oxides of silicon, aluminum, iron, and calcium. Fly ash is the unburned material from coal combustion that is light enough to be entrained in the flue gas stream, carried out of the process, and collected as a dry material in the APC equipment. Bottom ash and boiler slag are not affected by post-combustion APC technology and, therefore, these materials are not being evaluated as part of this study. Bottom ash is the unburned material that is too heavy to be entrained in the flue gas stream and drops out in the furnace. Boiler slag, unburned carbon or inorganic material in coal that does not burn, falls to the bottom of the furnace and melts.

The properties of fly ash and flue gas desulfurization residues are likely to change as a result of APC changes to reduce emissions of concern from coal-fired power plants. The chemical and physical properties may also change as a result of sorbents and other additives being used to improve air pollution control.

1.4. RESIDUE MANAGEMENT PRACTICES

CCRs can be disposed in landfills or surface impoundments or used in commercial applications to produce concrete and gypsum wallboard, among other products. Research on the impact of CCR disposal on the environment has been conducted by many researchers and has been summarized by the (EPA, 1988; EPA, 1999). However, most of the existing CCR data are for CCRs prior to implementation of mercury or multi-pollutant controls.

1.4.1. Beneficial Use

In the United States, approximately 43% percent (or 54 million tons out of total 125 million tons produced) of all CCRs produced are reused in commercial applications or other uses that are considered beneficial and avoid landfilling. Of the 125 million tons of CCRs produced as of 2006, about 60 percent (72.4 million tons of fly ash out of 125 million tons of CCRs) of CCRs is fly ash which is potential candidate for use in commercial applications such as making concrete/grout, cement, structural fill, and highway construction (ACAA, 2007; Thorneloe, 2003). Twelve million tons of the FGD gypsum was produced in 2006 with 7.6 million tons (i.e., 62% or 7.6 million out of 12 million) used in making wall board (ACAA, 2007). Table 3 and Figure 5 present the primary commercial uses of CCRs, and a breakdown of U.S. production and usage by CCR type.

Some beneficial uses may involve high temperature processing that may increase the potential for release of mercury and other metals. In cement manufacturing, for example, CCRs may be raw feed for producing clinker in cement kilns. Because of the high temperatures (~1450 ^{o}C), virtually all mercury will be volatilized from CCRs when they are used as feedstock to cement kilns. EPA has proposed (74 FR 21136m May 6, 2009) regulations to reduce mercury emissions from cement kilns, which may result in use of air pollution control technology similar to that used at coal-fired power plants (e.g, wet scrubbers and sorbents for enhanced Hg capture). The addition of air pollution control at cement kilns should not affect the ability to use fly ash or FGD gypsum in the production of clinker. However, to avoid installation of air pollution control, kiln inputs (such as fly ash) containing mercury may be avoided which could impact usage of some CCRs.

Through a separate study by EPA’s Air Pollution Prevention and Control Division, three high-temperature processes using coal ash have been evaluated for stability of mercury and other COPCs found in coal ash. This research is documented in a separate EPA report (Thorneloe, 2009).

The fate of mercury and other metals is also a potential concern when CCRs are used on the land (mine reclamation, building highways, soil amendments, agriculture and in making concrete, cement) or to make products that are subsequently disposed (e.g., disposal of wallboard in unlined landfill). The potential for leaching is a function of the characteristics of the material and the conditions under which it is managed.

For some commercial uses, it appears unlikely that mercury in CCRs will be reintroduced into the environment, at least during the lifetime of the product (e.g., encapsulated uses such as in the production of concrete). However, the impact of advanced mercury emissions control technology (e.g., activated carbon injection) on beneficial use applications is uncertain. There is concern that the presence of increased concentrations of mercury, certain other metals, or high carbon content may reduce the suitability of CCRs for use in some applications (e.g., carbon content can limit fly ash use in Portland cement concrete).

1.4.2. Land Disposal

There are approximately 600 land-based CCR waste disposal units (landfills or surface impoundments) being used by the approximately 500 coal-fired power plants in the United States (EPA, 1999). About 60% of the 125 million tons of CCRs generated annually are land disposed. Landfills may be located either on-site or off-site while surface impoundments are almost always located on-site with the combustion operations. Although the distribution of units is about equal between landfills and surface impoundments, there is a trend toward increased use of landfills as the primary disposal method.

Table 3. Beneficial uses of CCRs (ACAA, 2007). Total production of CCRs during 2006 was 124,795,124 short tons (values indicated are as reported in the primary reference and precision should not be inferred from the number of significant figures reported).

CCR Categories (Short Tons)	**Fly Ash**	**Bottom Ash**	**FGD Gypsum**	**FGD Wet Scrubbers**	**Boiler Slag[1]**	**FGD Dry Scrubbers[1]**	**FGD Other**
CCR Production Category Totals[2]	72,400,000	18,600,000	12,100,000	16,300,000	2,026,066	1,488,951	299,195
CCR Used Category Totals[3]	32,423,569	8,378,494	9,561,489	904,348	1,690,999	136,639	29,341
CCR Use By Application[4]	**Fly Ash**	**Bottom Ash**	**FGD Gypsum**	**FGD Wet Scrubbers**	**Boiler Slag [1]**	**FGD Dry Scrubbers[1]**	**FGD Other**
1. Concrete/Concrete Products/Grout	15,041,335	597,387	1,541,930	0	0	9,660	0
2. Cement/Raw Feed for Clinker	4,150,228	925,888	264,568	0	17,773	0	0
3. Flowable Fill	109,357	0	0	0	0	9,843	0
4. Structural Fills/Embankments	7,175,784	3,908,561	0	131,821	126,280	0	0
5. Road Base/Sub-base/Pavement	379,020	815,520	0	0	60	249	0
6. Soil Modification/Stabilization	648,551	189,587	0	0	0	299	1,503
7. Mineral Filler in Asphalt	26,720	19,250	0	0	45,000	0	0
8. Snow and Ice Control	0	331,107	0	0	41,549	0	0
9. Blasting Grit/Roofing Granules	0	81,242	0	232,765	1,445,933	0	0
10. Mining Applications	942,048	79,636	0	201,011	0	115,696	0
11. Wallboard	0	0	7,579,187	0	0	0	0
12. Waste Stabilization/Solidification	2,582,125	105,052	0	0	0	0	27,838
13. Agriculture	81,212	1,527	168,190	0	0	846	846
14. Aggregate	271,098	647,274	0	0	416	0	0
15. Miscellaneous/Other	1,016,091	676,463	7,614	338,751	13,988	46	46
CCR Category Use Tools	**32,423,569**	**8,378,494**	**9,561,489**	**904,348**	**1,690,999**	**136,639**	**29,341**
Application Use to Production Rate	44.8%	45.0%	79.0%	5.5%	83.5%	9.2%	9.8%

[1] As submitted based on 54 percent coal burn.

[2] CCR Production totals for Fly Ash, Bottom Ash, FGD Gypsum, and Wet FGD are extrapolated estimates rounded off to nearest 50,000 tons.

[3] CCR Used totals for Fly Ash, Bottom Ash, FGD Gypsum, and Wet FGD are per extrapolation calculations (not rounded off).

[4] CCR Uses by application for Fly Ash, Bottom Ash, FGD Gypsum, and Wet FGD are calculated by proportioning the CCR Used Category Totals by the same percentage as each of the individual application types' raw data contributions to the as-submitted raw data submittal total (not rounded off).

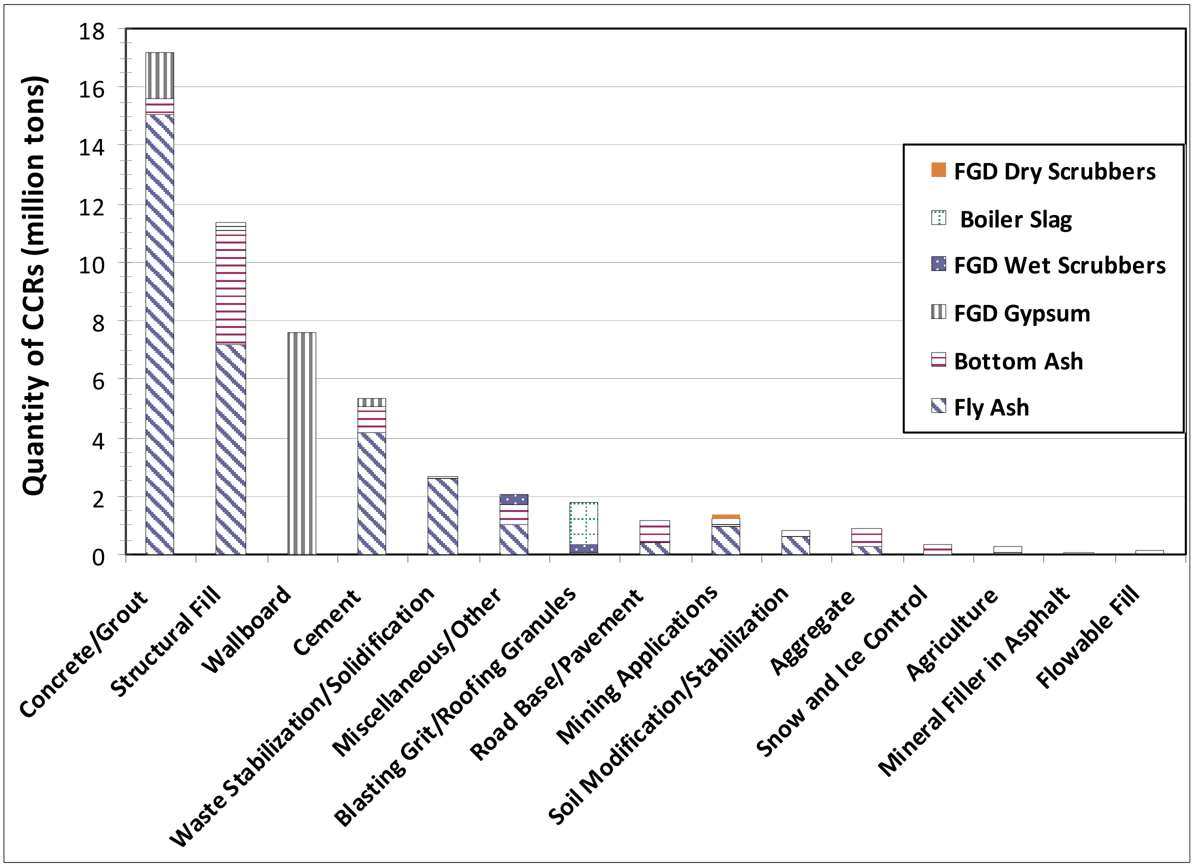

Figure 5. Uses of CCRs based on 2006 industry statistics (ACAA, 2007).

1.5. LEACHING PROTOCOL

One of the major challenges initially facing this research was identification of an appropriate test protocol for evaluating the leaching potential of CCRs that may have increased levels of several metals, particularly mercury. The goal of this research is to develop more accurate estimates of likely constituent leaching when CCRs are used or disposed on land. These estimates of leaching need to be appropriate for assessing at a national level the likely impacts through leaching of pollutants from CCRs that is a consequence of installation of enhanced mercury and, or, multi-pollutant controls. Because management conditions are known to affect the leaching of many metals, evaluation of leaching potential for CCRs over a range of test conditions is needed to consider a range of as managed scenarios (to the degree this is known), and provide leach testing results that can be appropriately extrapolated to a national assessment. A significant consideration in this research has been to identify and evaluate CCR samples collected from the most prevalent combinations of power plant design (with a focus on air pollution control technology configurations) and coal rank used. In addition, the resulting data set is expected to serve as foundation for evaluation of CCR management options for different types of CCRs at specific sites.

As a key part of this assessment approach, data have been collected on the actual disposal conditions for CCRs. These conditions are determined by a number of factors, and conditions will vary over time, which also needs to be considered when evaluating leaching (EPA, 1999; EPA, 2002; EPA, 2007b). When disposed, CCRs are typically monofilled[23] or disposed with other CCRs, so initial conditions may be determined largely by the tested material, and any co-disposed CCRs. However, CCR composition can change over time, due to reactions with the atmosphere (e.g., carbonation and oxidation), leaching out of soluble species, creation of reducing conditions at lower landfill levels, changes in the source of coal or coal rank burned, or due to installation of additional pollution control equipment.

Many leaching tests have been developed by regulatory agencies, researchers, or third-party technical standards organizations, and are described in the published literature. States and others have expressed concern with the variety of leaching protocols in use, the lack of correlation of test results with field conditions and actual leaching, and lack of comparability of available data because of incomplete reporting of test conditions. There is also limited or no quality assurance (QA) information for many of these tests. Leaching tests such as the Toxicity Characterization Leaching Procedure (TCLP)[24] (which reflects municipal solid waste co-disposal conditions) or the synthetic precipitation leaching procedure (SPLP), or any number of deionized water based tests may be inappropriate, or are at least not optimal for evaluating the leaching potential of CCRs as they are actually managed (i.e., monofilled or co-disposed with other CCRs). These tests either presume a set of prevailing landfill conditions (which may or may not exist at CCR disposal sites; e.g., TCLP), try to account for an environmental factor considered to be important in leaching (e.g., SPLP), or presume that the waste as tested in the laboratory will define the disposal conditions [such as deionized (DI) water tests]. Most existing leaching tests are empirical, in that results are presented simply as the contaminant concentrations leached when using the test, and without measuring or reporting values for factors that may occur under actual management and affect waste leaching, or that provide insight into the chemistry that is

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[23] The term “monofilled” refers to when a CCR is the only or dominant component in a landfill or disposal scenario.

[24] The Toxicity Characterization Leaching Procedure (TCLP) was not included as part of this study for several reasons. First, EPA previously made a waste status determination under RCRA that coal combustion residues are non-hazardous (65 FR 32214, May 22, 2000). Therefore, use of TCLP was not required as indicated under the RCRA toxicity characteristic regulation for determination of whether or not CCRs were hazardous. Second, TCLP was developed to simulate co-disposal of industrial waste with municipal solid waste as a mismanagement scenario, and to reflect conditions specific to this scenario. However, although MSW co-disposal of CCRs is plausible, the vast majority of CCRs are not being managed through co-disposal with municipal solid waste, and the test conditions for TCLP are different from the actual management practices for most CCRs. Third, SAB and NAS expressed concerns that a broader set of conditions and test methods other than TCLP are needed to evaluate leaching under conditions other than co-disposal with municipal solid waste. In seeking a tailored, “best-estimate” of CCR leaching, the leaching framework is responsive to SAB and NAS concerns and provides the flexibility to consider the effects of actual management conditions on these wastes, and so will be more accurate in this case.

occurring in leaching. Most tests are performed as a single batch test, and so do not consider the effect of variations in conditions on waste constituent leaching[25].

In searching for a reliable procedure to characterize the leaching potential of metals from the management of CCRs, EPA sought an approach that (i) considers key aspects of the range of known CCR chemistry and management conditions (including re-use); and (ii) permits development of data that are comparable across U.S. coal and CCR types. Because the data resulting from this research will be used to support regulations, scrutiny of the data is expected. Therefore, the use of a published, peer-reviewed (but not promulgated) protocol is also considered to be an essential element of this work.[26]

EPA ORD has worked closely with EPA's Office of Solid Waste and Emergency Response (OSWER) to identify an appropriate leaching protocol for evaluating CCRs. The protocol that has been adopted is the "Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials" (Kosson et al., 2002) and referred to here as the "leaching framework." The leaching framework consists of a tiered approach to leaching assessment. The general approach under the leaching framework is to use laboratory testing to measure intrinsic leaching characteristics of a material (i.e., liquid-solid equilibrium partitioning as a function of pH and LS ratio, mass transfer rates) and then use this information in conjunction with mass transfer models to estimate constituent release by leaching under specific management scenarios (e.g., landfilling). Unlike other laboratory leaching tests, under this approach, laboratory testing is not intended to directly simulate or mimic a particular set of field conditions. Development work to-date on the leaching framework has focused on assessing metals leaching, and this work includes equilibrium batch testing (over a range of pH and LS ratio values), diffusion-controlled mass transfer, and percolation-controlled (column) laboratory test methods in conjunction with mass transfer models, to estimate release for specific management scenarios based on testing results from a common set of leaching conditions. EPA OSWER and ORD believe that this approach successfully addresses the concerns identified above, in that it seeks to consider the effect of key disposal conditions on constituent leaching, and to understand the leaching chemistry of wastes tested.

The following attributes of the leaching framework were considered as part of the selection process:

- The leaching framework will permit development of data that are comparable across U.S. coal and CCR types;
- The leaching framework will permit comparison with existing laboratory and field leaching data on CCRs;

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[25] Many factors are known or may reasonably be expected to affect waste constituent leaching. The solubility of many metal salts is well known to vary with pH; adsorption of metals to the waste matrix varies with pH; redox conditions may determine which metal salts are present in wastes; temperature may affect reaction rates; water infiltration can affect the leaching rate, and also affect leaching chemistry and equilibrium.

[26] EPA is working to include the leaching test methods used in this research as part of standard methods in SW-846.

- The leaching framework was published in the peer-reviewed scientific literature (Kosson et al., 2002);
- On consultation with EPA’s OSWER, it was recommended as the appropriate protocol based on review of the range of available test methods and assessment approaches; and
- On consultation with the Environmental Engineering Committee of the Science Advisory Board (SAB, 2003), the committee considered the leaching framework responsive to earlier SAB criticisms of EPA’s approach to leaching evaluation, and also was considered broadly applicable and appropriate for this study

For this study, the primary leaching tests used from the leaching framework were Solubility and Release as a Function of pH (SR002.1) and Solubility and Release as a Function of the Liquid-Solid Ratio (LS) (SR003.1)[27]. These tests represent equilibrium-based leaching characterization (Kosson et al., 2002). The range of pH and LS ratio used in the leaching tests is within the range of conditions observed for current CCR management practices. Results of these tests provide insights into the physical-chemical mechanisms controlling constituent leaching. When used in conjunction with mass transfer and geochemical speciation modeling, the results can provide conservative[28] but realistic estimates of constituent leaching under a variety of environmental conditions (pH, redox, salinity, carbonation) and management scenarios.

This test set is considered Tier 2 testing (equilibrium-based) for detailed characterization, which was selected to develop a comprehensive data set of CCR characteristics (Kosson et al., 2002). Mass transfer rate testing (Tier 3, detailed characterization) may be carried out in the future for specific cases where results from equilibrium-based characterization indicate a need for detailed assessment.

Eluates from leaching tests were analyzed for more than 35 constituents (e.g., elements, anions, DIC, DOC) and characteristics (e.g., pH and conductivity), however, 13 constituents were selected to be the focus of this report based on input from OSWER due to potential concern for human health and the environment.

Laboratory testing for leaching assessment was carried out at EPA’s National Risk Management Research Laboratory (Research Triangle Park, NC) with technical assistance from Vanderbilt University.

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[27] LS refers to liquid to solid ratio (mL water/g CCR or L water/kg CCR) occurring during laboratory leaching tests or under field conditions. SR002.1 is carried out at LS=10 with several parallel batch extractions over a range of pH, while SR003.1 is carried out using several parallel batch extractions with deionized water at LS= 0.5, 1, 2, 5 and 10. Under field conditions, LS refers to the cumulative amount of water passing through the total mass of CCR subject to leaching. SR002.1 and SR003.1 are Vanderbilt University test method designations. An appropriately defined and structured version of test method SR002.1 is being proposed as SW-846 Draft Method 1313 – Leaching Test (Liquid-Solid Partitioning as a Function of Extract pH) of Constituents in Solid Materials Using a Parallel Batch Extraction Test; similarly, test method SR003.1 is being proposed as SW-846 Draft Method 1316 – Leaching Test (Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ration) of Constituents in Solid Materials Using a Parallel Batch Extraction Test.

[28] In this report, “conservative” implies that the constituent release estimates are likely to be equal to or greater than actual expected release under field conditions.

2. MATERIALS AND METHODS

The following sections discuss the specific CCR materials evaluated in this report and the specific methods of characterization, including physical and chemical properties, elemental composition and leaching characteristics. The Quality Assurance Project Plan supporting this work is provided as Appendix B and assessment of quality assurance results is discussed in section 2.4.

2.1. CCR MATERIALS FOR EVALUATION

The 73 CCR samples tested in this study (inclusive of all three reports) include 27 fly ashes without Hg sorbent injection, 7 fly ashes with Hg sorbent injection, 2 spray dryers with fabric filter, 11 unwashed gypsum, 9 washed gypsum, 5 scrubber sludges, 8 blended CCRs (7 mixed fly ash and scrubber sludges; 1 mixed fly ash and gypsum) from 31 coal fired power plants (Table 4). Most coal fired power plants providing samples are identified by a single or two letter code (i.e., Facility T or Facility Ba) to allow specific facilities to remain anonymous. In addition, 4 filter cake samples from the waste water treatment process associated with the management of CCRs were evaluated. Table 5 summarizes the CCR samples evaluated, grouped by residue type, coal type and air pollution control (APC) configuration. Description of the facilities and CCR sampling points is provided in Appendix A.

The facilities and CCRs that were sampled were selected to allow comparisons:

1. Between fly ashes for different coal types (bituminous *vs*. sub-bituminous *vs*. lignite[29]), particulate control devices (cold-side ESP *vs*. hot-side ESP *vs*. fabric filter), and NO_x control (none or by passed, SNCR or SCR);
2. Between fly ashes from the same facility without and with Hg sorbent injection (Brayton Point, Salem Harbor, Pleasant Prairie, and Facilities J, L, C, and Ba);
3. Between unwashed and washed gypsum from the same facility (Facilities N, O, S, T, W, X, and Aa); and,
4. On the impact of different FGD scrubber types on scrubber sludge (Facilities A, B, and K), blended fly ash and scrubber sludge (Facilities A, B, K and M), and blended fly ash and gypsum (Facility U).

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[29] This project had a difficult time obtaining coal ash samples from lignite coal. Samples (fly ash and FGD gypsum) were obtained from one facility using Gulf Coast lignite. For facility Ba, the obtained fly ash was from a coal blend of PRB and North Dakota lignite.

Table 4. Summary of facility configurations, CCR sample types and sample codes.

Facility Information						**CCR Sample Types and Sample Codes**								
Facility Code	**Coal Type**	**NO_x Control**	**PM Control**	**FGD Scrubber**		**Fly Ash**	**Spray Dryer Ash**	**Gypsum**		**ScS**	**Blended CCRs**			**Filter Cake**
				Limestone or Mg Lime	**Oxidation**			**Gyp-U**	**Gyp-W**		**FA+ Gyp**	**FA+ ScS**	**FA+ ScS+ Lime**	
[1]Brayton Point	East-Bit	None	CS-ESP	None	None	BPB								
[1]Brayton Point	East-Bit	None	ACI+ CS-ESP	None	None	BPT								
[1]Pleasant Prairie	PRB Sub-Bit	None	CS-ESP	None	None	PPB								
[1]Pleasant Prairie	PRB Sub-Bit	None	ACI+ CS-ESP	None	None	PPT								
[1]Salem Harbor	Low S East-Bit	SNCR	CS-ESP	None	None	SHB								
[1]Salem Harbor	Low S East-Bit	SNCR	ACI+ CS-ESP	None	None	SHT								
[2]A	East-Bit	SNCR-BP[3]	Fabric Filter	Limestone	Natural	CFA						CCC		
[2]A	East-Bit	SNCR	Fabric Filter	Limestone	Natural	AFA			CGD			ACC		
[2]B	East-Bit	SCR-BP*	CS-ESP	Mg Lime	Natural	BFA				BGD			BCC	
[2]B	East-Bit	SCR	CS-ESP	Mg Lime	Natural	DFA			AGD				DCC	
[1]C	Low S Bit	None	HS-ESP with COHPAC	None	None	GAB			DGD					
[1]C	Low S Bit	None	HS-ESP + ACI + COHPAC	None	None	GAT								
E	Med S East-Bit	SCR (in use and BP)	CS-ESP	None	None	EFA, EFB								

Table 4. Summary of facility configurations, CCR sample types and sample codes.

Facility Information						**CCR Sample Types and Sample Codes**								
Facility Code	**Coal Type**	**NO$_x$ Control**	**PM Control**	**FGD Scrubber**		**Fly Ash**	**Spray Dryer Ash**	**Gypsum**		**ScS**	**Blended CCRs**			**Filter Cake**
				Limestone or Mg Lime	**Oxidation**			**Gyp-U**	**Gyp-W**		**FA+ Gyp**	**FA+ ScS**	**FA+ ScS+ Lime**	
E	High S East-Bit	SCR (in use and BP)	CS-ESP	None	None	EFC								
F	Low S Bit	None	CS-ESP	None	None	FFA								
G	Low S Bit	SNCR	CS-ESP	None	None	GFA								
H	High S Bit	SCR	CS-ESP	Limestone	Forced	HFA								
[1]J	Sub-Bit	None	CS-ESP	None	None	JAB								
[1]J	Sub-Bit	None	Br-ACI + CS-ESP	None	None	JAT								
[2]K	Sub-Bit	SCR	CS-ESP	Mg Lime	Natural	KFA							KCC	
[1]L	Southern Appala-chian	SOFA[4]	HS-ESP	None	None	LAB			KGD					
[1]L	Southern Appala-chian	SOFA	Br-ACI + HS-ESP	None	None	LAT								
[2]M	Bit	SCR-BP	CS-ESP	Limestone	Inhibited								MAD	
[2]M	Bit	SCR	CS-ESP	Limestone	Inhibited								MAS	
[2]N	Bit	None	CS-ESP	Limestone	Forced			NAU	NAW					
[2]O	Bit	SCR	CS-ESP	Limestone	Forced			OAU	OAW					
[2]P	Bit	SCR & SNCR[5]	CS-ESP	Limestone	Forced			PAD						
[2]Q	Sub-Bit	None	HS-ESP	Limestone	Forced			QAU						
R	Sub-Bit PRB	None	CS-ESP	Wet Limestone	Forced			RAU						

Table 4. Summary of facility configurations, CCR sample types and sample codes.

Facility Information						CCR Sample Types and Sample Codes								
Facility Code	**Coal Type**	**NO_x Control**	**PM Control**	**FGD Scrubber**		**Fly Ash**	**Spray Dryer Ash**	**Gypsum**		**ScS**	**Blended CCRs**			**Filter Cake**
				Limestone or Mg Lime	**Oxidation**			**Gyp-U**	**Gyp-W**		**FA+ Gyp**	**FA+ ScS**	**FA+ ScS+ Lime**	
S	High S Bit	SCR	CS-ESP	Limestone	Forced			SAU	SAW					
T	East-Bit	SCR	CS-ESP	Lime	Forced	TFA		TAU	TAW					TFC
U	Low S Bit	SCR	CS-ESP	Limestone	Forced	UFA		UAU			UGF			
V	Sub-Bit PRB	SCR	Spray Dryer / Baghouse	slaked lime	None		VSD							
W	East-Bit	SCR-BP	CS-ESP	Limestone Trona	Forced	WFA		WAU	WAW					WFC
X	Sub-Bit PRB	SCR	CS-ESP	Limestone	Forced	XFA		XAU	XAW					XFC
Y	Sub-Bit PRB	SCR before air preheater	Baghouse	Slaked Lime / Spray Dryer Adsorber	Natural		YSD							
Z	Sub-Bit PRB	None	CS-ESP	None	None	ZFA ZFB (totals only)								
Aa	East-Bit	SCR	CS-ESP	Limestone	Forced	AaFA AaFB AaFC		AaAU	AaAW					

Table 4. Summary of facility configurations, CCR sample types and sample codes.

Facility Information						**CCR Sample Types and Sample Codes**								
Facility Code	**Coal Type**	**NO$_x$ Control**	**PM Control**	**FGD Scrubber**		**Fly Ash**	**Spray Dryer Ash**	**Gypsum**		**ScS**	**Blended CCRs**			**Filter Cake**
				Limestone or Mg Lime	**Oxidation**			**Gyp-U**	**Gyp-W**		**FA+ Gyp**	**FA+ ScS**	**FA+ ScS+ Lime**	
Ba	Sub-Bit PRB / Lignite (Gulf Coast)		CS-ESP w/ COHPAC NH$_3$ inj. before ESP for flue gas conditioning	None	None	BaFA								
Ca	Gulf Coast Lignite	Low NO$_x$ burner	CS-ESP	Wet Limestone	Forced	CaFA			CaAW					
Da	East-Bit	SCR	CS-ESP	Limestone	Forced	DaFA			DaAW					DaFC

[1] (Sanchez et al., 2006)

[2] (Sanchez et al., 2008)

[3] BP – designates that the post-NO$_x$ combustion control (either SCR or SNCR) was not in use or by-passed during sample collection. Clean Air Interstate Rule requires year-round use of post-NO$_x$ combustion whereas previously if used, then it was seasonal during the summer months.

[4] SOFA - Separate overfire air, it is often added above the burner level to stage combustion.

[5] Facility P has one wet scrubber for two boilers. Both boilers have post-combustion NO$_x$ control – one with SCR and the other with SNCR. The sample collected for this facility is from the wet scrubber.

Table 5. CCR samples evaluated in this study, grouped by residue type, coal type and air pollution control configuration.

Facility	Sample ID	Coal Source (Region)	PM Capture	NO_x Control	Hg Sorbent Injection	SO_3 Control
Fly Ash without Hg Sorbent Injection						
Bituminous, Low S						
Brayton Point	BPB	Eastern bituminous	CS ESP	None	None	None
Facility F	FFA	Eastern bituminous	CS ESP	None	None	None
Facility B	DFA	Eastern bituminous	CS ESP	SCR-BP	None	None
Facility A	CFA	Eastern bituminous	Fabric F.	SNCR-BP	None	None
Facility B	BFA	Eastern bituminous	CS ESP	SCR	None	None
Facility U	UFA	Southern Appalachian	CS ESP	SCR	None	None
Salem Harbor	SHB	Eastern bituminous	CS ESP	SNCR	None	None
Facility G	GFA	Eastern bituminous	CS ESP	SNCR	None	None
Facility A	AFA	Eastern bituminous	Fabric F.	SNCR	None	None
Facility L	LAB	Southern Appalachian	HS ESP	SOFA	None	None
Facility C	GAB	Eastern bituminous	HS ESP w/ COHPAC	None	None	None
Bituminous, Med S						
Facility T	TFA	Eastern bituminous	CS ESP	None	None	None
Facility E	EFB	Eastern bituminous	CS ESP	SCR-BP	None	None
Facility W	WFA	Eastern bituminous	CS ESP	SCR-BP	None	Duct Sorbent injection - Trona
Facility E	EFA	Eastern bituminous	CS ESP	SCR	None	None
Facility K	KFA	Eastern bituminous	CS ESP	SCR	None	None
Facility Aa	AaFA	Eastern bituminous	CS ESP	SCR	None	None
Facility Aa	AaFB	Eastern bituminous	CS ESP	SCR	None	None
Facility Da	DaFA	Eastern bituminous	CS ESP	SCR	None	None
Facility Aa	AaFC	Eastern bituminous	HS ESP	SCR	None	None

Table 5 (continued). CCR samples evaluated in this study, grouped by residue type, coal type and air pollution control configuration.

Facility	Sample ID	Coal Source (Region)	PM Capture	NO_x Control	Hg Sorbent Injection	SO_3 Control
Fly Ash without Hg Sorbent Injection						
Bituminous, High S						
Facility E	EFC	Eastern bituminous	CS ESP	SCR	None	None
Facility H	HFA	Eastern bituminous	CS ESP	SCR	None	None
Sub-Bituminous & Sub-bit/bituminous mix						
Pleasant Prairie	PPB	Powder River Basin	CS ESP	None	None	None
Facility J	JAB	PRB (85%)/Bit (15%)	CS ESP	None	None	None
Facility Z	ZFA	Powder River Basin	CS ESP	None	None	None
Facility X	XFA	Powder River Basin	CS ESP	SCR	None	None
Lignite						
Facility Ca	CaFA	Gulf Coast	CS ESP	None	None	None

Table 5 (continued). CCR samples evaluated in this study, grouped by residue type, coal type and air pollution control configuration.

Facility	Sample ID	Coal Source (Region)	PM Capture	NO_x Control	Hg Sorbent Injection	SO_3 Control
Fly Ash without and with Hg Sorbent Injection Pairs						
Bituminous, Low S						
Brayton Point	BPB	Eastern bituminous	CS ESP	None	None	None
Brayton Point	BPT	Eastern bituminous	CS ESP	None	PAC	None
Salem Harbor	SHB	Eastern bituminous	CS ESP	SNCR	None	None
Salem Harbor	SHT	Eastern bituminous	CS ESP	SNCR	PAC	None
Facility L	LAB	Southern Appalachian	HS ESP	SOFA	None	None
Facility L	LAT	Southern Appalachian	HS ESP	SOFA	Br-PAC	None
Facility C	GAB	Eastern bituminous	HS ESP w/ COHPAC	None	None	None
Facility C	GAT	Eastern bituminous	HS ESP w/ COHPAC	None	PAC	None
Sub-bituminous						
Pleasant Prairie	PPB	Powder River Basin	CS ESP	None	None	None
Pleasant Prairie	PPT	Powder River Basin	CS ESP	None	PAC	None
Facility J	JAB	Other	CS ESP	None	None	None
Facility J	JAT	Other	CS ESP	None	Br-PAC	None
Lignite						
Facility Ba	BaFA	PRB/Lignite blend	CS ESP w/ COHPAC+ Ammonia Injection	None	PAC	None

Table 5 (continued). CCR samples evaluated in this study, grouped by residue type, coal type and air pollution control configuration.

Facility	Sample ID	Coal Source (Region)	PM Capture	NO_x Control	Hg Sorbent Injection	FGD Scrubber additive	SO_3 Control
Spray dryer with Fabric Filter (fly ash and FGD collected together)							
Sub-Bituminous							
Facility V	VSD	Powder River Basin	Fabric F.	SCR	None	Slaked Lime	None
Facility Y	YSD	Powder River Basin	Fabric F.	SCR	None	Slaked Lime	None

Table 5 (continued). CCR samples evaluated in this study, grouped by residue type, coal type and air pollution control configuration.

Gypsum, unwashed and washed

Bituminous, Low S

Facility	Sample ID	Region	Residue type	PM Capture	NO_x Control	Wet Scrubber type	FGD Scrubber additive	SO_3 Control
Facility U	UAU	Southern Appalachian	Gyp-U	CS ESP	SCR	Forced Ox.	Limestone	None

Bituminous, Med S

Facility	Sample ID	Region	Residue type	PM Capture	NO_x Control	Wet Scrubber type	FGD Scrubber additive	SO_3 Control
Facility T	TAU	Eastern bituminous	Gyp-U	CS ESP	None	Forced Ox.	Limestone	None
Facility T	TAW	Eastern bituminous	Gyp-W	CS ESP	None	Forced Ox.	Limestone	None
Facility W	WAU	Eastern bituminous	Gyp-U	CS ESP	SCR-BP	Forced Ox.	Limestone	Duct Sorbent inj. - Trona
Facility W	WAW	Eastern bituminous	Gyp-W	CS ESP	SCR-BP	Forced Ox.	Limestone	Duct Sorbent inj. - Trona
Facility Aa	AaAU	Eastern bituminous	Gyp-U	CS ESP	SCR	Forced Ox.	Limestone	None
Facility Aa	AaAW	Eastern bituminous	Gyp-W	CS ESP	SCR	Forced Ox.	Limestone	None
Facility Da	DaAW	Eastern bituminous	Gyp-W	CS ESP	SCR	Forced Ox.	Limestone	None
Facility P	PAD	Eastern bituminous	Gyp-U	CS ESP	SCR & SNCR	Forced Ox.	Limestone	None

Table 5 (continued). CCR samples evaluated in this study, grouped by residue type, coal type and air pollution control configuration.

Facility	Sample ID	Region	Residue type	PM Capture	NO_x Control	Wet Scrubber type	FGD Scrubber additive	SO_3 Control
Gypsum, unwashed and washed								
Bituminous, High S								
Facility N	NAU	Eastern bituminous	Gyp-U	CS ESP	None	Forced Ox.	Limestone	None
Facility N	NAW	Eastern bituminous	Gyp-W	CS ESP	None	Forced Ox.	Limestone	None
Facility S	SAU	Illinois Basin	Gyp-U	CS ESP	SCR	Forced Ox.	Limestone	None
Facility S	SAW	Illinois Basin	Gyp-W	CS ESP	SCR	Forced Ox.	Limestone	None
Facility O	OAU	Other	Gyp-U	CS ESP	SCR	Forced Ox.	Limestone	None
Facility O	OAW	Other	Gyp-W	CS ESP	SCR	Forced Ox.	Limestone	None
Sub-bituminous								
Facility R	RAU	Powder River Basin	Gyp-U	CS ESP	None	Forced Ox.	Limestone	None
Facility Q	QAU	Powder River Basin	Gyp-U	HS ESP	None	Forced Ox.	Limestone	Other
Facility X	XAU	Powder River Basin	Gyp-U	CS ESP	SCR	Forced Ox.	Limestone	None
Facility X	XAW	Powder River Basin	Gyp-W	CS ESP	SCR	Forced Ox.	Limestone	None
Lignite								
Facility Ca	CaAW	Gulf Coast	Gyp-U	CS ESP	None	Forced Ox.	Limestone	None

Table 5 (continued). CCR samples evaluated in this study, grouped by residue type, coal type and air pollution control configuration.

Facility	Sample ID	Region	Residue type	PM Capture	NO_x Control	Wet Scrubber type	FGD Scrubber additive	SO_3 Control
Scrubber Sludge								
Bituminous, Low S								
Facility B	DGD	Eastern bituminous	Scrubber sludge	Cold-side ESP	SCR-BP	Natural Ox.	Mg lime	None
Facility A	CGD	Eastern bituminous	Scrubber sludge	Fabric Filter	SNCR-BP	Natural Ox.	Limestone	None
Facility B	BGD	Eastern bituminous	Scrubber sludge	Cold-side ESP	SCR	Natural Ox.	Mg lime	None
Facility A	AGD	Eastern bituminous	Scrubber sludge	Fabric Filter	SNCR	Natural Ox.	Limestone	None
Bituminous, Med S								
Facility K	KGD	Eastern bituminous	Scrubber sludge	Cold-side ESP	SCR	Natural Ox.	Mg lime	None

Table 5 (continued). CCR samples evaluated in this study, grouped by residue type, coal type and air pollution control configuration.

Facility	Sample ID	Region	Residue type	PM Capture	NO_x Control	Wet Scrubber type	FGD Scrubber additive	SO_3 Control
Mixed Fly Ash and Scrubber Sludge (as managed)								
Bituminous, Low S								
Facility B	DCC	Eastern bituminous	FA+ScS+ lime	CS ESP	SCR-BP	Natural Ox.	Mg lime	None
Facility A	CCC	Eastern bituminous	FA+ScS	Fabric Filter	SNCR-BP	Natural Ox.	Limestone	None
Facility B	BCC	Eastern bituminous	FA+ScS+ lime	CS ESP	SCR	Natural Ox.	Mg lime	None
Facility A	ACC	Eastern bituminous	FA+ScS	Fabric Filter	SNCR	Natural Ox.	Limestone	None
Bituminous Med S								
Facility K	KCC	Eastern bituminous	FA+ScS+ lime	CS ESP	SCR	Natural Ox.	Mg lime	None
Bituminous Med S								
Facility M	MAD	Illinois Basin	FA+ScS+ lime	CS ESP	SCR-BP	Inhibited Ox.	Limestone	None
Facility M	MAS	Illinois Basin	FA+ScS+ lime	CS ESP	SCR	Inhibited Ox.	Limestone	None

2.2. LEACHING ASSESSMENT PROTOCOLS

Laboratory testing for this study focused on leaching as a function of pH and LS ratio as defined by the leaching framework. This test set is considered Tier 2 testing (equilibrium-based) for detailed characterization, which was selected to develop a comprehensive data set of CCR characteristics. Mass transfer rate testing (Tier 3, detailed characterization) may be carried out in the future for specific cases where results from equilibrium-based characterization indicate a need for detailed assessment.

2.2.1. Alkalinity, Solubility and Release as a Function of pH (SR002.1)

Alkalinity, solubility and release as a function of pH were determined according to method SR002.1 (Kosson et al., 2002). This method is currently under review as a preliminary version of Method 1313[30] for publication in SW-846. This protocol consists of 11 parallel extractions of particle size reduced material, at different pH values ranging from pH 2-13, and at a LS ratio of 10 mL extractant/g dry sample. In this method, particle-size reduction is used when necessary to prepare large-grained samples for extraction so that the approach toward liquid-solid equilibrium concentrations of the COPCs is enhanced. For the samples evaluated in this study, particle size reduction was required infrequently. Each extraction condition was carried out with replication as appropriate[31] using 40 g of material for each material evaluated. In addition, three method blanks were included, consisting of the DI water, nitric acid and potassium hydroxide used for extractions. Typical particle size of the tested materials was less than 300 µm using standard sieves according to ASTM E-11-70 (1995). An acid or base addition schedule is formulated based on initial screening for eleven eluates with final solution pH values between 3 and 12, through addition of aliquots of nitric acid or potassium hydroxide as needed. The exact schedule is adjusted based on the nature of the material; however, the range of pH values includes the natural pH of the matrix that may extend the pH domain (e.g., for very alkaline or acidic materials). The final LS ratio is 10 mL extractant/g dry sample which includes DI water, the added acid or base, and the amount of moisture that is inherent to the waste matrix as determined by moisture content analysis. The eleven extractions were tumbled in an end-over-end fashion at 28 ± 2 rpm for 24 hours followed by filtration separation of the solid phase from the eluate using a 0.45 µm polypropylene filter. Each eluate then was analyzed for constituents of interest. The acid and base neutralization behavior of the materials is evaluated by plotting the pH of each eluate as a function of equivalents of acid or base added per gram of dry solid. Concentration of constituents of interest for each eluate is plotted as a function of eluate final pH to provide liquid-solid partitioning equilibrium as a function of pH. Initially, the SR002.1 test was carried out in triplicate; however, replication was reduced to two replicates of the test method for later

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[30] Preliminary version denotes that this method has not been endorsed by EPA but is under consideration for inclusion into SW-846. This method has been derived from published procedures (Kosson et al, 2002) using reviewed and accepted methodologies (USEPA 2006, 2008, 2009). The method has been submitted to the USEPA Office of Resource Conservation and Recovery and is currently under review for development of interlaboratory validation studies to develop precision and bias information.

[31] Initial replication was in triplicate (as indicated in Report 1 and for some of the samples in Report 2), which was reduced to duplicate based on quality assurance review of the triplicate analyses results.

samples based on good replication and consistency amongst the early results (Sanchez et al., 2006).

2.2.2. Solubility and Release as a Function of LS Ratio (SR003.1)

Solubility and release as a function of LS ratio was determined according to method SR003.1 (Kosson et al., 2002). This method is currently under review as a preliminary version of Method 1314[32] for promulgation in SW-846. This protocol consists of five parallel batch extractions over a range of LS ratios (i.e., 10, 5, 2, 1, and 0.5 mL/g dry material), using DI water as the extractant with aliquots of material that has been particle size reduced. Typical particle size of the material tested was less than 300 µm. Between 40 and 200 g of material were used for each extraction, based on the desired LS ratio. All extractions are conducted at room temperature (20 ± 2 °C) in leak-proof vessels that are tumbled in an end-over-end fashion at 28 ± 2 rpm for 24 hours. Following gross separation of the solid and liquid phases by centrifuge or settling, leachate pH and conductivity measurements are taken and the phases are separated by pressure filtration using 0.45-µm polypropylene filter membrane. The five leachates are collected, and preserved as appropriate for chemical analysis. Initially, the SR003.1 test was carried out in triplicate; however, replication was reduced to two replicates of the test method for later samples based on good replication and consistency amongst the early results.

2.3. ANALYTICAL METHODS

2.3.1. Surface Area and Pore Size Distribution

A Quantachrome Autosorb-1 C-MS chemisorption mass spectrometer was used to perform 5-point Brunauer, Emmett, and Teller (BET) method surface area, pore volume, and pore size distribution analyses on each as-received and size-reduced CCR. A 200 mg sample was degassed under vacuum at 200 ºC for at least one hour in the sample preparation manifold prior to analysis with N_2 as the analysis gas. Standard materials with known surface area were routinely run as a QC check. Tabular results for each CCR are provided in Appendix C.

2.3.2. pH and Conductivity

pH and conductivity were measured for all aqueous eluates using an Accumet 925 pH/ion meter. The pH of the leachates was measured using a combined pH electrode accurate to 0.1 pH units. A 3-point calibration was performed daily using pH buffer solutions at pH 4.0, 7.0 and 10.0. Conductivity of the leachates was measured using a standard conductivity probe. The conductivity probe was calibrated using appropriate standard conductivity solutions for the conductivity range of concern. Conductivity meters typically are accurate to ± 1% and have a precision of ± 1%.

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[32] Method SR003.1 was developed into a preliminary version of Method 1314: Leaching Test (Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio) for Constituents in Solid Materials using an Up-flow Percolation Column Test, 2009 (submitted to EPA Office of Solid Waste; under review for inclusion in SW-846).

2.3.3. Moisture Content

Moisture content of the “as received” CCRs was determined using American Society for Testing and Materials (ASTM) D 2216-92. This procedure supersedes the method indicated in the version of the leaching procedure published by (Kosson et al., 2002). Tabular results are provided in Appendix C.

2.3.4. Carbon Content - Organic Carbon/Elemental Carbon Analyzer

Organic carbon (OC) and elemental carbon (EC) content of each CCR tested was measured using a Sunset Lab thermal-optical EC/OC analyzer using the thermal/optical method (NIOSH Method 5040). The sample collected on quartz fiber filters is heated under a completely oxygen-free helium atmosphere in a quartz oven in four increasing temperature steps (375 °C, 540 °C, 670 °C and 870 °C) at 60 second ramp times for the first three temperatures and a ramp time of 90 seconds for the final temperature. The heating process removes all organic carbon on the filter. As the organic compounds are vaporized, they are immediately oxidized to carbon dioxide in an oxidizer oven which follows the sample oven. The flow of helium containing the produced carbon dioxide then flows to a quartz methanator oven where the carbon dioxide is reduced to methane. The methane is then detected by a flame ionization detector (FID). After the sample oven is cooled to 525 ºC, the pure helium eluent is switched to an oxygen/helium mixture in the sample oven. At that time, the sample oven temperature is stepped up to 850 ºC. During this phase, both the original elemental carbon and the residual carbon produced by the pyrolysis of organic compounds during the first phase are oxidized to carbon dioxide due to the presence of oxygen in the eluent. The carbon dioxide is then converted to methane and detected by the FID. After all carbon has been oxidized from the sample, a known volume and concentration of methane is injected into the sample oven. Thus, each sample is calibrated to a known quantity of carbon as a means of checking the operation of the instrument. The calibration range for these analyses was from 10 to 200 µg/cm^2 of carbon using a sucrose solution as the standard. The detection limit of this instrument is approximately 100 ng/cm^2 with a linear dynamic range from 100 ng/cm^2 to 1 g/cm^2. Tabular results of OC and EC content are presented in Appendix C.

2.3.5. Dissolved Inorganic Carbon (DIC) and Dissolved Organic Carbon (DOC)

Analyses of total organic carbon and inorganic carbon were performed on a Shimadzu model TOC-V CPH/CPN. Five-point calibration curves, for both dissolved inorganic carbon (DIC) and non-purgeable dissolved organic carbon (DOC) analyses, were generated for an analytical range between 5 ppm and 100 ppm and are accepted with a correlation coefficient of at least 0.995. An analytical blank and check standard at approximately 10 ppm were run every 10 samples. The standard was required to be within 15% of the specified value. A volume of approximately 16 mL of undiluted sample was loaded for analysis. DIC analysis was performed first for the analytical blank and standard and then the samples. DOC analysis was carried out separately after completion of DIC analysis. DOC analysis began using addition of 2 M (mole/L) of hydrochloric acid to achieve a pH of 2 along with a sparge gas flow rate of 50 mL/min to purge inorganic carbon prior to analysis. Method detection limit (MDL) and minimum level of quantification (ML) are shown in Table 6. All DIC and DOC results will be made available separately through an electronic format as part of the leaching assessment tool (LeachXS Lite®).

Table 6. MDL and ML of analysis of DIC and DOC.

	MDL (µg/L)	**ML (µg/L)**
DIC	130	410
DOC	170	550

2.3.6. Mercury (CVAA, Method 3052, and Method 7473)

Liquid samples were preserved for mercury analysis by additions of nitric acid and potassium permanganate and then prepared prior to analysis according to the following method. For each 87 mL of sample, 3 mL of concentrated nitric acid and 5 mL of 5 wt% aqueous potassium permanganate solution were added prior to storage. Immediately before cold vapor atomic absorption (CVAA) analysis, 5 mL of hydroxylamine were added to clear the sample and then the sample was digested according to ASTM Method D6784-02 (i.e., Ontario Hydro) as described for the permanganate fraction (ASTM, 2002). On completion of the digestion, the sample was analyzed for mercury by CVAA. Samples with known additions of mercury for matrix analytical spikes also were digested as described above prior to CVAA analysis.

Sample preparation of the solids and filters was carried out by HF/HNO_3 microwave digestion according to Method 3052 (EPA, 1996) followed by CVAA analysis as indicated above. No additional preservation or digestion was carried out prior to CVAA analysis.

Mercury analysis of each digest, eluate and leachate was carried out by CVAA according to EPA SW846 Method 7470A “Mercury in Liquid Waste (Manual Cold Vapor Technique)” (EPA, 1998a). A Perkin Elmer FIMS 100 Flow Injection Mercury System was used for this analysis. The instrument was calibrated with known standards ranging from 0.025 to 1 µg/L mercury.

Solids also were analyzed by Method 7473 “Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry” (EPA, 1998b). A Nippon MD-1 mercury system was used for this analysis. The instrument was calibrated with known standards ranging from 1 to 20 ng of mercury. The method detection limit for mercury in solids is 0.145 µg/kg.

2.3.7. Other Metals (ICP-MS, ICP-AES, Method 3052, Method 6020, and Method 6010)

Liquid samples for ICP-MS and ICP-AES analysis were preserved through addition of 3 mL of concentrated nitric acid (trace metal grade) per 97 mL of sample. Known quantities of each analyte were also added to sample aliquots for analytical matrix spikes. Solid samples were digested by EPA Method 3052 (EPA, 1996) prior to ICP-MS and ICP-AES analysis. Table 7 indicates the switch from ICP-MS to ICP-AES for specific elements and samples.

Table 7. ICP instrument used for each element.* Elements indicated in bold are discussed in this report; results for all other indicated elements will be available through the leaching assessment tool.

Symbol	**Instrument**	**Used**	**Switch Date**
Al		ICP-OES	Report 3 Samples
Sb	ICP-MS	ICP-OES*	Only SR003.1 Report 1 Samples*
As	ICP-MS		
Ba	ICP-MS		
Be	ICP-MS		
B		ICP-OES	Report 1 and 3 Samples
Cd	ICP-MS		
Ca		ICP-OES	Report 3 Samples
Cr	ICP-MS		
Co	ICP-MS		
Cu	ICP-MS		
Fe		ICP-OES	Report 3 Samples
Pb	ICP-MS		
Mg		ICP-OES	Report 3 Samples
Mn	ICP-MS		
Mo	ICP-MS	ICP-OES*	*Only Report 1 Samples
Ni	ICP-MS		
K		ICP-OES	Report 3 Samples
Re	ICP-MS		
Se	ICP-MS		
Si		ICP-OES	Report 3 Samples
Na		ICP-OES	Report 3 Samples
Sr		ICP-OES	Report 3 Samples
Tl	ICP-MS	ICP-OES*	Only SR003.1 Report 1 Samples*
Sn	ICP-MS		
Ti		ICP-OES	Report 3 Samples
U	ICP-MS		
V	ICP-MS		
Zn	ICP-MS		

*Samples were analyzed on the ICP-OES for the indicated elements. Measurements for the same elements on Facility T samples (TFA, TFC, TAW, and TAU) were also completed on the ICP-MS for comparison. Precision of results was within 15% for concentrations above 100 µg/L and within 25% for concentrations below 100 µg/L.

2.3.7.1. ICP-MS Analysis (SW-846 Method 6020)

ICP-MS analyses of aqueous samples from laboratory leaching tests were carried out at Vanderbilt University (Department of Civil and Environmental Engineering) using a Perkin Elmer model ELAN DRC II in both standard and dynamic reaction chamber (DRC) modes. Standard analysis mode was used for all analytes except for As and Se, which were run in DRC mode with 0.5 mL/min of oxygen as the reaction gas. Seven-point standard curves were used for an analytical range between approximately 0.5 µg/L and 500 µg/L and completed before each analysis. Analytical blanks and analytical check standards at approximately 50 µg/L were run every 10 to 20 samples and required to be within 15% of the specified value. Samples for analysis were diluted gravimetrically to within the targeted analytical range using 1% v/v Optima grade nitric acid (Fisher Scientific). Initially, analyses for 10:1 dilutions were performed to minimize total dissolved loading to the instrument. Additional dilutions at 100:1 and 1000:1 were analyzed if the calibration range was exceeded with the 10:1 dilution. 50 µL of a 10 mg/L internal standard consisting of indium (In) (for mass range below 150) and bismuth (Bi) (for mass range over 150) was added to 10 mL of sample aliquot prior to analysis. Analytical matrix spikes were completed for one of each of the replicate eluates from SR002.1. For each analytical matrix spike, a volume between 10 µL and 100 µL of a 10 mg/L standard solution was added to 10 mL of sample aliquot. Table 8 provides the element analyzed, method detection limit (MDL) and minimum level of quantification (ML). Analyte concentrations measured that are less than the ML and greater than the MDL are reported as estimated value using the instrument response. The values reflect the initial 10:1 dilution used for samples from laboratory leaching tests.

Table 8. Method detection limits (MDLs) and minimum level of quantification (ML) for ICP-MS analysis on liquid samples. Elements indicated in bold are discussed in this report; results for all other indicated elements will be available through the leaching assessment tool.

Symbol	Units	MDL	ML
Al	µg/L	0.96	3.06
Sb	µg/L	0.08	0.25
As	µg/L	0.64	2.04
Ba	µg/L	0.57	1.82
Be	µg/L	0.64	2.03
B	µg/L	0.65	2.06
Cd	µg/L	0.17	0.54
Ca	µg/L	1.02	3.24
Cr	µg/L	0.50	1.58
Co	µg/L	0.41	1.32
Cu	µg/L	0.70	2.23
Fe	µg/L	0.94	3.00
Pb	µg/L	0.23	0.73
Mg	µg/L	0.57	1.83
Mn	µg/L	0.34	1.09
Mo	µg/L	0.76	2.41
Ni	µg/L	0.73	2.31
K	µg/L	1.38	4.38
Re	µg/L	0.24	0.77
Se	µg/L	0.52	1.65
Si	µg/L	1.56	4.97
Na	µg/L	0.74	2.35
Sr	µg/L	0.52	1.66
Tl	µg/L	0.51	1.61
Sn	µg/L	0.70	2.22
Ti	µg/L	0.52	1.66
U	µg/L	0.30	0.95
V	µg/L	0.31	0.98
Zn	µg/L	0.92	2.94
Zr	µg/L	0.47	1.48

2.3.7.2. ICP-OES Analysis (SW-846 Method 6010)

ICP-OES analyses of aqueous samples from laboratory leaching tests were carried out at Vanderbilt University (Department of Civil and Environmental Engineering) using a Varian ICP Model 720-ES. Five-point standard curves were used for an analytical range between approximately 0.1 mg/L and 25 mg/L for trace metals. Seven-point standard curves were used for an analytical range between approximately 0.1 mg/L and 500 mg/L for minerals. Analytical blanks and analytical check standards at approximately 0.5 mg/L were run every 10 to 20 samples and required to be within 15% of the specified value. Initially, analyses were performed on undiluted samples to minimize total dissolved loading to the instrument. Samples for analysis were diluted gravimetrically to within the targeted analytical range using 1% v/v Optima grade nitric acid (Fisher Scientific) if the maximum calibration was exceeded. Yttrium at 10 mg/L was used as the internal standard. Analytical matrix spikes were completed for three test positions from one of the replicate eluates from SR002.1. For each analytical matrix spike, a volume of 500 µL of a 10 mg/L standard solution was added to 5 mL of sample aliquot. Table 9 provides the element analyzed, method detection limit (MDL), and minimum level of quantification (ML). Analyte concentrations measured that are less than the ML and greater than the MDL are reported as estimated value using the instrument response.

Table 9. Method detection limits (MDLs) and minimum level of quantification (ML) for ICP-OES analysis on liquid samples.

Symbol	Units	MDL	ML
Al	µg/L	1.00	3.18
Sb	µg/L	8.00	25.4
As	µg/L	15.0	47.7
Ba	µg/L	1.00	3.18
Be	µg/L	5.00	15.9
B	µg/L	1.00	3.18
Cd	µg/L	6.00	19.1
Ca	µg/L	3.50	11.1
Cr	µg/L	1.00	3.18
Co	µg/L	1.00	3.18
Cu	µg/L	4.1	13.0
Fe	µg/L	2.90	9.22
Pb	µg/L	7.00	22.3
Li	µg/L	6.00	19.1
Mg	µg/L	1.00	3.18
Mn	µg/L	3.60	11.4
Mo	µg/L	1.00	3.18
Ni	µg/L	2.20	7.00
K	µg/L	1.50	4.77
P	µg/L	6.2	19.7
Se	µg/L	17.0	54.1
Si	µg/L	2.80	8.90
Ag	µg/L	18.00	57.2
Na	µg/L	3.50	11.1
Sr	µg/L	1.00	3.18
S	µg/L	8.30	26.4
Tl	µg/L	5.00	15.9
Sn	µg/L	17.0	54.1
Ti	µg/L	6.40	20.3
V	µg/L	1.30	4.13
Zn	µg/L	2.50	7.95
Zr	µg/L	2.70	8.59

2.3.8. X-Ray Fluorescence (XRF)

XRF analysis was performed on each CCR to provide additional information on each CCR total elemental composition. For each CCR two pellets were prepared as follows. 3000 mg of material was weighed and mixed with 1.5 mL (100 mg dry solids) of liquid binder to give a 32 mm diameter pellet weighing 3150 mg with a material-to-diluent ratio of 0.05. For high carbon content samples 3.0 ml (100 mg dry solids) of liquid binder was used to give a 32 mm diameter pellet weighing 3300 mg with a material-to-diluent ratio of 0.1. XRF intensities were collected on each side of each pellet using Philips SuperQ data collection software and evaluated using Omega Data System’s UniQuant 4 XRF “standardless” data analysis software. The UQ/fly ash calibration was used to analyze the samples. The pellets were evaluated as oxides. Known fly ash Standard Reference Materials (SRMs) were also run to assess the accuracy of the analysis. This information is useful in supplementing CVAA and ICP results.

X-Ray Fluorescence Spectrometry was used in the Research Triangle Park laboratories of EPA-NRMRL to analyze these samples. A Philips model PW 2404 wavelength dispersive instrument, equipped with a PW 2540 VRC sample changer, was used for these analyses. The manufacturer’s software suite, “SuperQ”, was used to operate the instrument, collect the data, and perform quantification.

The instrument was calibrated at the time of installation of the software plus a new X-ray tube using a manufacturer-supplied set of calibration standards. On a monthly basis, manufacturer-supplied drift correction standards were used to create an updated drift correction factor for each potential analytical line. On a monthly basis, a dedicated suite of QC samples were analyzed before and after the drift correction procedure. This data was used to update and maintain the instrument’s QC charts.

The software suite’s “Measure and Analyze” program was used to collect and manage the sample data. Quantification was performed post-data collection using the program “IQ+”. IQ+ is a “first principles” quantification program that includes complex calculations to account for a wide variety of sample-specific parameters. For this reason, sample-specific calibrations were not necessary. This program calculates both peak heights and baseline values. The difference is then used, after adjustment by drift correction factors, for elemental quantification versus the calibration data. Inter-element effects are possible and the software includes a library of such parameters. Data from secondary lines may be used for quantification where inter-element effects are significant or the primary peak is overloading the data acquisition system. Where the difference between the calculated peak height and baseline is of low quality, the program will not identify a peak and will not report results. IQ^+ permits the inclusion of data from other sources by manual entry. Carbon was an example of this for these samples. Entry of other source data for elements indeterminable by XRF improves the mass balance.

Table 10 presents detection limit data in two forms. The two forms are not mutually exclusive. The “reporting limit” is built into the software and reflects the manufacturer’s willingness to report low-level data. Data listed in the “detection limit” column were based upon the short-term reproducibility of replicate analyses (two standard deviations, 2σ) and were sample matrix specific. These calculations are likely to report higher detection limits for elements present at high concentrations than what would be reported if the same element was present at trace levels. In this data set, calcium is a likely example of this behavior.

Table 10. XRF detection limits.

Analyte	**Reporting Limit** mg/kg	**Detection Limit, wt %** 2σ (wt. %)
Al	20	0.016
As	20	0.038
Ba	20	0.0084
Br	20	0.02
Ca	20	0.1
Cd	20	0.064
Ce	20	0.022
Cl	20	0.0046
Co	20	0.0024
Cr	20	0.0028
Cu	20	0.0014
F	20	0.082
Fe	20	0.034
Ga	20	0.0016
Ge	20	0.0014
K	20	0.0048
La	20	0.0054
Mg	20	0.01
Mn	20	0.0032
Mo	20	0.0026
Na	20	0.0076
Nb	20	0.0018
Ni	20	0.0048
Pb	20	0.0034
Px	20	0.004
Rb	20	0.0016
Sc	20	0.0016
Se	20	0.0018
Si	20	0.092
Sr	20	0.0016
Sx	20	0.05
Ti	20	0.003
V	20	0.0038
W	20	0.0036
Y	20	0.0018
Zn	20	0.0014
Zr	20	0.0024

2.3.9. XAFS

XANES and EXAFS spectra were collected using the MR-CAT (Sector 10 ID) beamline at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL, Argonne, IL) and beamline X18B at the National SynchrotronLight Source (NSLS) at Brookhaven National Laboratory (BNL, Upton, NY) and analyzed according to the methods previously described (Hutson et al., 2007).

2.3.10. Determination of Hexavalent Chromium (Cr^{6+}) and Total Chromium Species in CCR Eluates

Fly ash samples were leached at three different pH values in duplicate using the SR002.1.1 leaching procedure for the determination of hexavalent and total chromium concentrations. The pH target values for the leachates were defined as 7-7.5, 10.5-11, and the natural CCR pH. The eluates were split into three samples for analysis by Eastern Research Group (ERG) and Vanderbilt University. ERG received one unpreserved and one nitric acid preserved sample. Vanderbilt University received one nitric acid preserved sample. Samples were preserved by adding 97 mL of leachate with 3 mL concentrated nitric acid.

Hexavalent chromium concentrations of the un-preserved CCR leachate eluates were determined using ion-chromatography. This procedure was modified from the EPA Urban Air Toxics Monitoring Programs (UATMP) method developed by ERG for the determination of Cr^{6+} in air by analyzing the eluates from sodium-bicarbonate impregnated cellulose filters (EPA, 2007a). The ion chromatography system was comprised of a guard column, an analytical column, a post-column deriviatization module, and a UV/VIS detector. In the analysis procedure, Cr^{6+} exists as chromate due to the near neutral pH of the eluent. After separation through the column, the Cr^{6+} forms a complex with 1,5-diphenylcarbohydrazide (DPC) and was detected at 530 nm (EPA, 2006c). This method had a reporting limit (RL) of 0.03 ng/mL.

The total chromium species for the nitric acid preserved samples were analyzed by ERG and Vanderbilt University using inductively-couples plasma / mass spectroscopy (ICP/MS) found in SW-846 Method 6020.

2.3.11. MDL and ML for Analytical Results

The MDL is defined by 40 CFR Part 136, Appendix B, July 1, 1995, Revision 1.11 as “the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.”

The MDL was determined statistically from data generated by the analysis of seven or more aliquots of a spiked reagent matrix[33] and verified by the analysis of calibration standards near the calculated MDL according to (EPA, 2004). The MDL then was determined by multiplying the

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[33] Establishing spikes in an actual leaching extract matrix is not possible because the sample being extracted dictates the matrix composition by virtue of the constituents that partition into the resulting aqueous extract, which varies by test position and material being tested. However, the extract aliquots are diluted at least 10:1 with 1% nitric acid (prepared from Optima grade nitric acid, Fisher Scientific), and the COPCs are dilute in the resulting analytical sample. Therefore, the 1% nitric acid solution was used as the matrix for MDL and ML determinations.

standard deviation of the replicate measurements by the appropriate Students t value for a 99% confidence level (two tailed) and n-1 (six) degrees of freedom and also multiplying by the minimum dilution factor required for matrix preservation and analysis.

The ML is defined by 40 CFR Part 136, 1994 as "the lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte." According to (EPA, 2004), the ML is intended to be the nearest integer value (i.e., 1, 2 or $5x10^n$, where n is an integer) to 10 times the standard deviation observed for determination of the MDL. This value is also multiplied by the minimum dilution factor required for preservation and analysis of the sample matrix to obtain the ML reported here.

The above methodology for determination of MDL and ML values was used for all ICP-MS and ICP-OES measurements (Table 8 and Table 9).

Mercury, as measured by CVAA, required modification of the calculation of the MDL and ML because very consistent replication resulted in calculation of a MDL lower than the instrument detection limit. For this case, the standard deviation of seven replicate analyses of 0.025 µg/L was 0.00069. Therefore, the MDL was set equal to the instrument detection limit of 0.001 µg/L times the minimum dilution factor from sample preparation (3.59) to result in an MDL of 0.0036 µg/L. The ML was set to 10 times the instrument detection limit and rounded to the nearest integer value as above. The resulting ML was 0.01 µg/L.

2.4. QUALITY ASSURANCE ASSESSMENT

2.4.1. Homogenization of Individual CCR Samples and Aliquots for Analyses

To ensure sample homogeneity the fly ashes were mixed using a Morse single can tumbler model 1-305 as described in (Sanchez et al., 2006). Scrubber sludges that were flowable slurries were mixed using a paddle mixer. Gypsum and CCRs samples were mixed by repetitively coning and quartering while passing through a mesh screen.[34] After mixing, ten subsamples were taken from sample MAD (blended CCRs) and analyzed by XRF to evaluate the homogeneity of the resultant material; the total content variability for primary and most trace constituents was less than 20% for this set of samples [see Report 2 (Sanchez et al., 2008)].

2.4.2. Leaching Test Methods and Analytical QA/QC

One of the requirements of this project was to establish a QA/QC framework for the leaching assessment approach developed by (Kosson et al., 2002). The developed QA/QC framework incorporates the use of blanks, spiked samples, and replicates. Appendix B provides the complete Quality Assurance Project Plan, as updated for this phase of the study. For each designated leaching test condition (i.e., acid or base addition to establish end-point pH values and LS value), triplicate leaching test extractions were completed (i.e., three separate aliquots of CCR were each extracted at the designated test condition) for early samples, while duplicate extractions were

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[34] "Coning and quartering" is a term used to describe how the material is mixed. The approach is to pass the material through a screen so that a "cone" forms in the collection container. Then the cone is bisected twice into quarters (quarter sections of the cone) and each section then is passed sequentially through the screen again to form a new cone. This sequence is repeated several times to achieve desired mixing.

used after evaluation of initial results. The three types of method blanks were the deionized water case, the most concentrated nitric acid addition case, and the most concentrated potassium hydroxide addition case. Each method blank was carried through the entire protocol, including tumbling and filtration, except an aliquot of CCR was not added.

During analysis for mercury by CVAA and elemental species by ICP-MS and ICP-OES, multipoint calibration curves using at least seven standards and an initial calibration verification (ICV) using a standard obtained from a different source than the calibration standards were completed daily or after every 50 samples, whichever was more frequent. In addition, instrument blanks and continuing calibration verification (CCV) standards were analyzed after every 10 analytical samples and required to be within 10 percent of the expected value based on the standards used. Samples were rerun if they were not within 10 percent of the expected value. CCV standards and instrument blanks also were run at the end of each batch of samples.

For ICP-MS and CVAA analyses, analytical spikes (aliquot of the sample plus a known spike concentration of the element of interest) for the constituents of interest were carried out for one replicate of each test case to assess analytical recoveries over the complete range of pH and liquid matrix conditions. For ICP-OES analyses, analytical matrix spikes were completed for three test positions from one of the replicate eluates. The “spike recovery” was required to be within 80 – 120% of the expected value for an acceptable analytical result.

2.4.3. Improving QA/QC Efficiency

Throughout the study, the approach to QA/QC was regularly reviewed to seek out opportunities for increased evaluation efficiency without unacceptable degradation of precision or accuracy in results. Based on evaluation of results from the first several facilities [Report 1, (Sanchez et al., 2006)], the number of replicates for Method SR002.1 (solubility as a function of pH) and Method SR003.1 (solubility as a function of liquid/solid ratio) was reduced from three to two [Report 2, (Sanchez et al., 2008)]. Results from Report 1 (Sanchez et al., 2006) and Report 2 (Sanchez et al., 2008) show that the precision between duplicate analyses is acceptable and that the triplicate set does not significantly increase the quality of the data set. This finding follows from recognition that (i) the data sets generated by Method SR002.1 and SR003.1 must provide both consistency between replicate extractions and analyses, and internal consistency between results at different pH and LS ratio, and (ii) precision is controlled primarily by the degree of homogeneity of the CCR under evaluation and representative sub-sampling, rather than by the intrinsic variability of the leaching test methods.

Data were screened for outliers based on comparison of individual data points (i) relative to replicate extractions (i.e., parallel extractions of aliquots of the same material under the same extraction conditions), and (ii) relative to the other data points in the extraction series [i.e., parallel extractions of aliquots of the same material at different pH (SR002.1) and LS conditions (SR003.1)] because of the expected systematic response behavior. The pH was considered an outlier when the final pH of the eluate deviated from the other replicates by more than 0.5 pH units and the corresponding constituent analyses did not follow systematic behavior indicated by other eluates across multiple constituents. Individual constituent results were considered outliers when results of constituent analyses deviated from the systematic behavior indicated by results in the extraction series (as a function of pH or as a function of LS) by more than one-half to one order of magnitude. Results were screened through inspection of the appropriately plotted results.

There were more than 80,000 final data observations required to complete this study, not including additional observations required for quality control and quality assurance purposes. Leaching test results required 69,733 observations considering all leaching test eluate analytes. The 13 constituents analyzed in leaching test eluates evaluated in detail in this report required 27,849 final observations.

As part of the QA/QC review of the data, two authors independently reviewed the data. The observations were screened for outliers based on comparison of individual observations as noted above. Anomalous observations were flagged for further review by the other reviewing author before a determination of outlier status was made.

Of the final 27,849 observations, 28 eluate concentration observations were considered as outliers relative to the data set. Additionally, 20 pH observations out of a total of 2,042 pH observations were considered as outliers relative to the data set. A pH observation was considered to be an outlier when the reported pH value was clearly incorrect in the context of the test method and other results. When a pH observation was determined to be an outlier, then all eluate concentration observations associated with the particular eluate were also considered outliers because they would be evaluated as a function of pH at an incorrect pH value. This resulted in an additional 252 eluate concentrations being considered as outliers based on the pH observation. The 300 total outlier observations were excluded from the statistical, graphical, and tabular evaluations. The specific outliers are tabulated in Appendix K.

Overall, these results indicate an error rate of approximately 0.1 percent for determination of constituent concentrations in leaching test eluates and an error rate of less than 1.0 percent for pH measurements.

Data quality indicators (DQIs) were measured for all parameters continuously during the leaching experiments and during analytical tasks. Chemical (ICP, CVAA, XRF, IC, EC/OC) and physical (surface area, pore size distribution and density) characterization data were reduced and reports were generated automatically by the instrument software. The primary analyst reviewed 100% of the report data for completeness to ensure that quality control checks met established criteria. Sample analysis was repeated for any results not meeting acceptance criteria. A secondary review was performed by the Inorganic Laboratory Manager to validate the analytical report.

2.4.4. Data Management

Data quality indicator (DQI) goals for critical measurements in terms of accuracy, precision and completeness are shown in Table 11.

Table 11. Data quality indicator goals.

Measurement	Method	Accuracy	Precision	Completeness
Hg Concentration	CVAA/7470A	80 – 120 %	10%	>90%
Non-Hg Metals Concentration	ICP/6010	80 – 120 %	10%	>90%

Accuracy was determined by calculating the percent bias from a known standard. Precision was calculated as relative percent difference (RPD) between duplicate values and relative standard deviation (RSD) for parameters that have more than two replicates. Completeness is defined as the percentage of measurements that meet DQI goals of the total number measurements taken. Types of QC samples used in this project included blanks, instrument calibration samples, replicates, and matrix spikes.

Accuracy and precision for the samples analyzed for mercury concentration leachate determinations were made using replicates and matrix spike analyses. Data validation for the mercury samples was performed after the analyses and outliers for accuracy were re-analyzed to improve results. Mercury samples not meeting the accuracy goals occurred most often in samples at the alkaline end of the pH testing and with the blank samples. The greatest mercury leaching occurred in the samples with the lower pH where there was greater availability. The samples not meeting the accuracy goals for matrix spiking did not affect the quality of the data. Limited volume of leachate collected for the SR003.1 samples resulted in only one spike being performed per replicate set.

QC samples required for CVAA analysis are detailed in Method 7470A. The mercury analyzer software was programmed with the acceptance criteria for Method 7470A with respect to independent calibration verifications, continuous calibration verifications, and blank solution concentrations. All calibrations and samples analysis parameters passed the QA/ QC criteria and may be considered valid samples.

The pH meter was calibrated daily before each batch of measurements. Standards purchased from Thomas scientific (Swedesboro, NJ) were used to calibrate the probe at pH values of 4, 7, and 10. Each solution was certified to a precision of ±0.01 at 25 °C and was traceable to the National Institute of Standards Technology (NIST) standard reference material (SRM) SRM-186-I-c and 186-II-c.

2.5. INTERPRETATION AND PRESENTATION OF LABORATORY LEACHING DATA

Complete laboratory leaching test results for each facility are presented in Appendix F. For each facility, results are organized by constituent of interest in the alphabetic order of the symbol (aluminum [Al], arsenic [As], boron [B], barium [Ba], cadmium [Cd], cobalt [Co], chromium [Cr], mercury [Hg], molybdenum [Mo], lead [Pb], antimony [Sb], selenium [Se], and thallium [Tl]). For each constituent, results of Solubility and Release as a Function of pH (from test method SR002.1) and results of Solubility and Release as a Function of LS ratio (from test method SR003.1) are presented side by side. Results of pH as a function of acid or base addition (from test method SR002.1) are presented in Appendix G.

In addition, comparisons of results of Solubility and Release as a function of pH (SR002.1) are provided in Section 3.2.1. Comparisons are grouped by residue type (fly ash, gypsum, scrubber sludge, spray dryer absorber residues, and blended CCRs), followed by coal type and air pollution control configurations, and are organized by constituent of interest. For each grouping, selected results of Solubility and Release as a Function of pH (SR002.1) are also presented to illustrate characteristic leaching behaviors.

For Solubility and Release as a Function of pH (SR002.1), results are presented as eluate concentrations as a function of pH. The “own pH[35]” of the system is indicated by a circle surrounding the corresponding data point. Included with each figure are horizontal lines at the drinking water maximum concentration level (MCL) or drinking water equivalent level (DWEL)[36], or action limit (AL, for lead) and analytical limits (ML and MDL) to provide a frame of reference for the results. Also included with each figure are vertical lines indicating the 5th and 95th percentiles of pH from field observations of leachates from landfills and surface impoundments containing combustion residues (see Section 2.5.2). An annotated example of the results is provided as Figure 6. Actual results are presented in the following sections.

For Solubility and Release as a Function of LS ratio (SR003.1), results are presented as eluate concentrations as a function of LS ratio. Also indicated are the relevant ML, MDL, MCL, DWEL, or AL. An annotated example of the results is provided as Figure 7.

2.5.1. Interpretation of Mechanisms Controlling Constituent Leaching

Constituent (e.g., mercury, arsenic, and selenium) concentrations observed in laboratory leach test eluates and in field leachate samples may be the result of several mechanisms and factors. The discussion presented here focuses on constituent leaching and source term modeling approaches. Source term is defined here as the flux or amount of constituent released from the waste or secondary material (e.g., CCRs). Factors controlling constituent release and transport in and within the near field of the CCRs are often distinctly different from the factors and

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[35] The “own pH” of a material refers to the equilibrium pH when the material is placed in deionized water at a ratio of 10 g CCR per 100 mL of water.

[36] MCL, DWEL, and AL values used are as reported in (EPA, 2006a).

mechanisms which are important for subsequent vadose zone or groundwater transport outside of the near field area.

In general, constituents are present in the waste or secondary material either as adsorbed species, co-precipitated as amorphous or crystalline solid phases, or incorporated as trace components in solid phases. These three different cases can often be distinguished from one another based on the results of these leaching tests, either through direct interpretation of leaching results or in conjunction with geochemical speciation modeling. If chemical equilibrium conditions are approached (as is the approximate case for the laboratory and field sample conditions discussed in this report), then the functional behavior of the aqueous solution concentrations reflects the nature of the constituent species in the waste or secondary material, the presence of any co-constituents in the aqueous phase influencing aqueous solution speciation (e.g., effects of high ionic strength, chelating or complexing constituents), and the presence of species in the solution that may compete for adsorption sites if adsorption is the controlling solid phase mechanism. If the constituent is present in the waste or secondary material as an adsorbed species, many different adsorption/desorption characteristic patterns are possible (Duong, 1998; Ruthven, 1984).

The simplest case is when the constituent of interest is present at very low concentration in the waste or secondary material, relatively weakly adsorbed, and the presence of complexing and/or, competing species in solution is at a constant concentration. For this case, leaching test results will indicate a constant concentration as a function of pH at a fixed LS ratio, and linearly increasing concentration as LS ratio decreases at constant pH. This case is represented mathematically as a linear equilibrium partitioning function, where the critical constant of proportionality is the partitioning coefficient, commonly known as K_d. Linear partitioning and use of K_d values is a common approach for mathematically modeling contaminant transport at low contaminant concentrations in soils. Assumption of linear partitioning is a valid and useful approach when the necessary conditions (discussed above) are fulfilled[37].

A different case is when mercury is adsorbed on activated carbon. For mercury adsorbed on activated carbon or char particles in fly ash, a complex combination of adsorption mechanisms is indicated. During laboratory leaching tests, mercury concentrations in the leaching test eluates are relatively constant over the pH range and LS ratio of interest, and independent of total mercury content in the CCR. In addition, the total mercury content in the CCR is very low. These results are indicative of adsorption phenomena where, in the adsorbed state, interactions between adsorbed mercury species are stronger (thermodynamically) than the interactions between the adsorbed mercury species and carbon surface[38]. This observation has been supported by the observation of mercury dimer formation during sorption (Munro et al., 2001) and the occurrence

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[37] Often specific K_d values are a function of pH because of competition for adsorption sites by hydrogen ions. Therefore, in cases where hydrogen ions do compete for binding sites, the varying of pH would violate the condition that competing species are at constant concentration, and the leaching curve would not be linear. However, often a single K_d or range of K_d values are used in contaminant fate and transport models, without accounting for any specific relationship between pH and K_d which can result in misrepresentation of actual contaminant behavior.

[38] For this case, the first mercury molecule is adsorbed more weakly than subsequent mercury molecules because the adsorbed mercury-mercury interaction is stronger than the adsorbed mercury-carbon surface interaction [see (Sanchez et al., 2006) for further discussion].

of chemisorption as the dominant adsorption mechanism at temperatures above 75 °C (consistent with conditions in air pollution control devices (Vidic, 2002). In other studies, this phenomenon has been observed as the formation of molecular clusters on the adsorbent surface (Duong, 1998; Rudzinski et al., 1997; Ruthven, 1984). For this case, use of a K_d approach would underestimate release because desorption is best represented as a constant aqueous concentration until depletion occurs, rather than the linearly decreasing aqueous concentration indicated by a K_d approach.

A third case is encountered when the constituent of interest is present in the waste or secondary material (e.g., CCR) as a primary or trace constituent in either an amorphous or crystalline solid phase and there may be complexing or chelating co-constituents in the aqueous phase. Observed aqueous concentrations are a non-linear function of pH and LS ratio, and reflect aqueous saturation with respect to the species of interest under the given conditions (pH, co-constituents). For these cases, an approximation of field conditions can be made empirically based on laboratory testing and observed saturation over the relevant domain (as applied in this report), or geochemical speciation modeling coupled with mass transfer modeling can be used to assess release under specific field scenarios (the subject of a future report). Use of a K_d approach would not be appropriate for these cases because constituent concentrations will remain relatively constant at a given pH until the controlling solid phase is depleted and control is shifted to a new solid phase or mechanism.

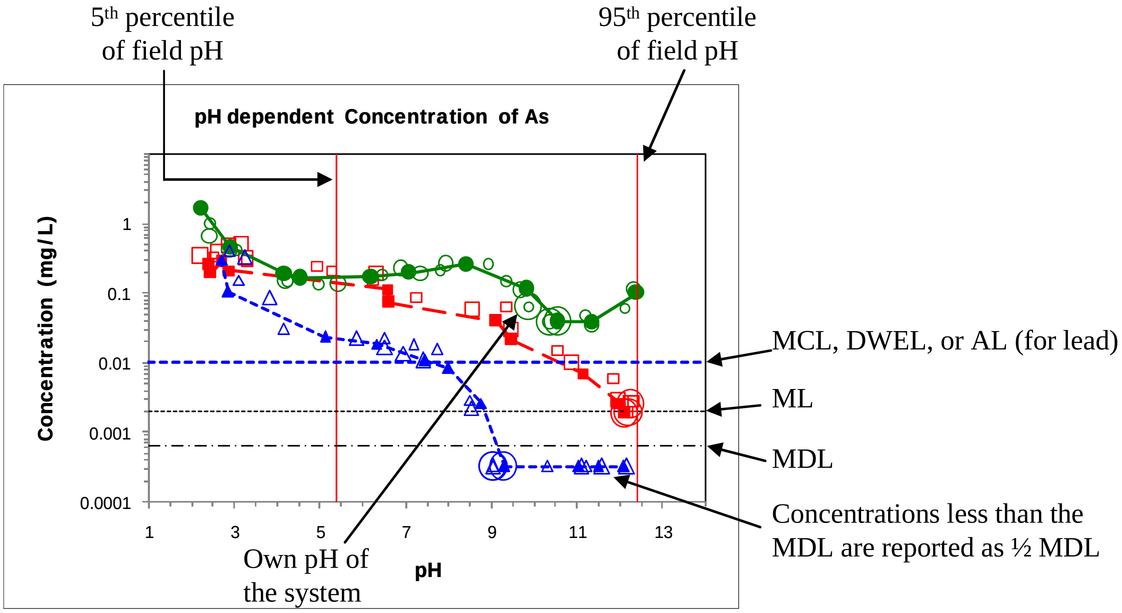


Figure 6. An example of eluate concentrations as a function of pH from SR002.1. Different colors, symbols and line types are used to represent different data sets. In this example figure, green, red, and blue indicate different CCR samples and open symbols are used to represent replicate data.

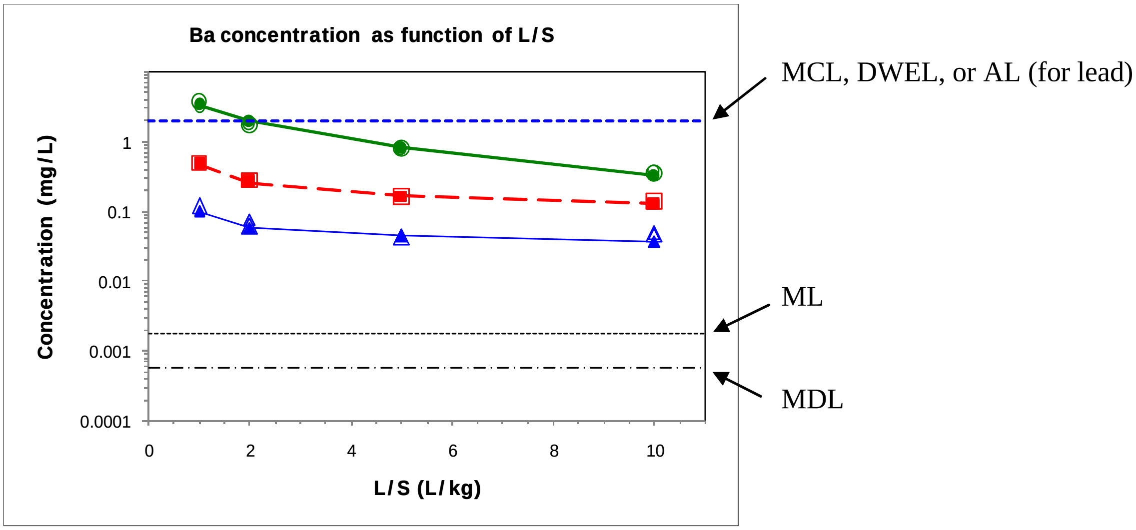


Figure 7. An example of eluate concentrations as a function of LS ratio from SR003.1.

2.5.2. Field pH Probability Distribution

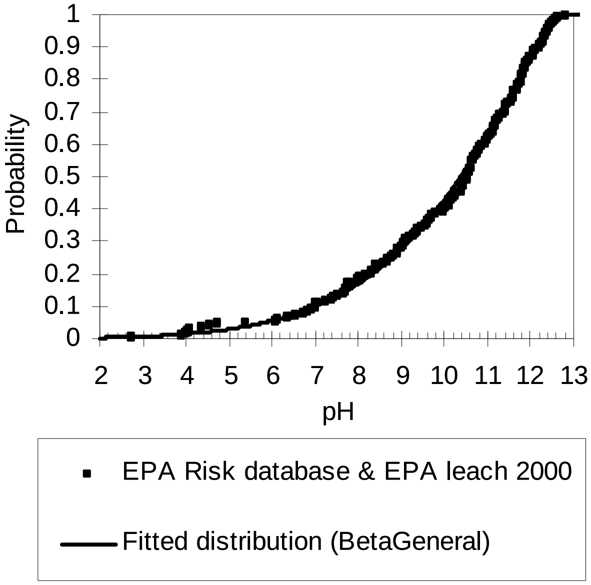
A probability distribution of field leachate pH values from coal combustion waste landfills was derived, as described below, from the set of field pH observations included in the EPA Risk Report (EPA, 2007b). The data set developed for the EPA Risk Report included (i) observations from the comprehensive database of landfill leachate characteristics developed by the EPA's Office of Solid Waste (EPA, 2000), (ii) field observations from literature, primarily from EPRI reports, (iii) additional data reported to EPA, and (vi) pH observations from laboratory leaching tests.

Only pH measurements from field samples (i.e., leachate, pore water) were selected for use in development of the resulting pH probability distribution. The resulting data set included 580 observations from 42 CCR landfill disposal facilities and was highly unbalanced, with some sites having only a few (e.g., less than five) observations and some sites having many observations (e.g., greater than 20). To prevent the unbalanced data from skewing the resulting probability distribution, the minimum, 25th, 50th, 75th percentile, and maximum values of observations for each individual facility were compiled into a single data set. For facilities with fewer than five observations, all observations for that facility were included. This data set then served as the basis for determining a balanced statistical distribution function of field leachate pH values from the disposal sites with reported values. Different distribution functions were used to fit the data and the one providing the best data fit based on the chi-square test was selected. The resulting field pH probability distribution was truncated and normalized to the pH range of the field data (Figure 8) (EPA, 2000; EPA, 2007b; EPRI, 2006).

Field pH observations were also evaluated for surface impoundments that receive CCRs from coal combustion facilities with FGD scrubbers in use. Pore water pH values measured in samples obtained from within the settled CCRs were extracted from the EPRI database. These pH observations were across the same range as the landfill field pH observations, but were insufficient to develop an independent pH probability distribution for surface impoundments.

Therefore, the same pH probability distribution was used for both landfill and surface impoundment facilities.

The resulting 5th and 95th percentiles of observed field pH values, equal to pH 5.4 and 12.4, respectively, are indicated on the figures of eluate concentrations as a function of pH (Figure 6).



pH	Field data	Fitted distribution	Simulated
Min	2.75	-7.42	2.76
5th percentile	5.40	5.84	5.85
50th percentile	10.53	10.38	10.24
90th percentile	12.20	12.18	11.94
95th percentile	12.40	12.43	12.43
Max	12.80	12.81	12.43

Distributions

BetaGeneral(9.0369, 1.5076, -7.4214, 12.814)

Figure 8. Probability distributions for field pH. Summary statistics for the field data and the probability distribution are provided to the right of the graph (EPA, 2000; EPA, 2007b; EPRI, 2006).

3. RESULTS AND DISCUSSION

The EPA Risk Report (EPA, 2007b) identified the following COPCs based on the potential for either human health or ecological impacts using a screening risk assessment: aluminum (Al), arsenic (As), antimony (Sb), barium (Ba), boron (B), cadmium (Cd), cobalt (Co), chromium (Cr), lead (Pb), mercury (Hg), molybdenum (Mo), selenium (Se), and thallium (Tl).[39] Thus, the evaluation provided here focuses on the same thirteen constituents and can be used in future risk and environmental assessments.

3.1. TOTAL ELEMENTAL CONTENT

Total elemental content of CCR samples was analyzed by acid digestion (digestion Method 3052 and ICP-MS analysis by Method 6020; see Section 2.3.7) for constituents of potential concern (Al, As, Ba, Cd, Co, Cr, Mo, Pb, Sb, Se, Tl)[40] and mercury was analyzed by Method 7470 with selected samples also analyzed by Method 7473; results of these analyses are provided in Figure 9 through Figure 21, with tabular results in Appendix D. Total elemental content for boron was not analyzed because of interferences by the sample digestion method. Total elemental content also was analyzed by XRF for major constituents and other detectable constituents (Al, Ba, Ca, Cl, F, Fe, K, Mg, Na, P, S, Si, Sr, Ti) and carbon was analyzed independently; results of these analyses are provided in Figure 22 through Figure 36, with tabular results provided in Appendices E and C. Several of the COPCs analyzed by ICP-MS were below the detection limits for XRF analysis (e.g., As, Sb, Se).

Two elements, Al and Ba, were analyzed by both acid digestion and XRF methods. Measurement accuracy and precision is better by acid digestion for low concentrations (e.g., less than 10,000 µg/g) and better by XRF for higher concentrations (e.g., greater than 10,000 µg/g).

Results suggest higher content for some trace elements in CCRs when SCR is in use, however, these observations are based on single samples from a limited number of facilities and evaluation of additional samples from the same and additional facilities is warranted. Primary observations for the constituents of concern (Figure 9 through Figure 21 and Figure 22 through Figure 36) are as follows:

Aluminum (Al) (Figure 9 and Figure 22). Al content in fly ash was 6-15 percent, in gypsum between 0.3-1 percent, and in scrubber sludges 0.7-20 percent. There is no apparent systematic effect of coal type or air pollution control system on Al content in CCRs. One likely source of variability is the Al content of the additive used for flue gas desulfurization (e.g., limestone or magnesium lime).

Arsenic (As) (Figure 10). As content in fly ash was 10-200 µg/g, with a higher content (500 µg/g) observed in one sample from a COHPAC facility with ACI (Facility C, sample GAT). As content in gypsum was 1-10 µg/g, in scrubber sludge and blended CCRs 3-70 µg/g. There was

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[39] The database used in the EPA Risk Report (EPA, 2007b) for the assessment was based on both measurements of field samples (e.g., leachate, pore water) and single point laboratory leaching tests (e.g., TCLP, SPLP).

[40] The total elemental content of boron in CCRs was not measured for samples reported here because of analytical interference (digestion Method 3052 uses boron as part of the method).

no clear effect of coal type at the high level categorization based on coal rank and region on As content in CCRs, although coal from within a region has been observed to have considerable variability with respect to trace element total content.

Barium (Ba) (Figure 11 and Figure 23). Ba content in fly ash from bituminous and lignite coals was 0.06-0.2 percent, and 0.6-1.5 percent in fly ash from sub-bituminous coals. Ba content in gypsum was 2-80 µg/g, and in scrubber sludges 80-3,000 µg/g. Likely sources of variability of Ba content in gypsum include the source of limestone used in flue gas desulfurization and the extent of carryover of fly ash into the gypsum.

Cadmium (Cd) (Figure 12). Cd content in all CCRs was less than 2 µg/g, with lower content typically in gypsum than fly ash samples. An exception was the fly ash sample from Facility U (UFA) which had Cd content of 15 µg/g.

Cobalt (Co) (Figure 13)**.** Co content in fly ash was 20-70 µg/g, and 0.8-4 µg/g in gypsum. Results for scrubber sludge suggest less Co content in samples from facilities without NOx controls (1-2 µg/g) than for facilities with NO_x controls (SCR or SNCR) in operation (3-40 µg/g, including paired comparisons).

Chromium (Cr) (Figure 14)**.** Cr content in fly ash was 70-200 µg/g, and 1-20 µg/g in gypsum with no apparent relationship to coal type. Higher Cr content in scrubber sludges was associated with facilities using SCR (Facilities B and K, samples BGD and KGD; 50-300 µg/g compared to 9-20 µg/g for other samples).

Mercury (Hg) (Figure 15 and Figure 16)**.** Hg content in all CCRs was from 0.01-20 µg/g with highest Hg content associated with fly ash samples from facilities with ACI and gypsum from a facility burning lignite coal (Facility Ca, sample CaAW).

Molybdenum (Mo) (Figure 17)**.** Mo content in fly ash and scrubber sludges was similar at 8-30 µg/g, with one exception in fly ash at 80 µg/g (Facility U, sample UFA). Mo content in gypsum was 1-10 µg/g. No apparent relationship to coal type or air pollution control system was observed.

Lead (Pb) (Figure 18)**.** Pb content in fly ash was 20-100 µg/g, 0.4-10 µg/g in gypsum and 2-30 µg/g in scrubber sludges. No apparent relationship to coal type or air pollution control system was observed.

Antimony (Sb) (Figure 19)**.** Sb content in fly ash and scrubber sludge was 3-15 µg/g and 0.15-8 µg/g in gypsum. No apparent relationship to coal type or air pollution control system was observed.

Selenium (Se) (Figure 20)**.** Se content in all CCRs was distributed over range with typical content of 2-50 µg/g with two samples with approximately 200 µg/g (Brayton Point, sample BPT; Facility C, sample GAT).

Thallium (Tl) (Figure 21)**.** Tl content was 0.8-15 in fly ash and scrubber sludges, and 0.2-2 µg/g in gypsum. No apparent relationship to coal type or air pollution control system was observed.

Major species analysis by XRF (Figure 22 to Figure 36) indicated that fly ash from facilities burning sub-bituminous coals had greater content of Ba, Ca, Mg, Na, P and Sr than fly ash from facilities burning bituminous or lignite coals. Total Ca content in fly ash can be divided into three groupings related to coal types: (i) sub-bituminous, 10-20%, (ii) high calcium bituminous and lignite, 1-6%, and (iii) low calcium bituminous, 0.3-0.7%. Fly ash samples with low total calcium had acidic own pH values (typically 4 < pH < 5) compared to samples with medium and high calcium content that had alkali own pH values (typically pH > 10). The relationship between total calcium content (by XRF) and own pH for fly ash samples is illustrated in Figure 37. Higher calcium content results in greater fly ash alkalinity, as indicated by higher pH values.

Major species analysis also indicated that gypsum contained up to 5 wt% carbon and up to 7 wt% Si, both indicative of fly ash carry over into the FGD scrubber. Based on Si content in gypsum, this suggests up to 5% of the non-carbon content is comprised of fly ash.

In interpreting these results, please note that the CCRs analyzed in this report are not considered to be a representative sample of all CCRs produced in the U.S. For many of the observations, only a few data points were available. It is hoped that through broader use of the improved leach test methods (as used in this report), that additional data from CCR characterization will become available. That will help better define trends associated with changes in air pollution control at coal-fired power plants.

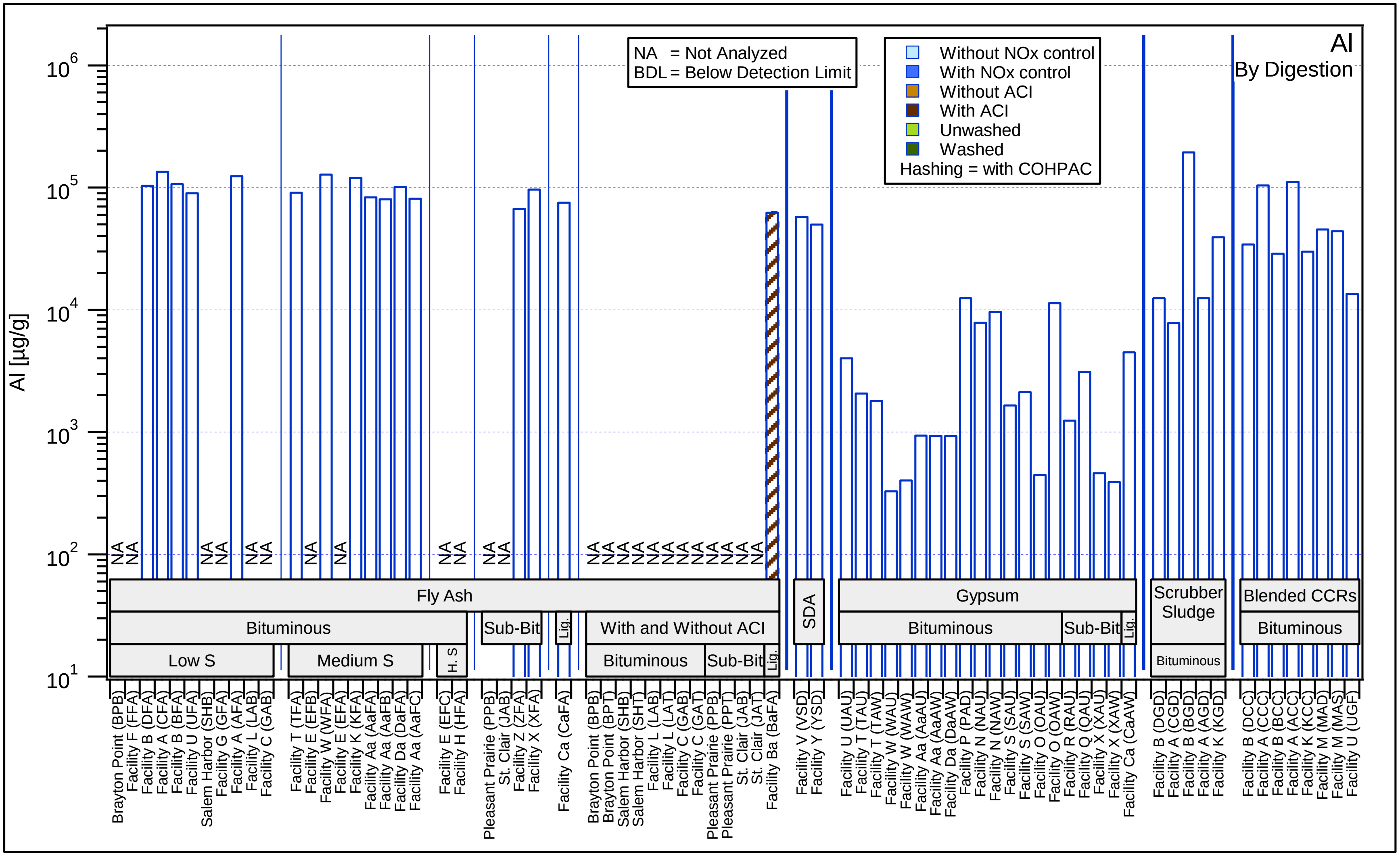

Figure 9. Aluminum. Comparison of total elemental content by digestion (Methods 3052 and 6020).

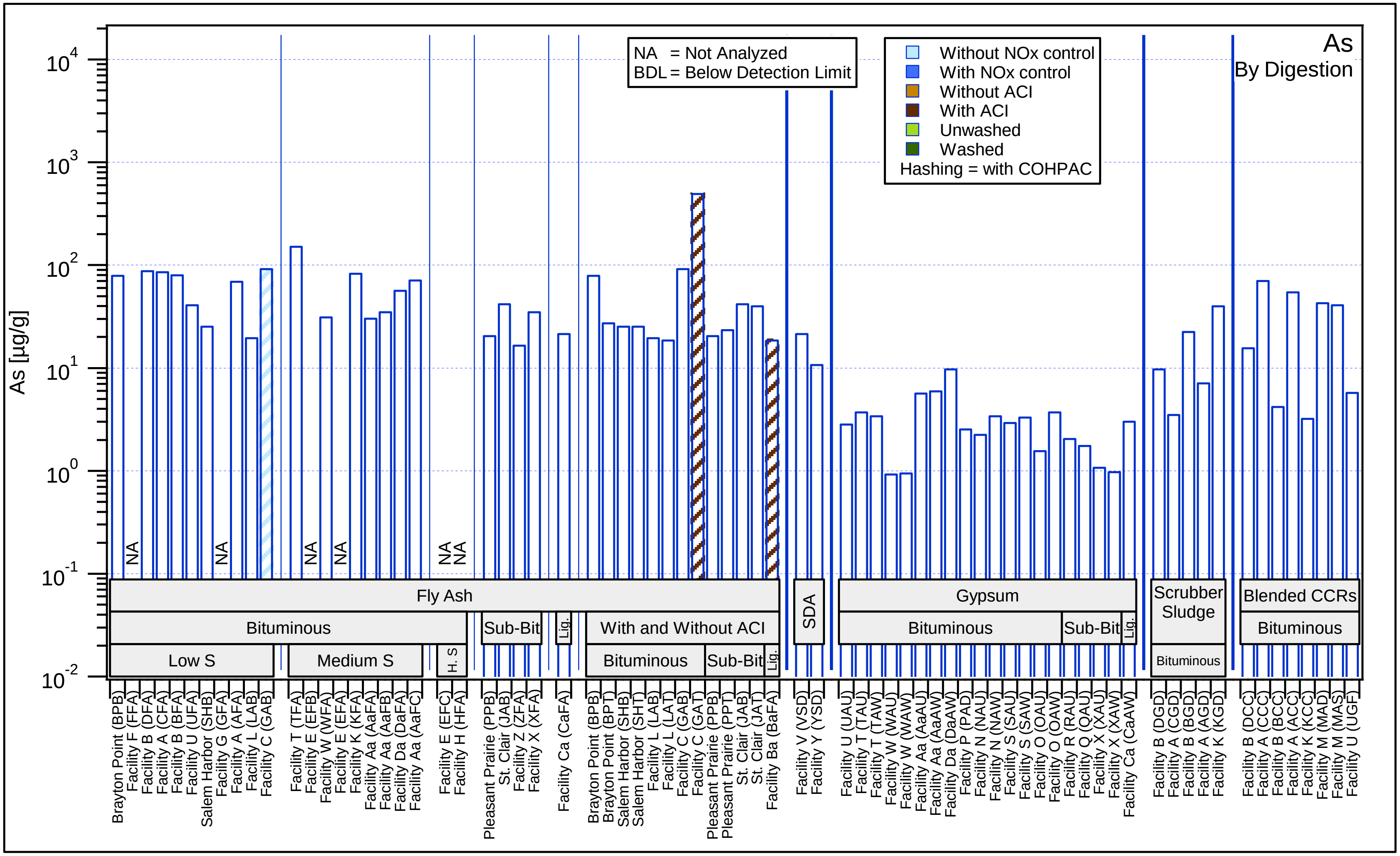

Figure 10. Arsenic. Comparison of total elemental content by digestion (Methods 3052 and 6020).

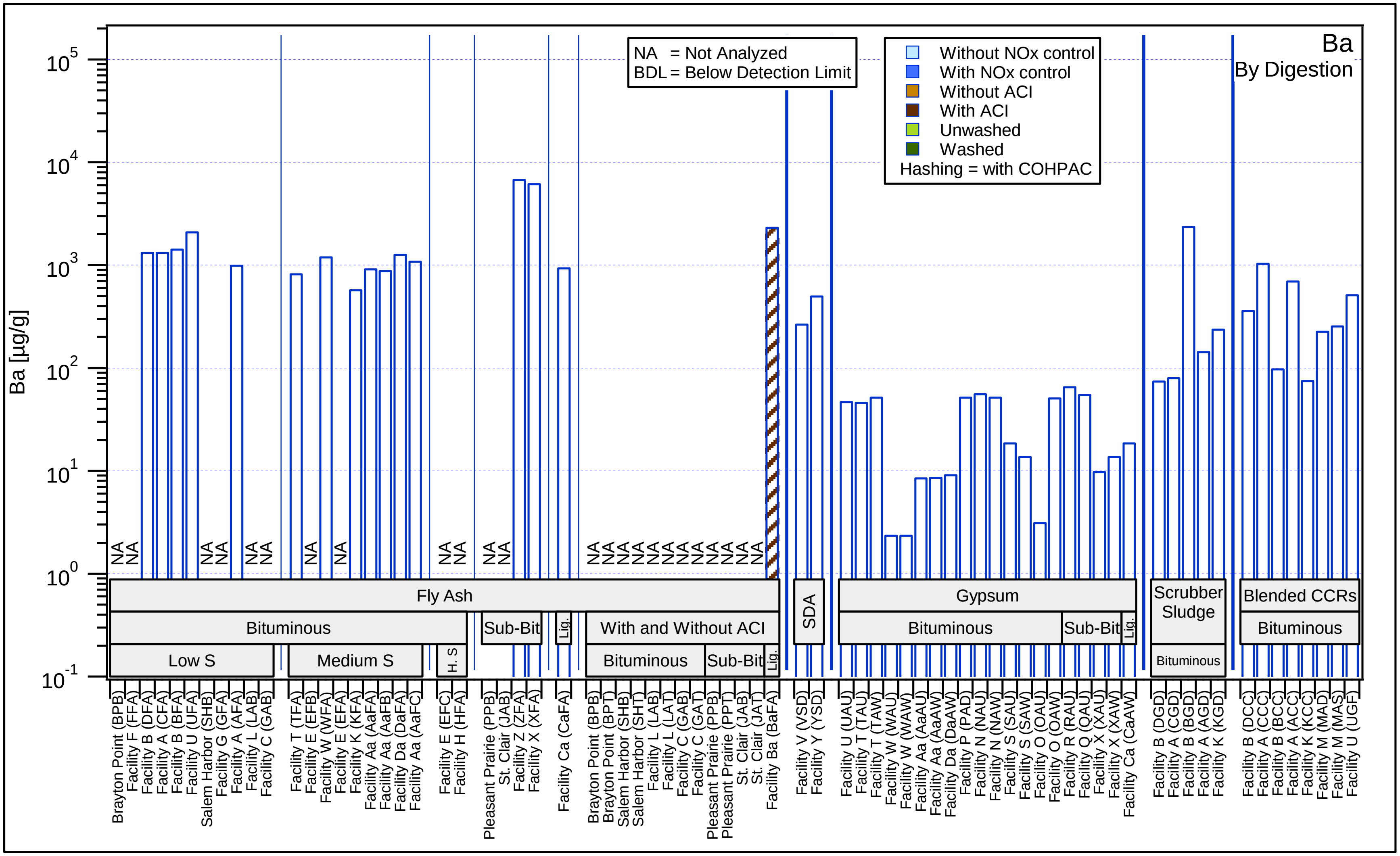

Figure 11. Barium. Comparison of total elemental content by digestion (Methods 3052 and 6020).

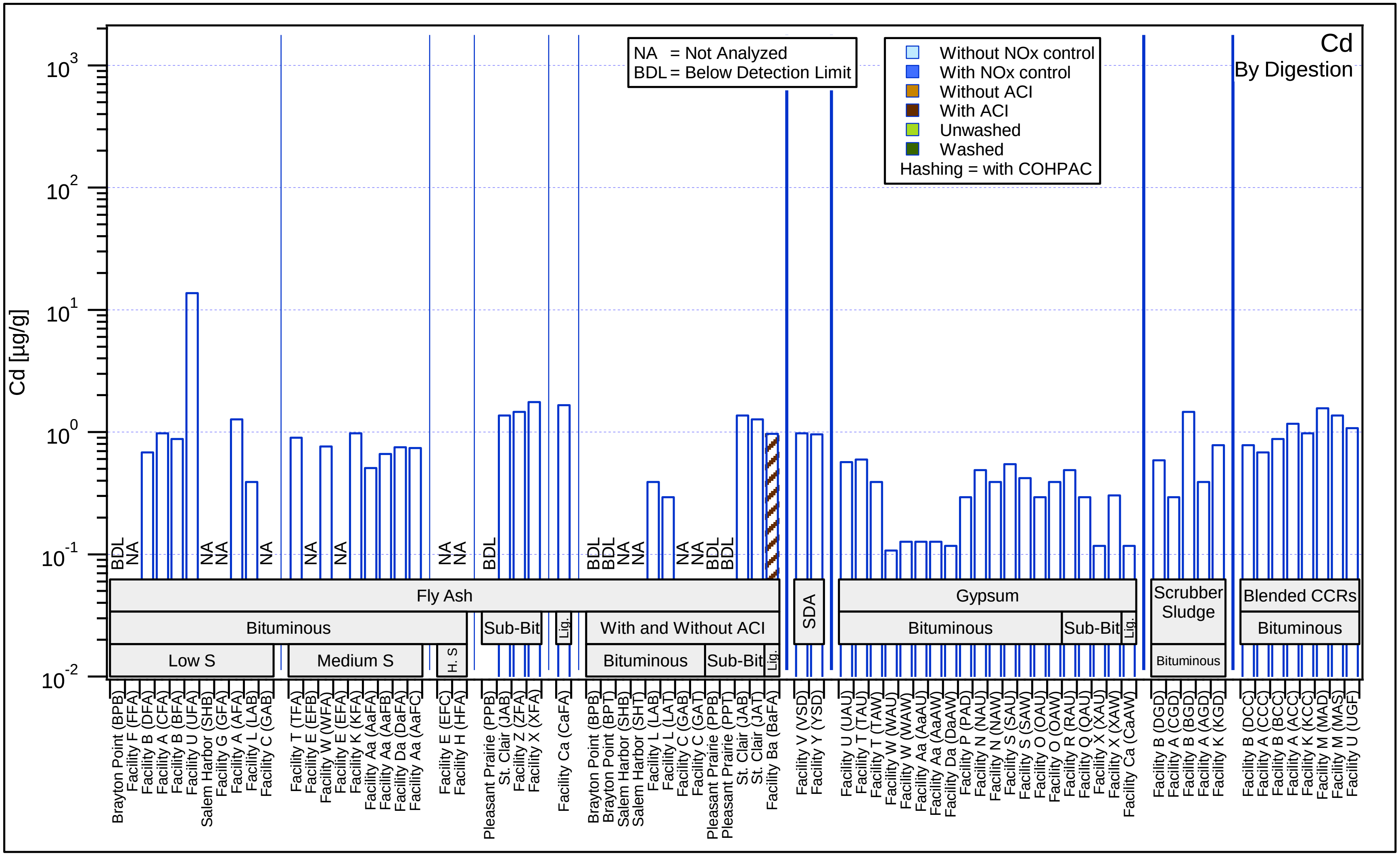

Figure 12. Cadmium. Comparison of total elemental content by digestion (Methods 3052 and 6020).

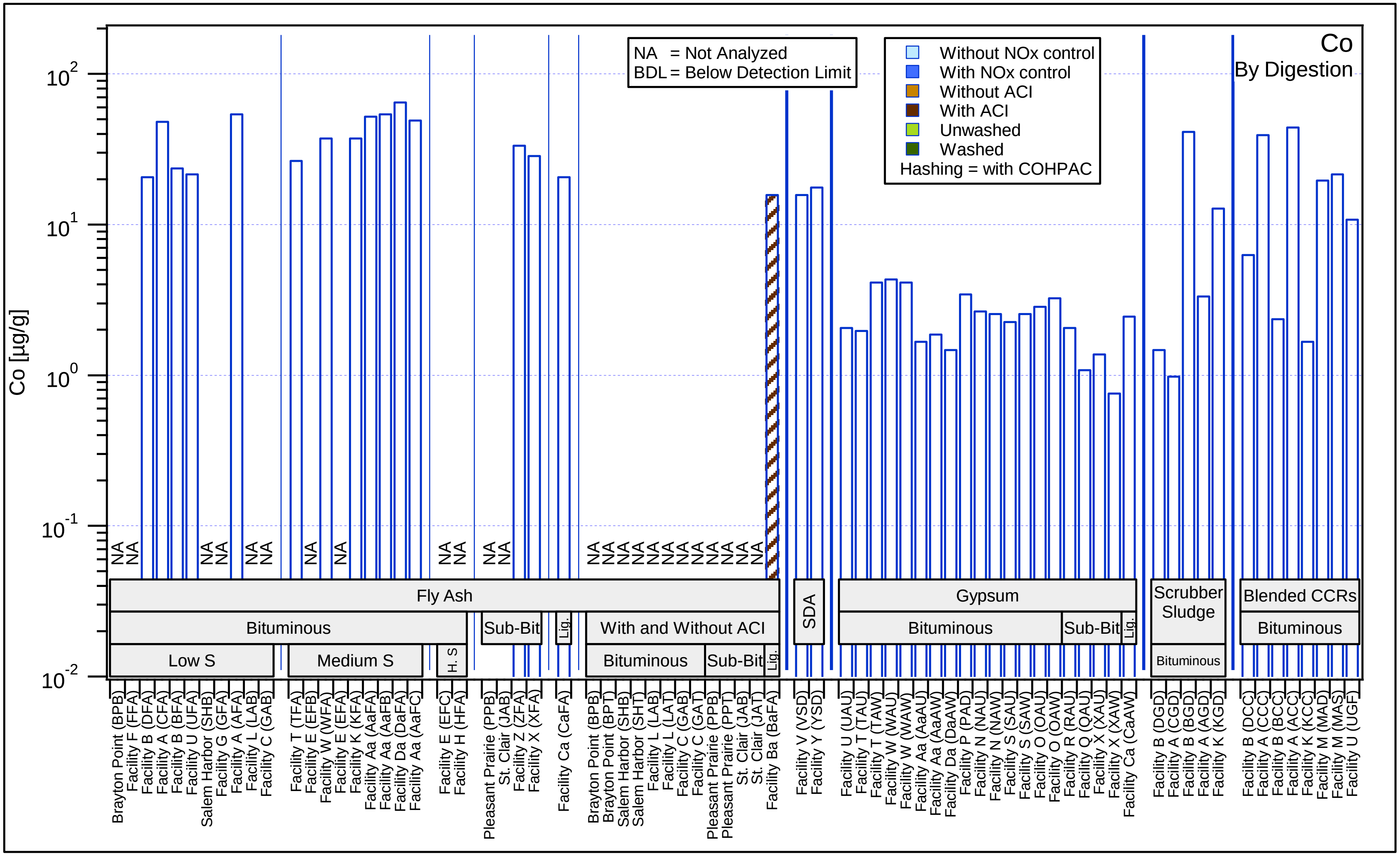

Figure 13. Cobalt. Comparison of total elemental content by digestion (Methods 3052 and 6020).

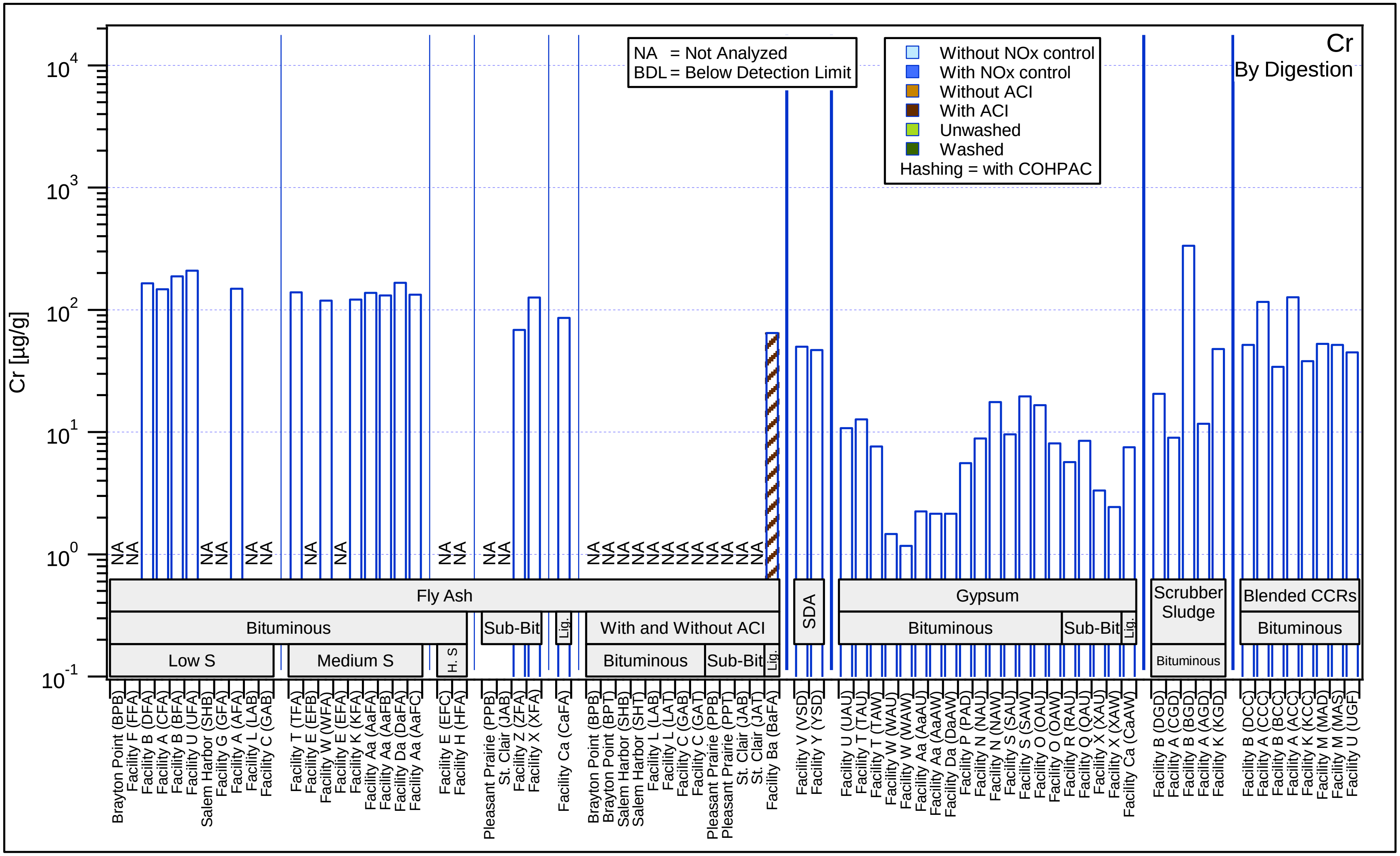

Figure 14. Chromium. Comparison of total elemental content by digestion (Methods 3052 and 6020).

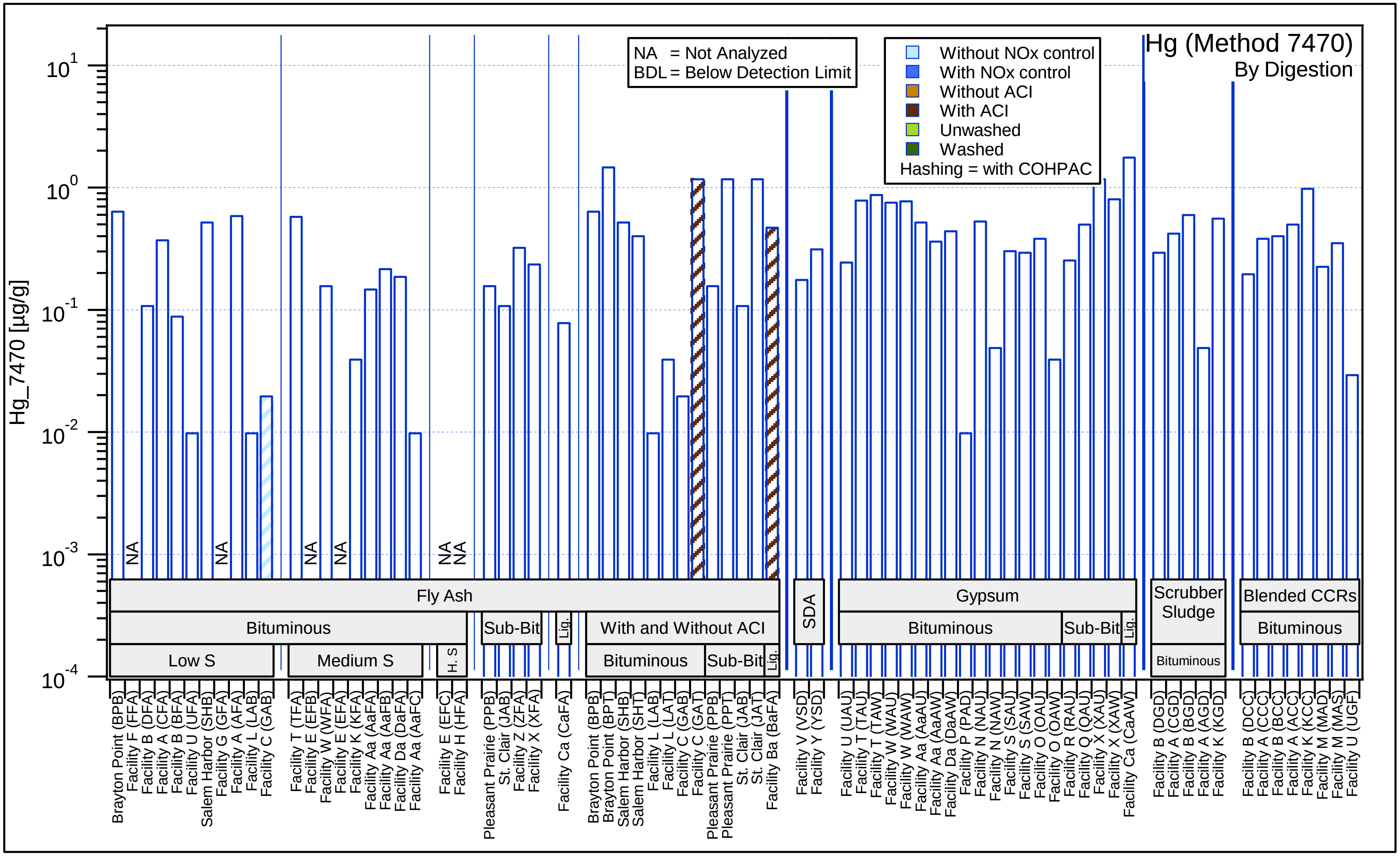

Figure 15. Mercury. Comparison of total elemental content by digestion (Method 7470).

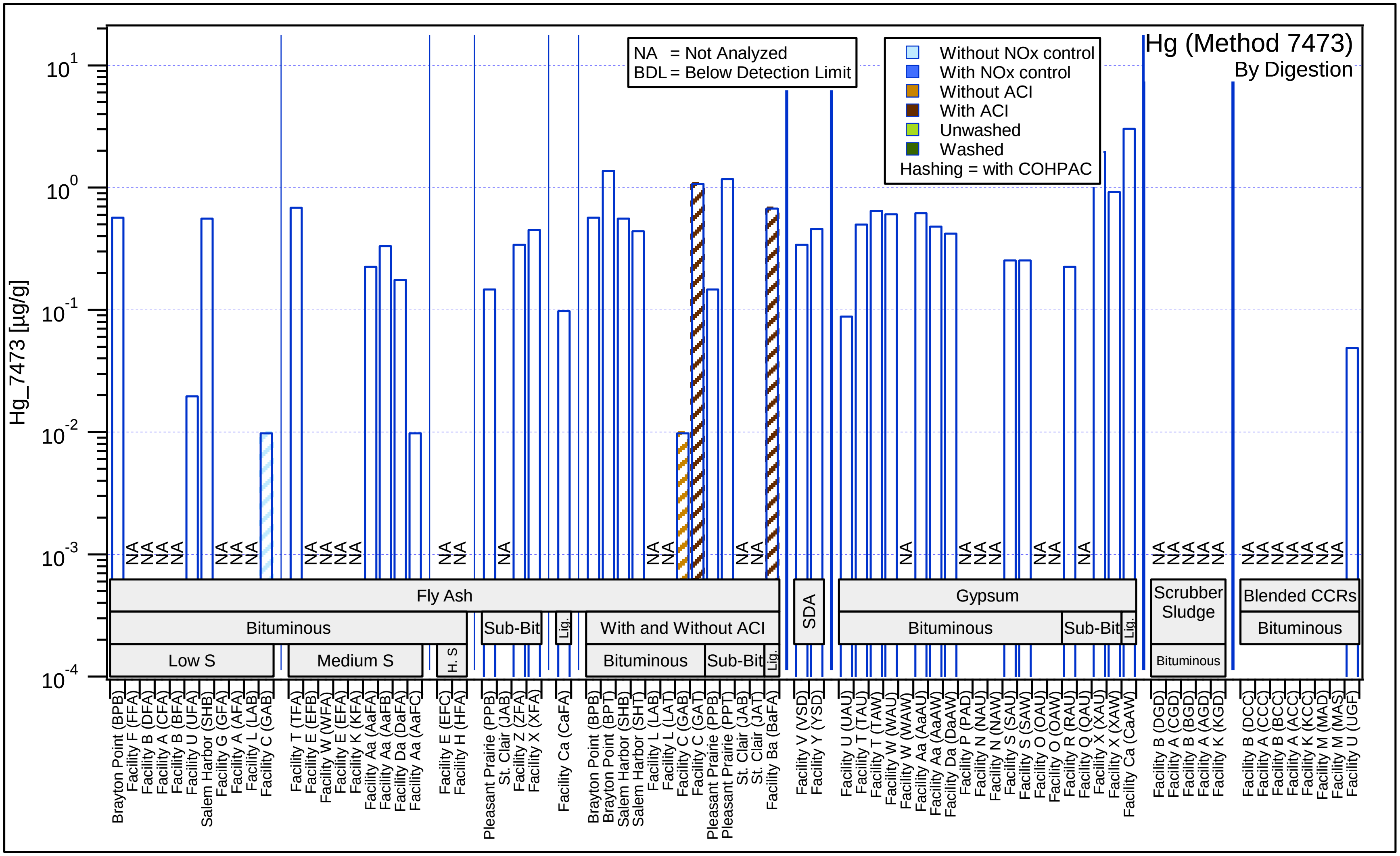

Figure 16. Mercury. Comparison of total elemental content by digestion (Method 7473).

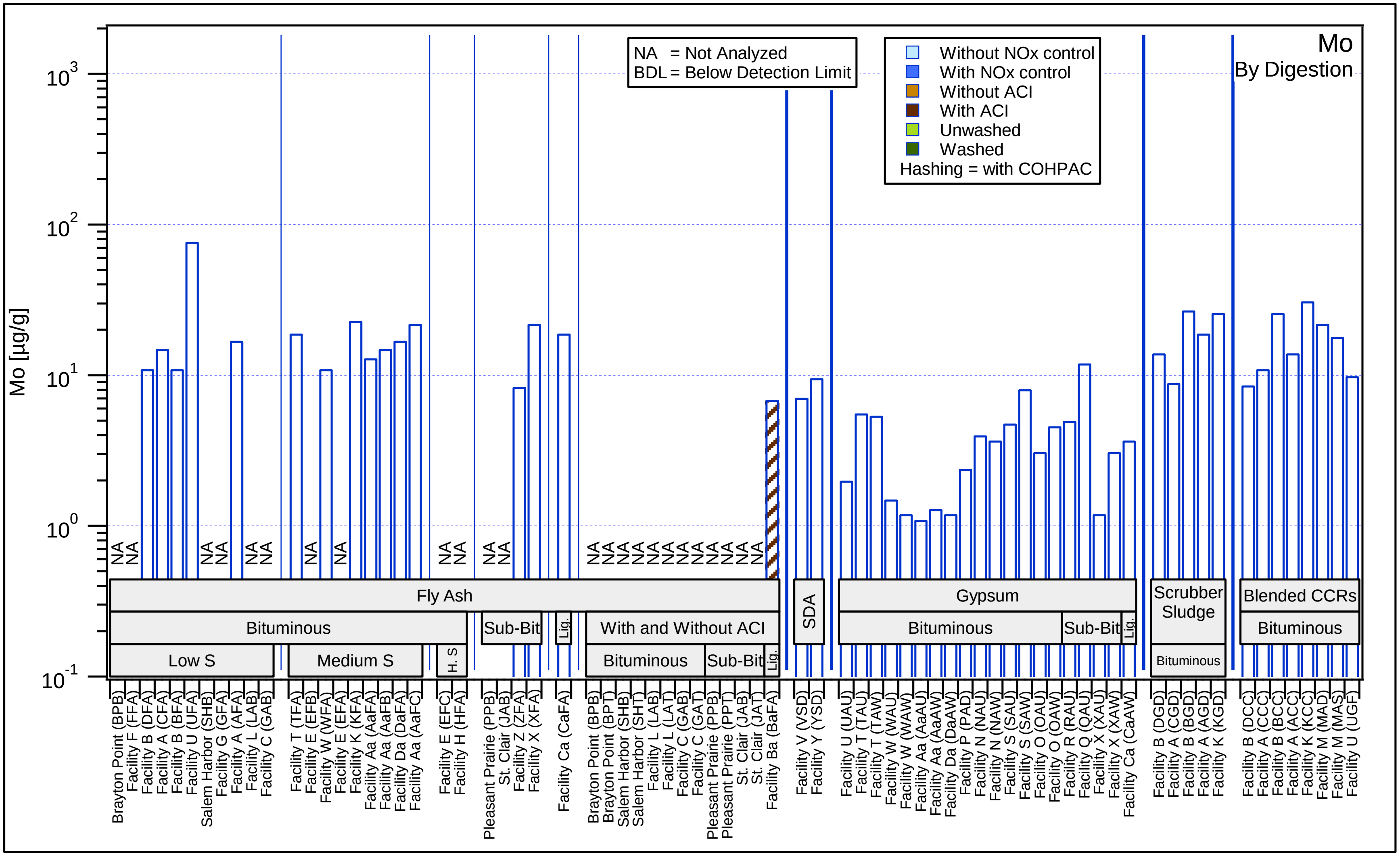

Figure 17. Molybdenum. Comparison of total elemental content by digestion (Methods 3052 and 6020).

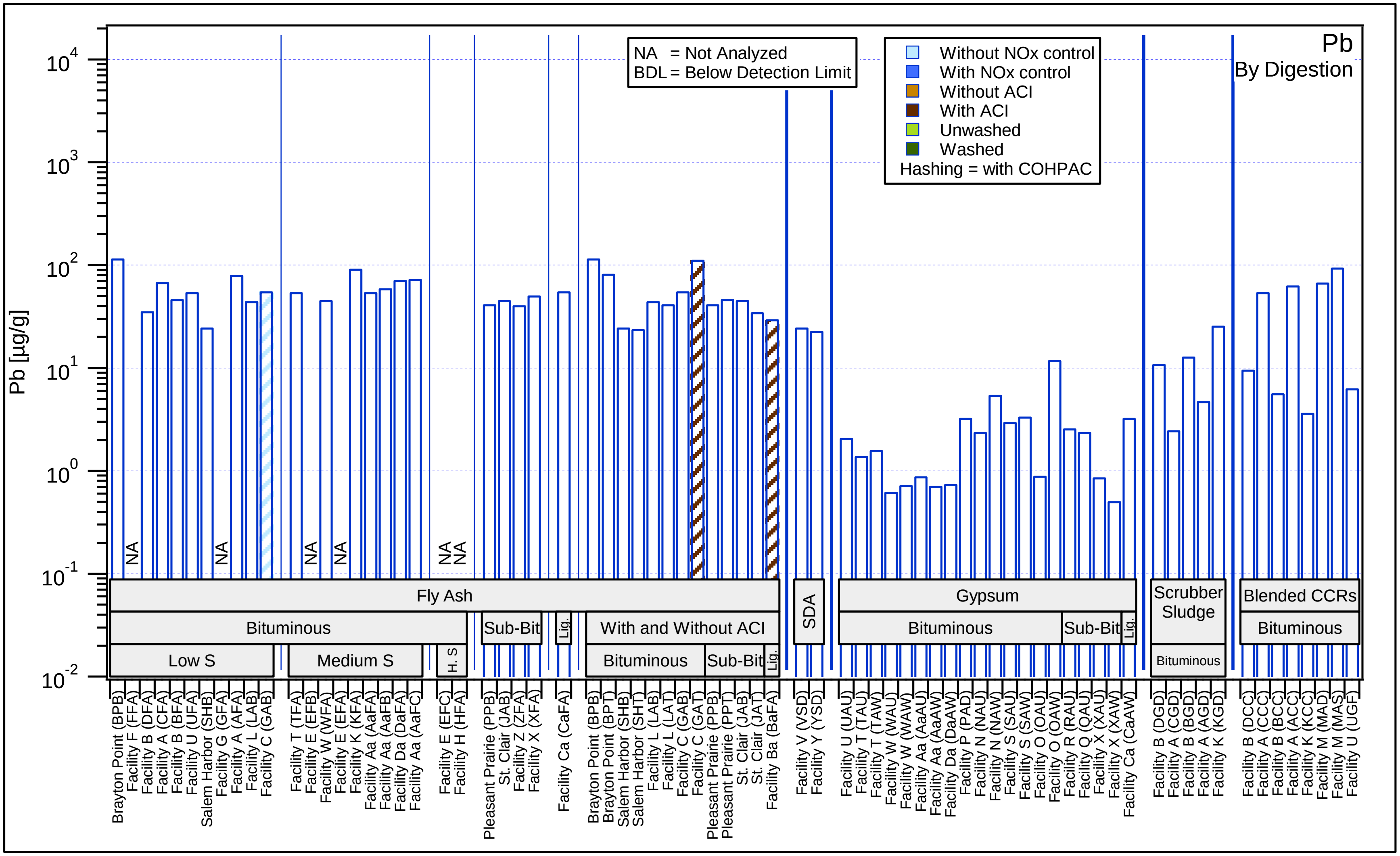

Figure 18. Lead. Comparison of total elemental content by digestion (Methods 3052 and 6020).

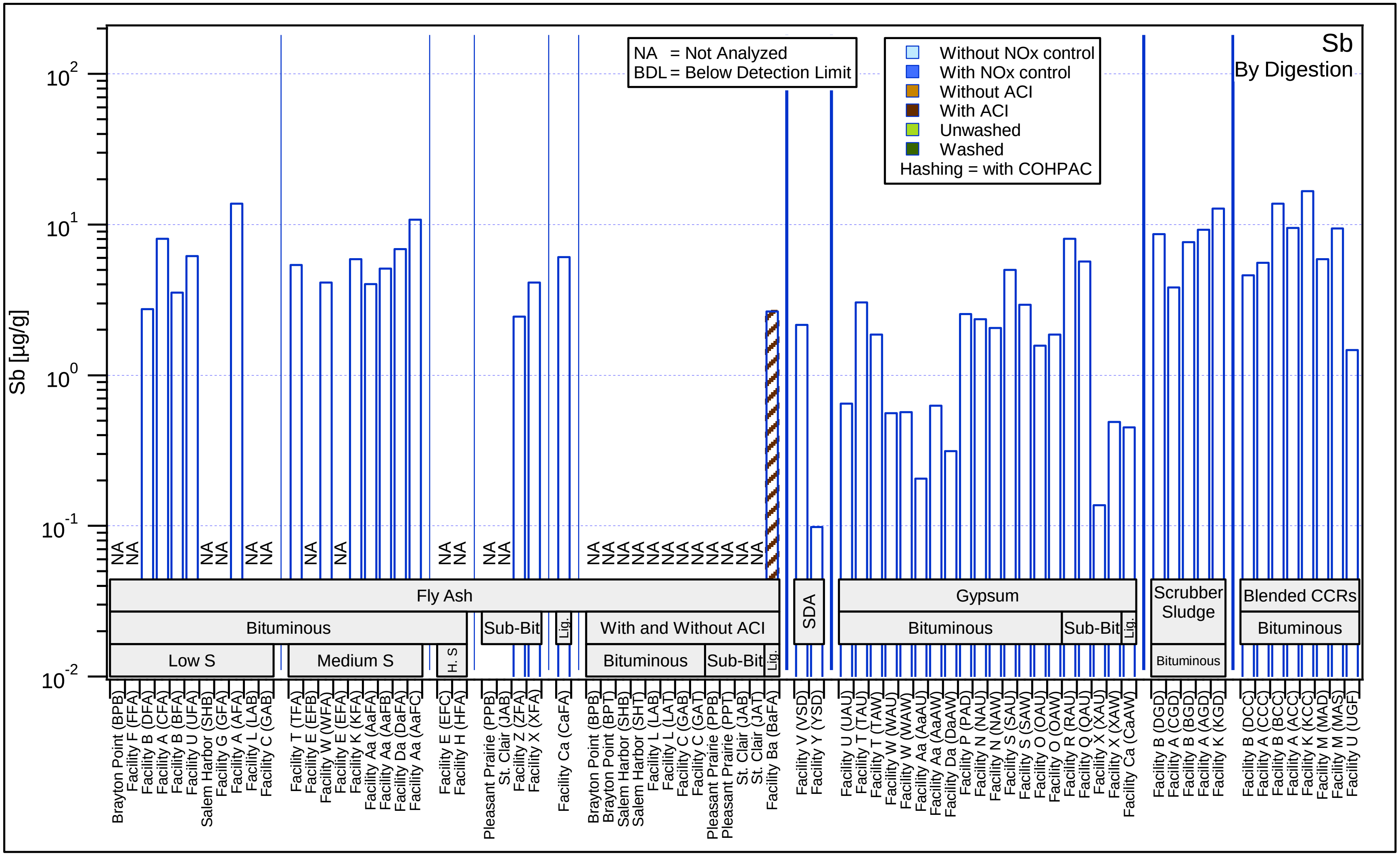

Figure 19. Antimony. Comparison of total elemental content by digestion (Methods 3052 and 6020).

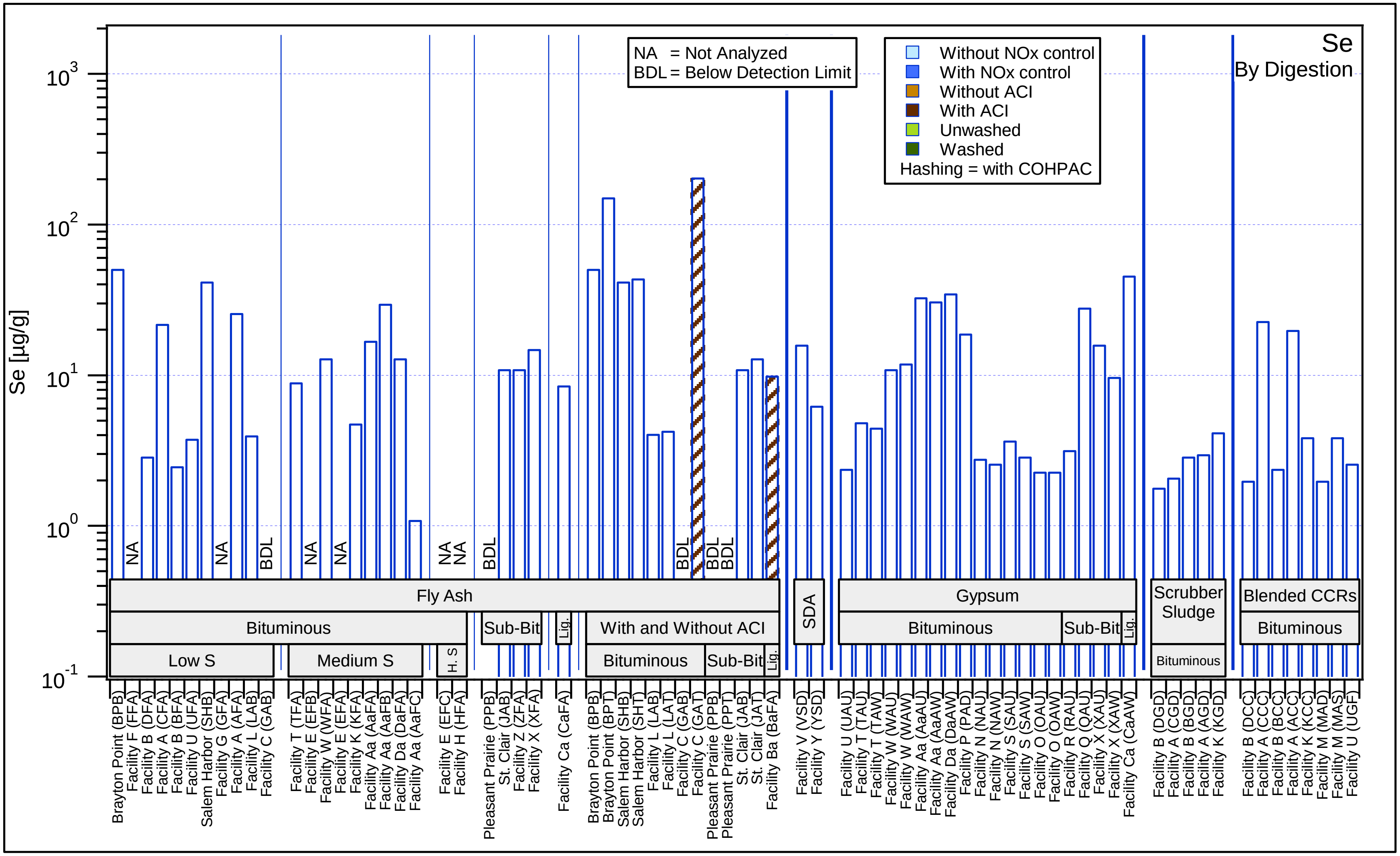

Figure 20. Selenium. Comparison of total elemental content by digestion (Methods 3052 and 6020).

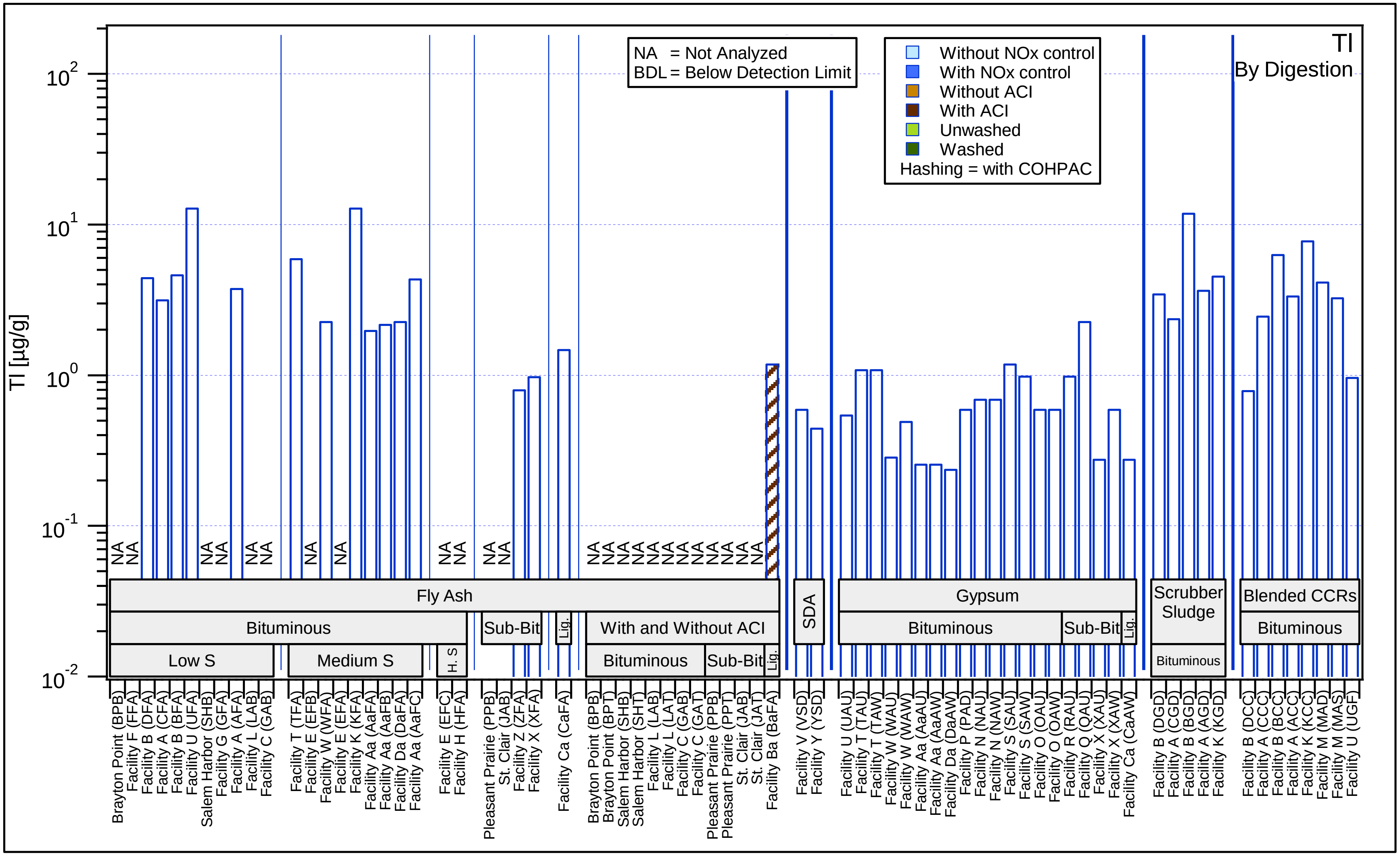

Figure 21. Thallium. Comparison of total elemental content by digestion (Methods 3052 and 6020).

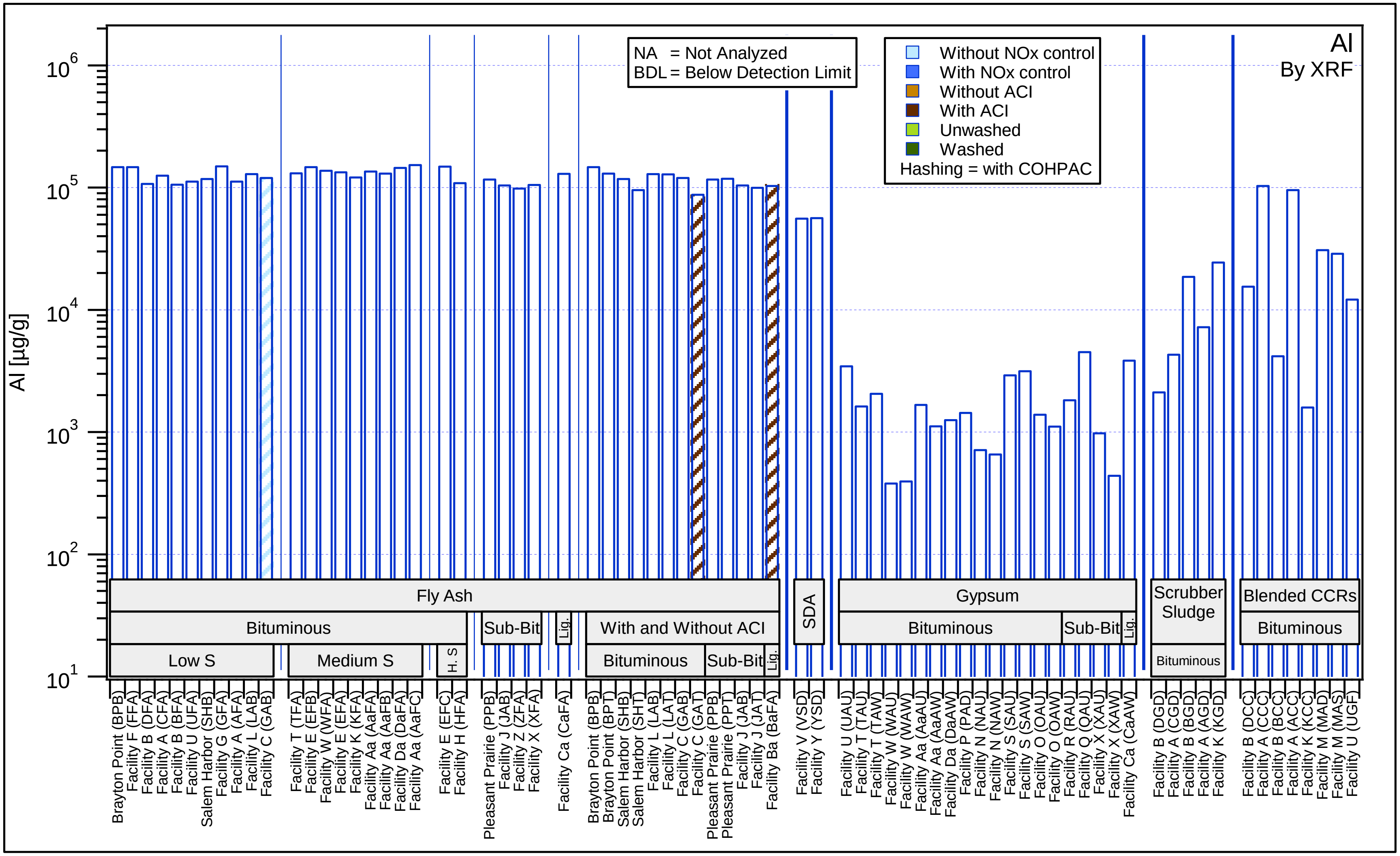

Figure 22. Aluminum. Comparison of total elemental content by XRF.

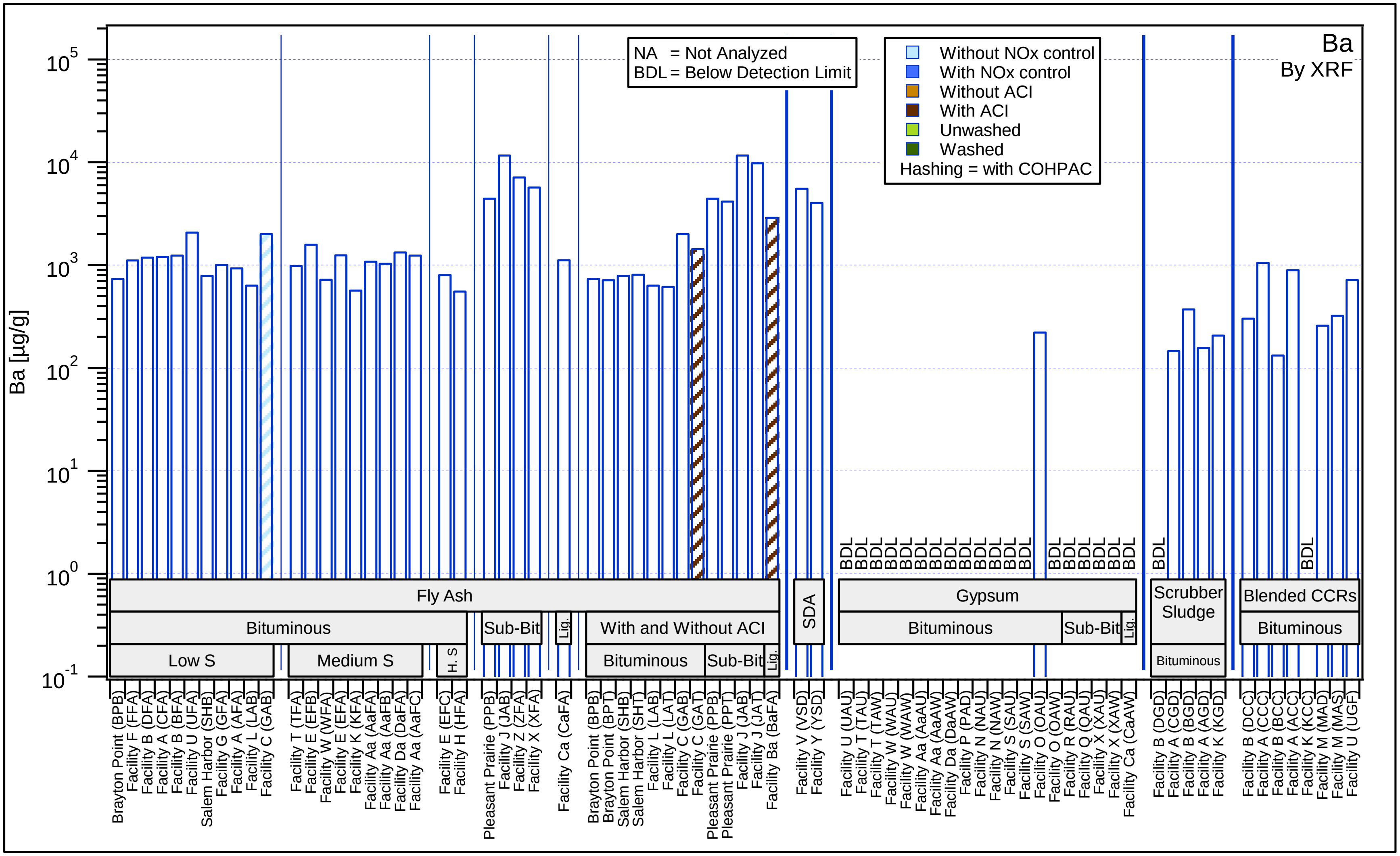

Figure 23. Barium. Comparison of total elemental content by XRF.

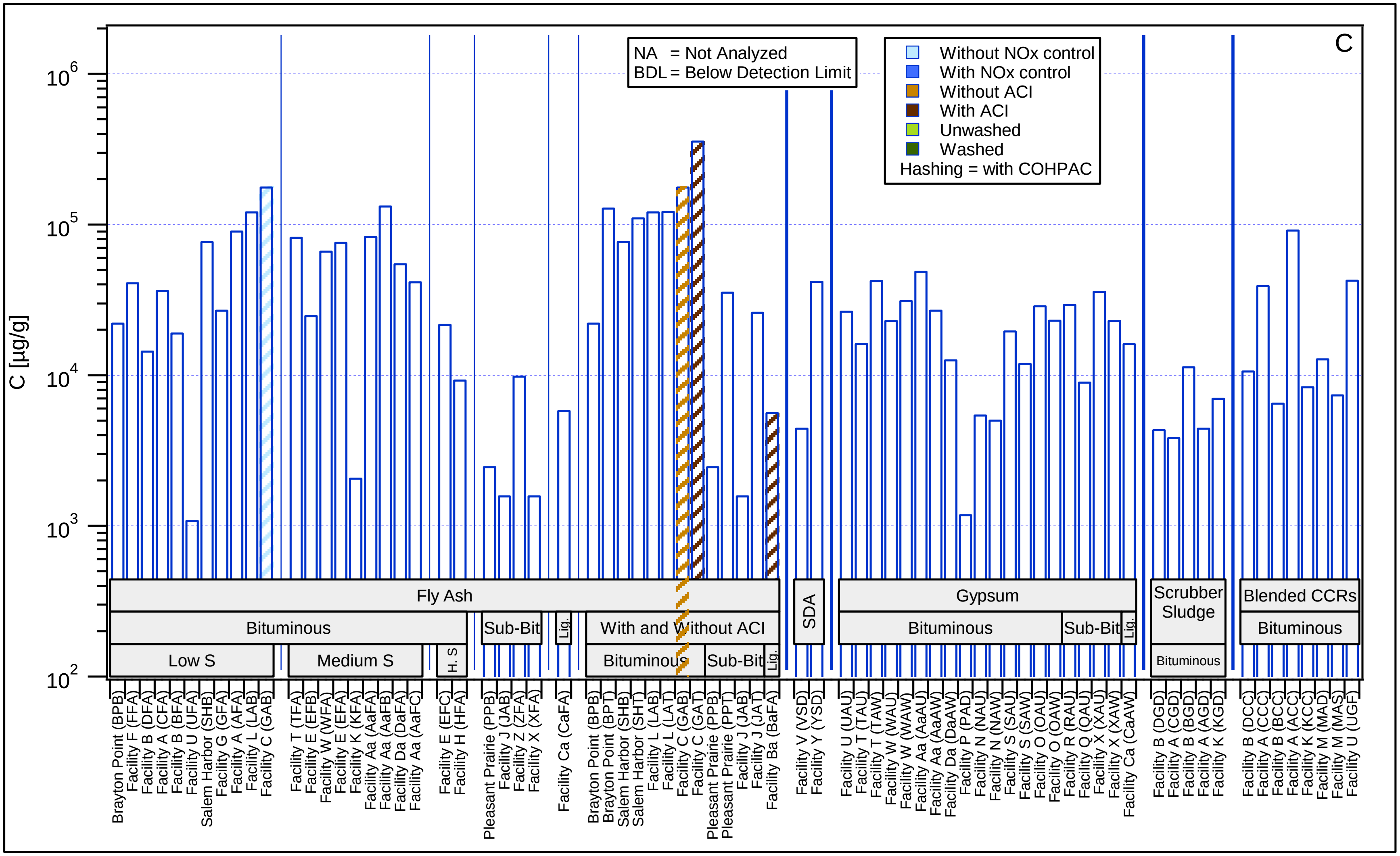

Figure 24. Carbon. Comparison of total elemental content.

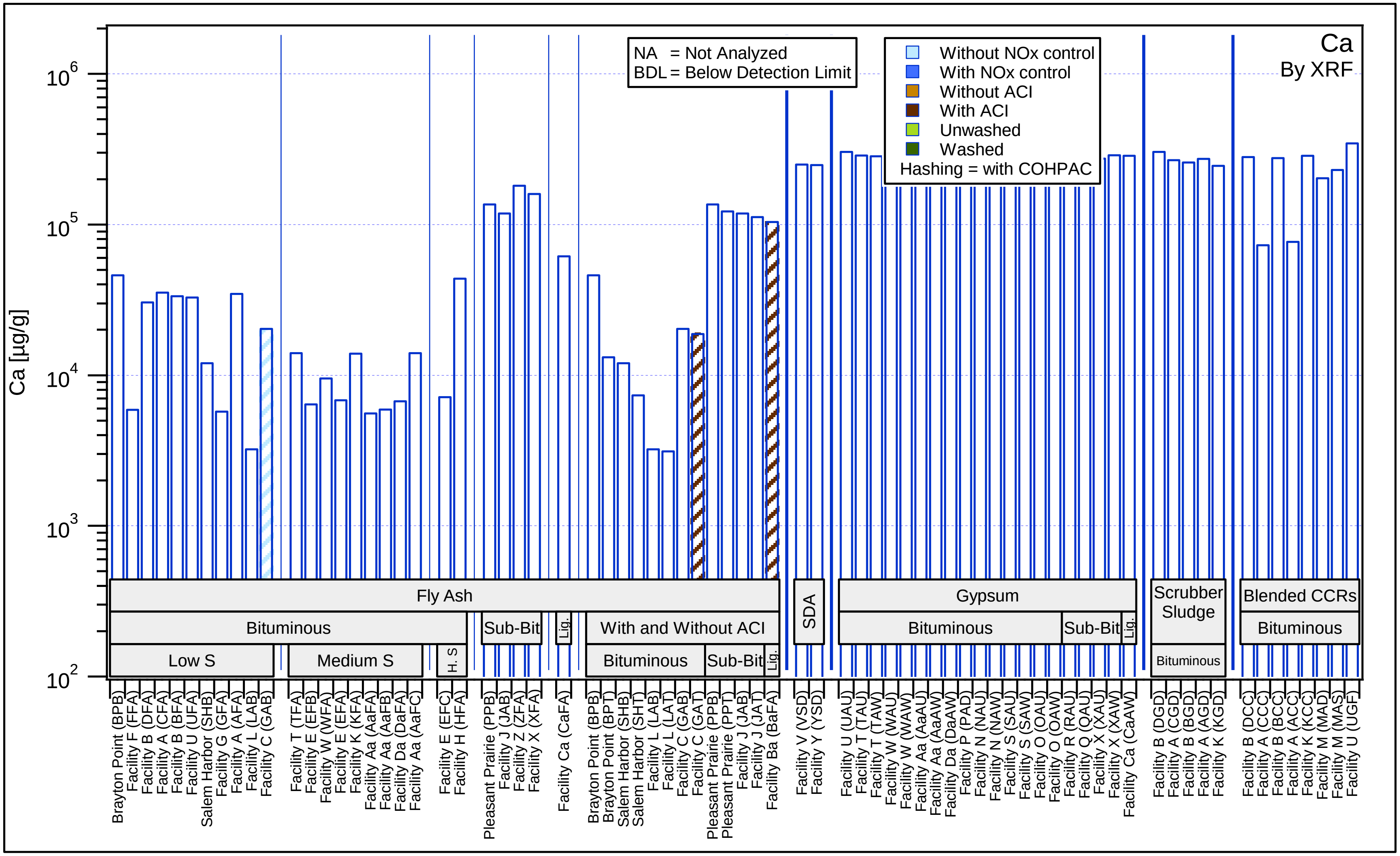

Figure 25. Calcium. Comparison of total elemental content by XRF.

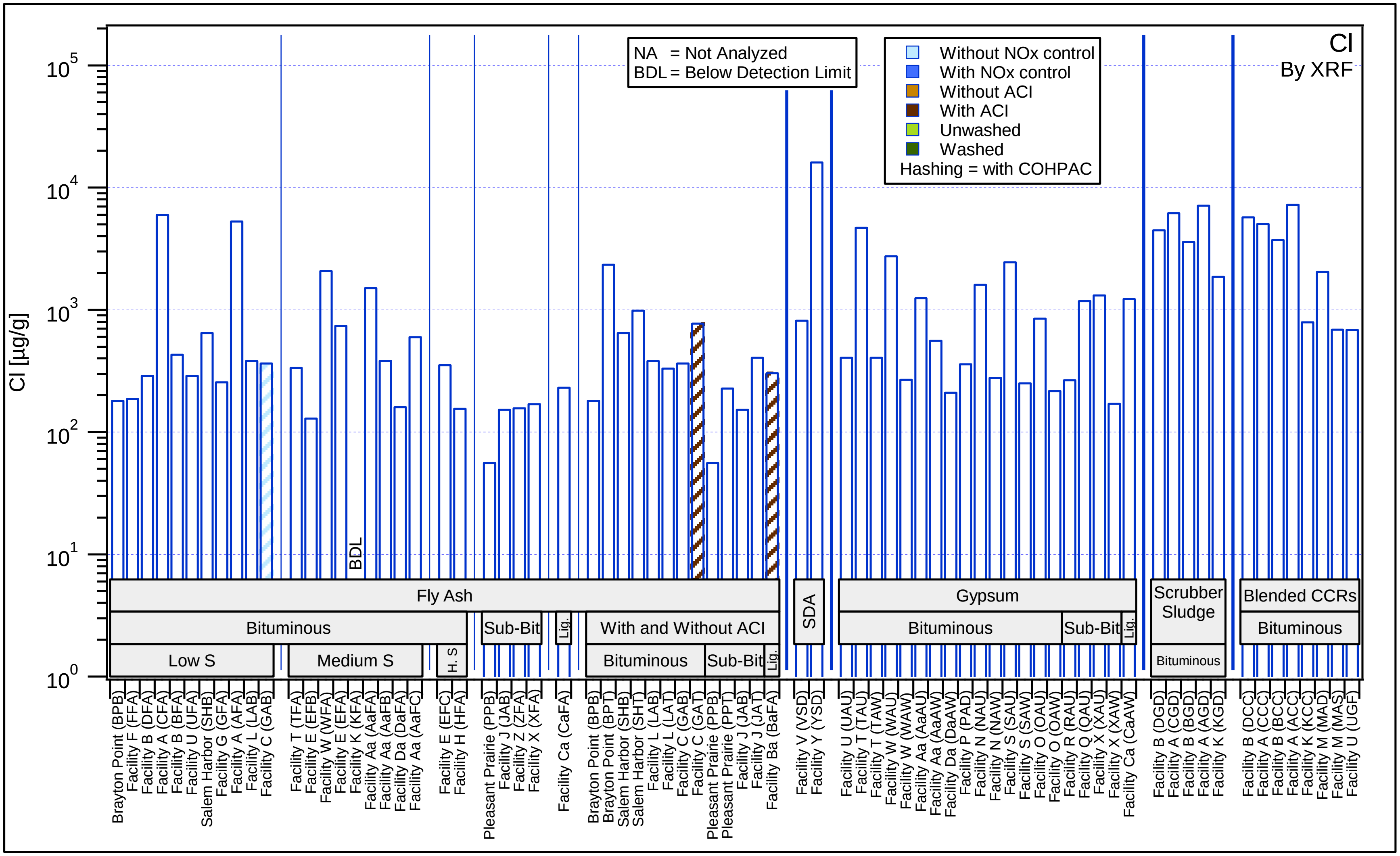

Figure 26. Chloride. Comparison of total elemental content by XRF.

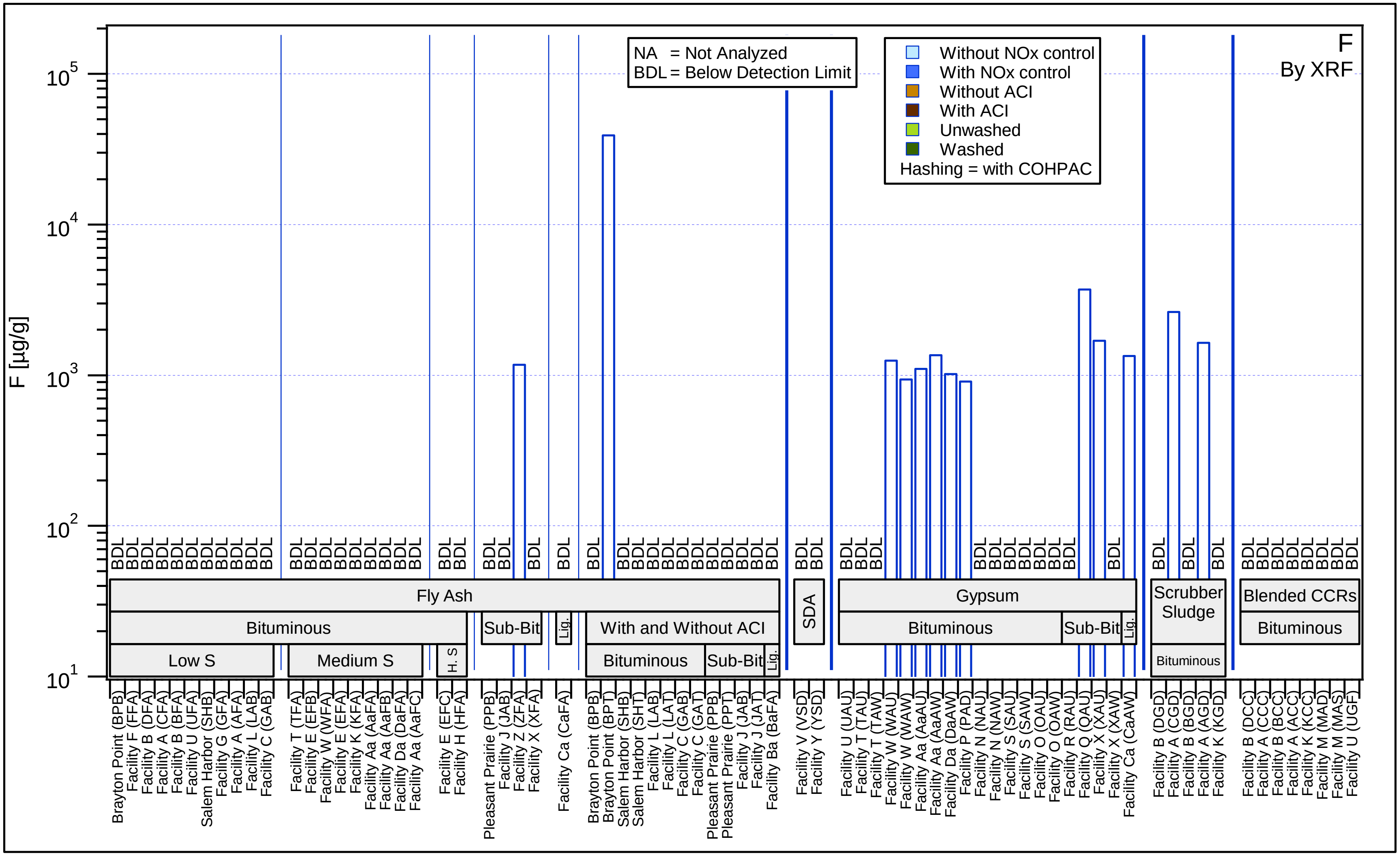

Figure 27. Fluoride. Comparison of total elemental content by XRF.

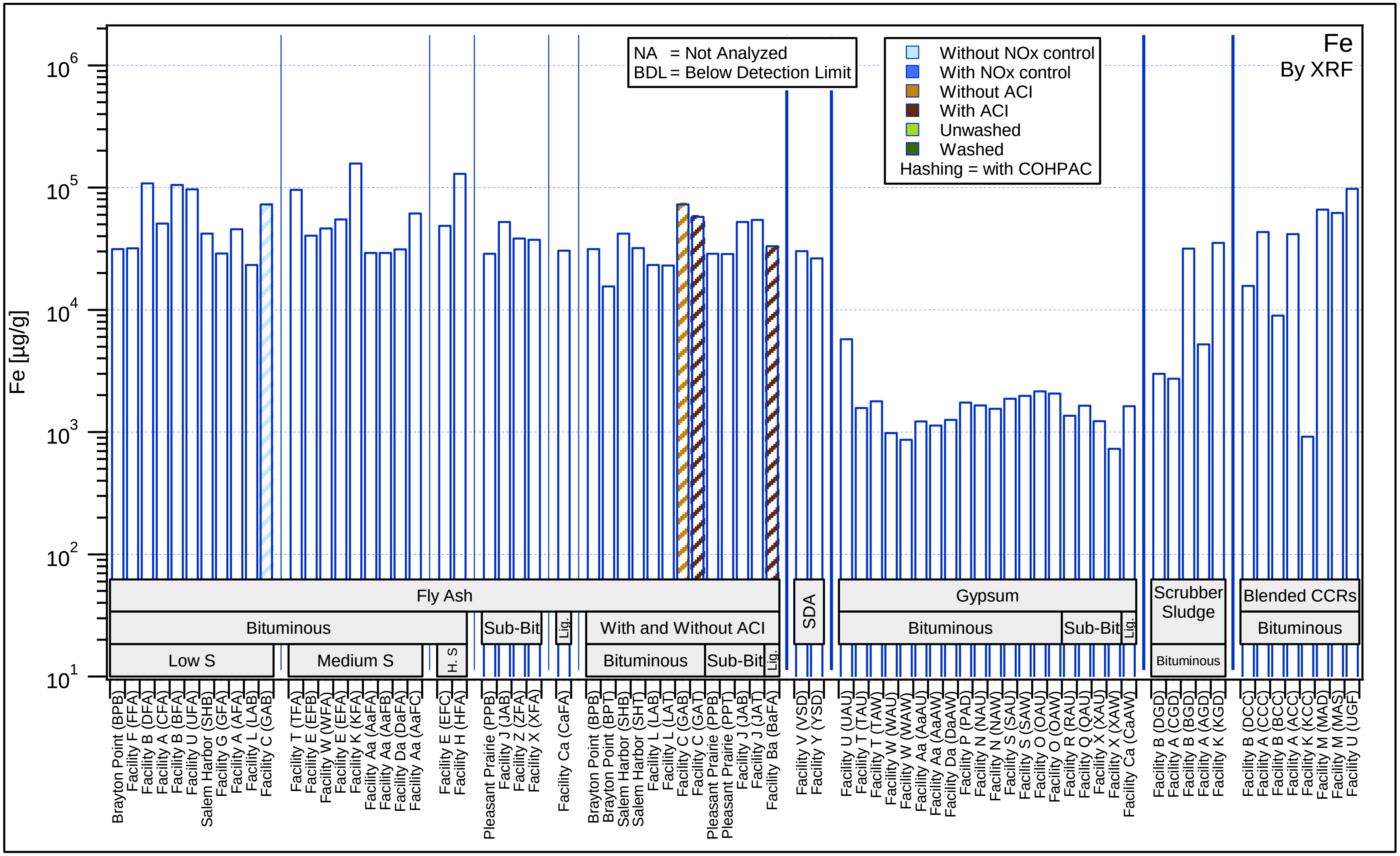

Figure 28. Iron. Comparison of total elemental content by XRF.

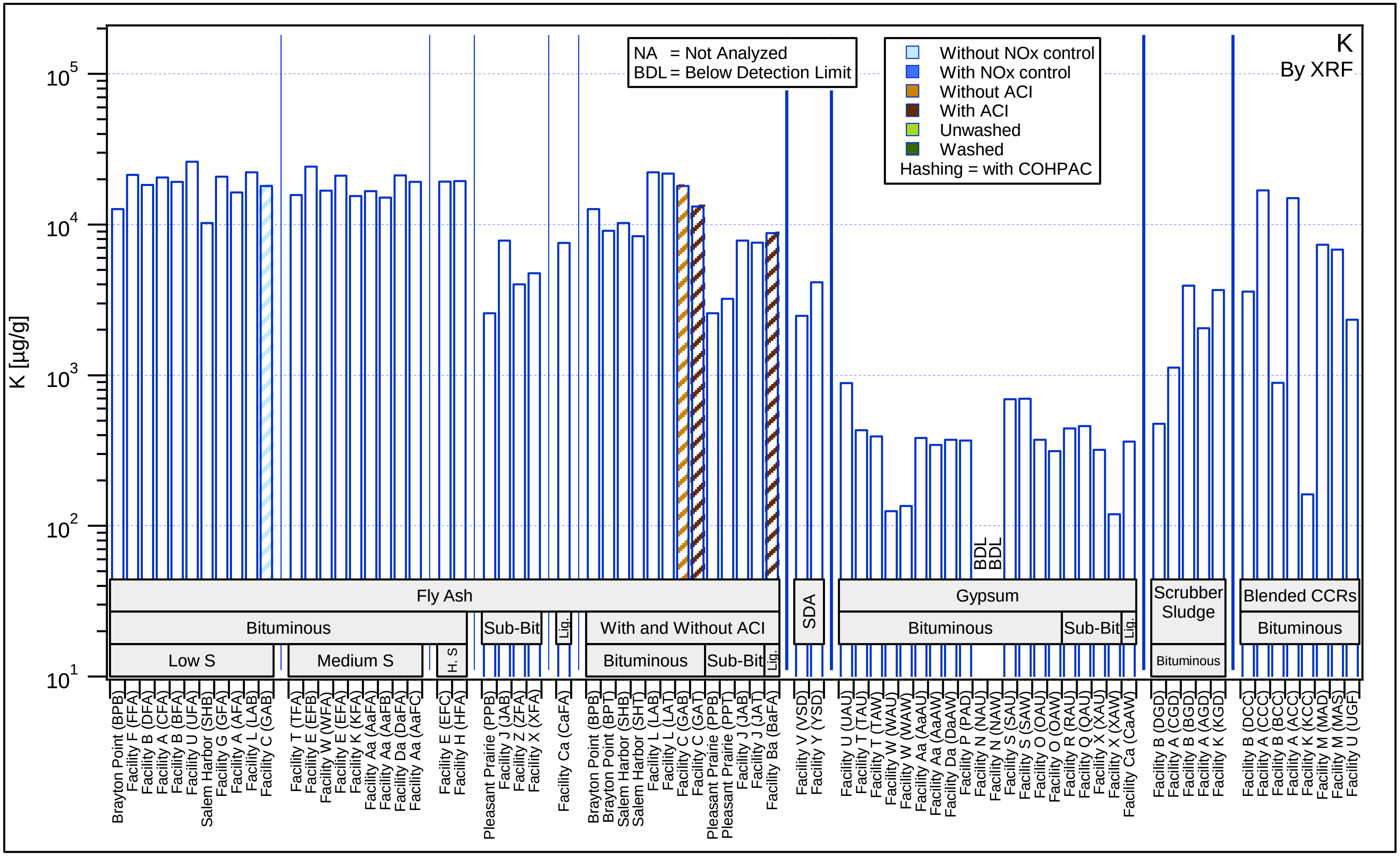

Figure 29. Potassium. Comparison of total elemental content by XRF.

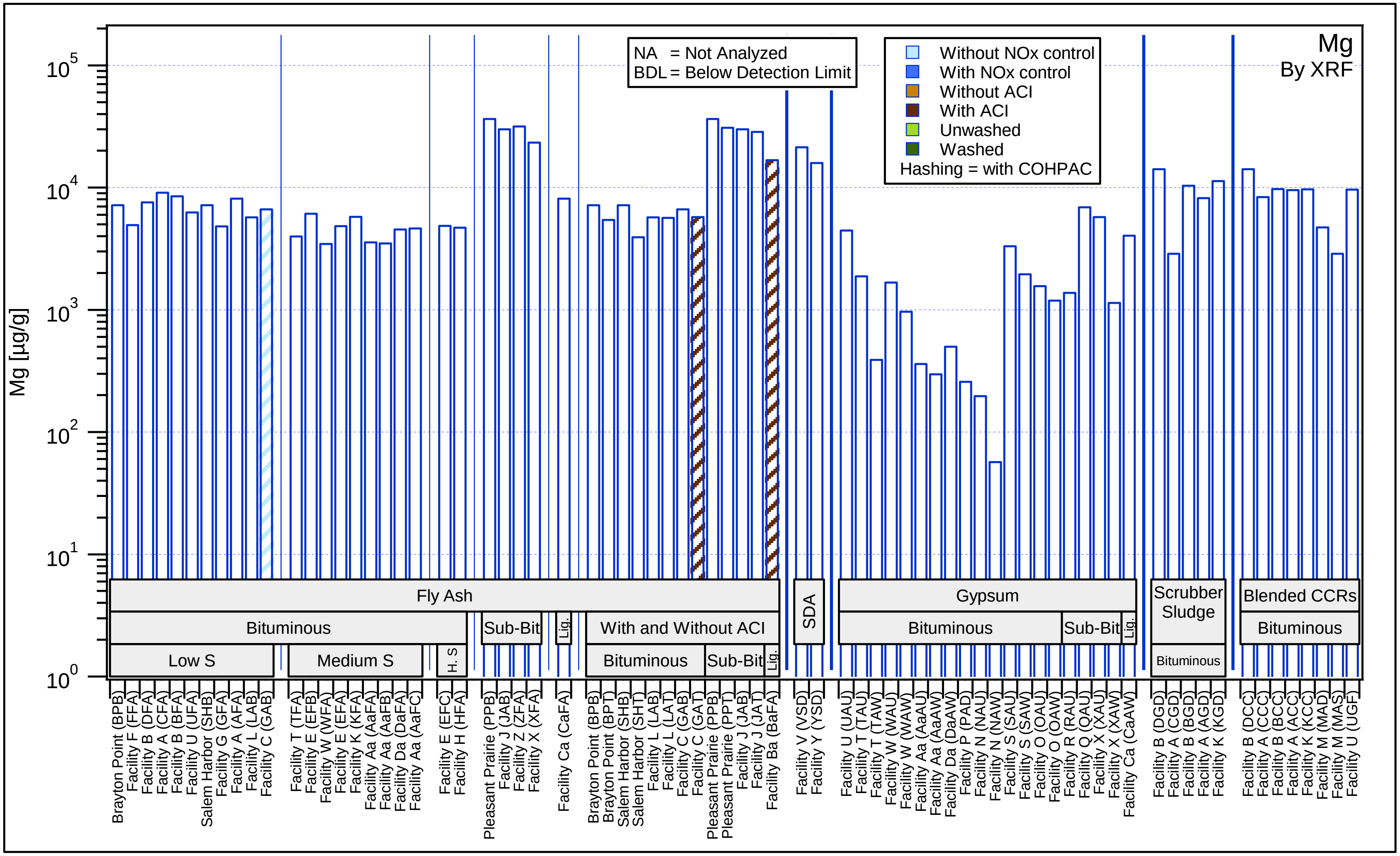

Figure 30. Magnesium. Comparison of total elemental content by XRF.

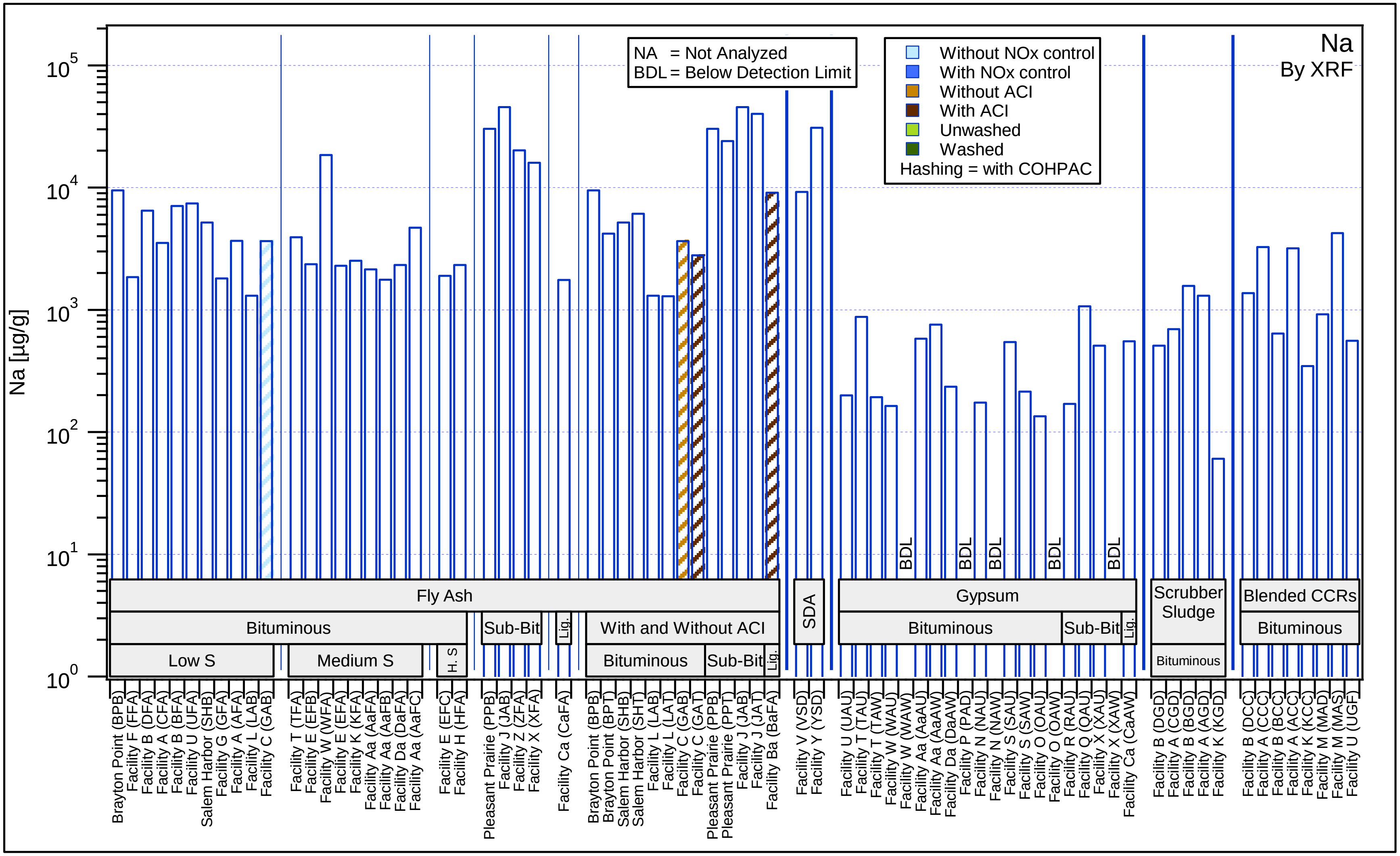

Figure 31. Sodium. Comparison of total elemental content by XRF.

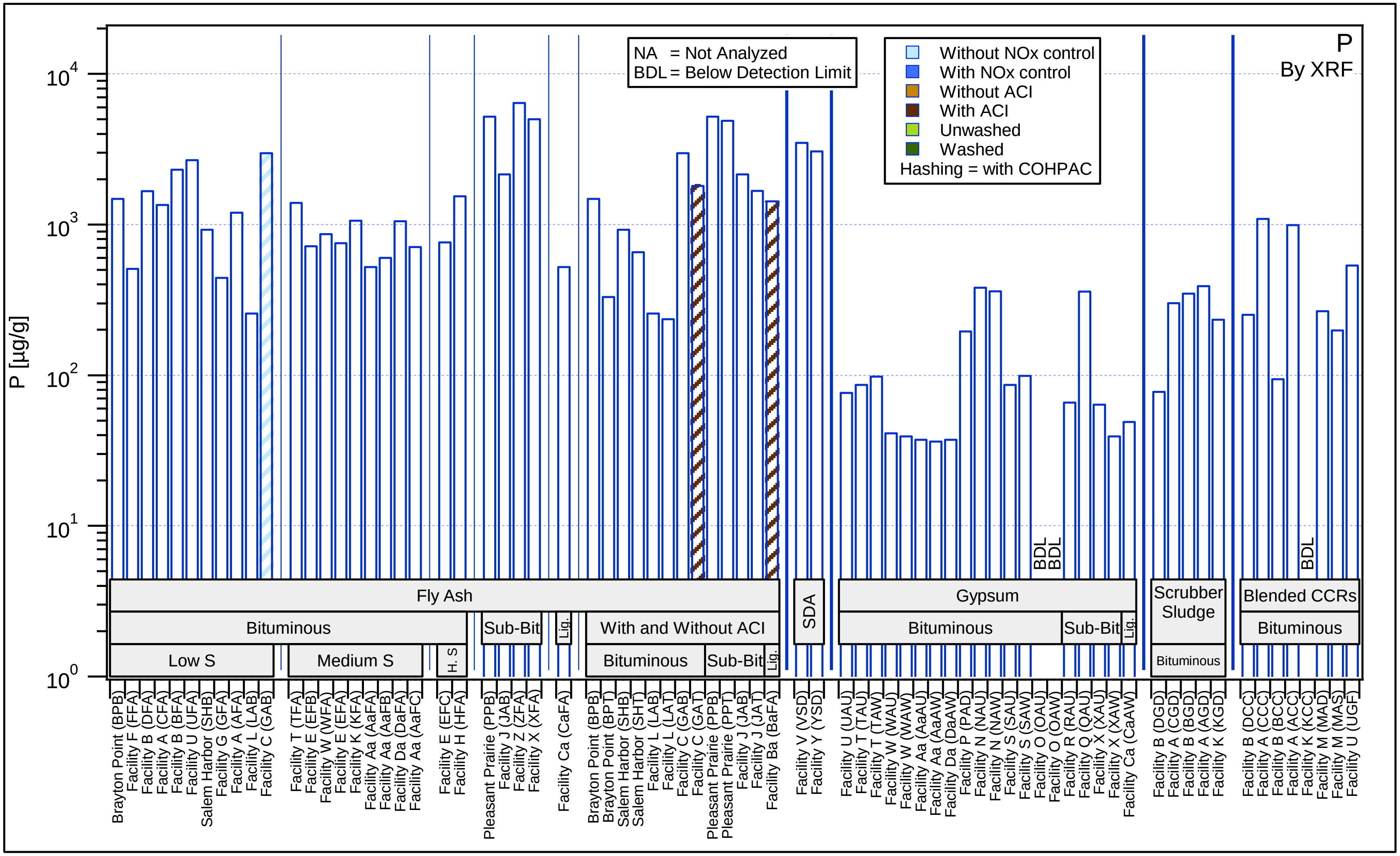

Figure 32. Phosphorous. Comparison of total elemental content by XRF.

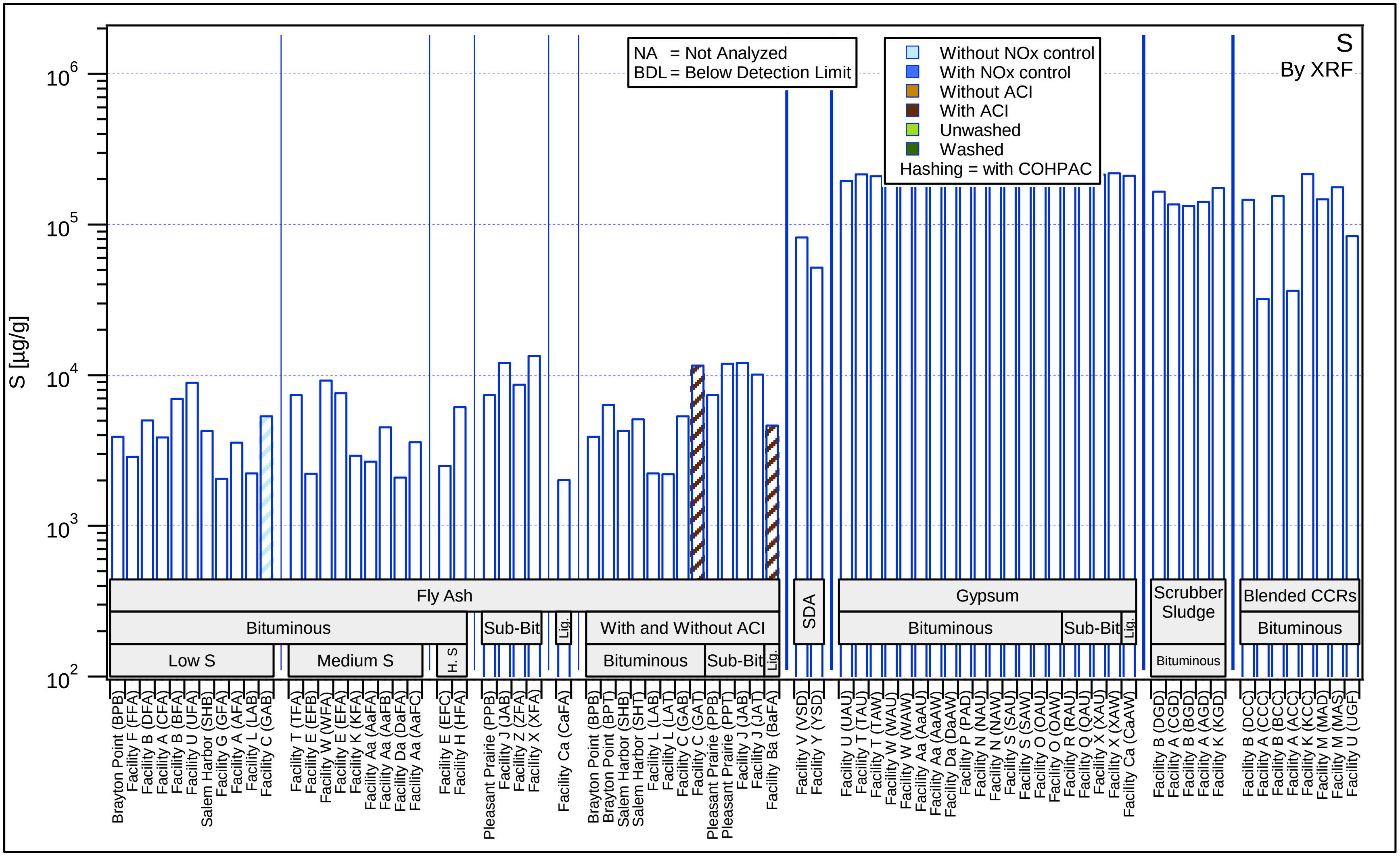

Figure 33. Sulfur. Comparison of total elemental content by XRF.

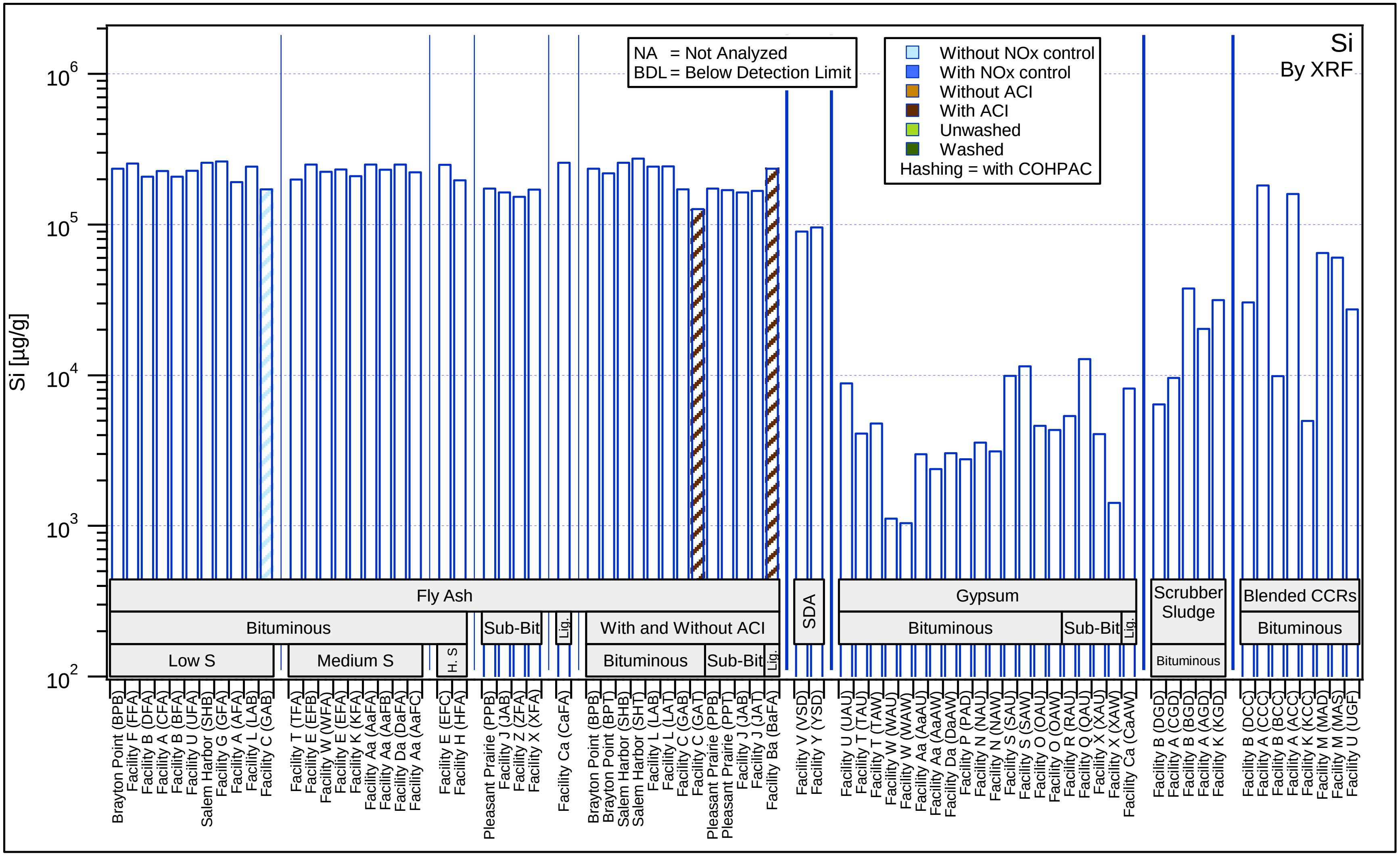

Figure 34. Silicon. Comparison of total elemental content by XRF.

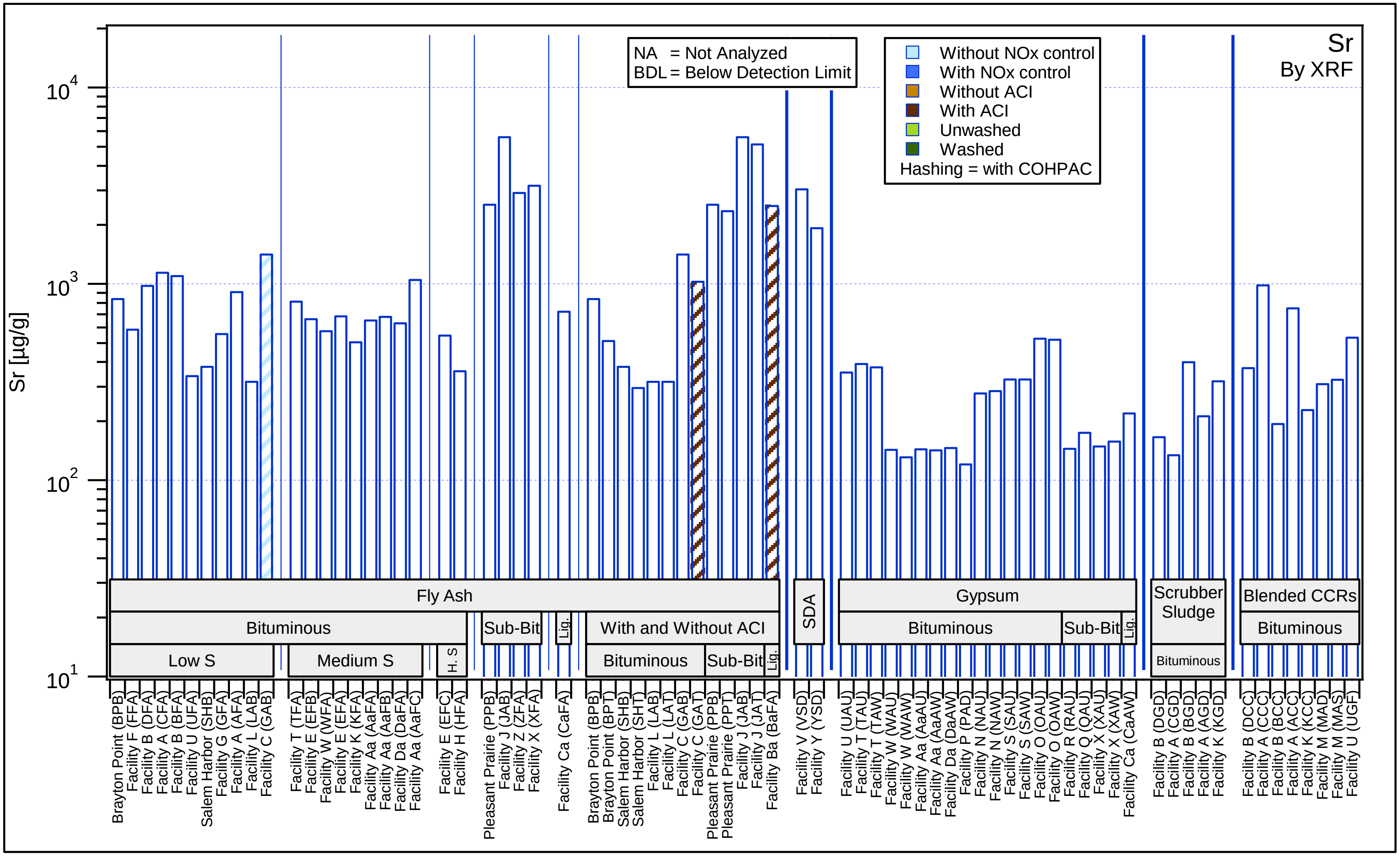

Figure 35. Strontium. Comparison of total elemental content by XRF.

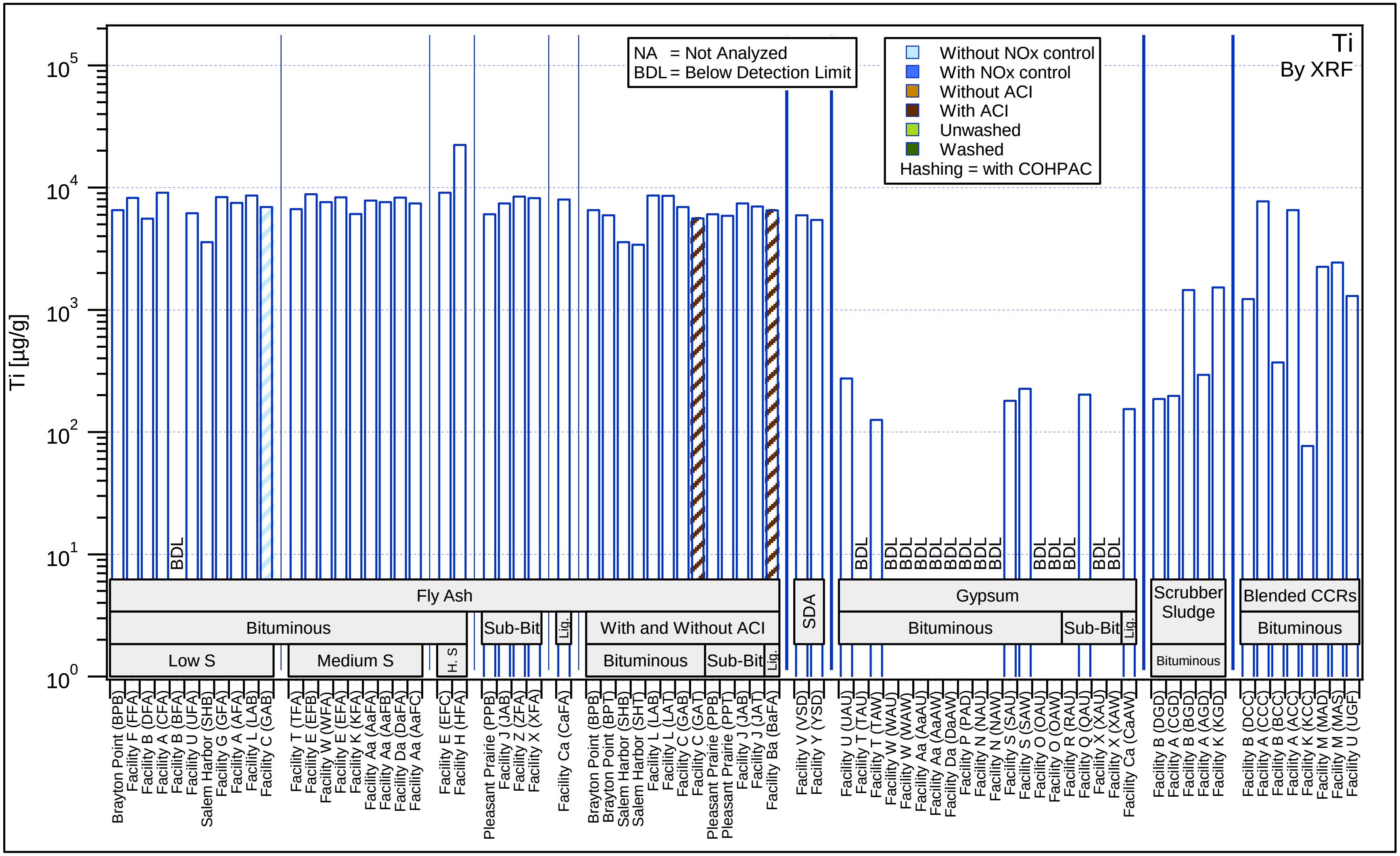

Figure 36. Thallium. Comparison of total elemental content by XRF.

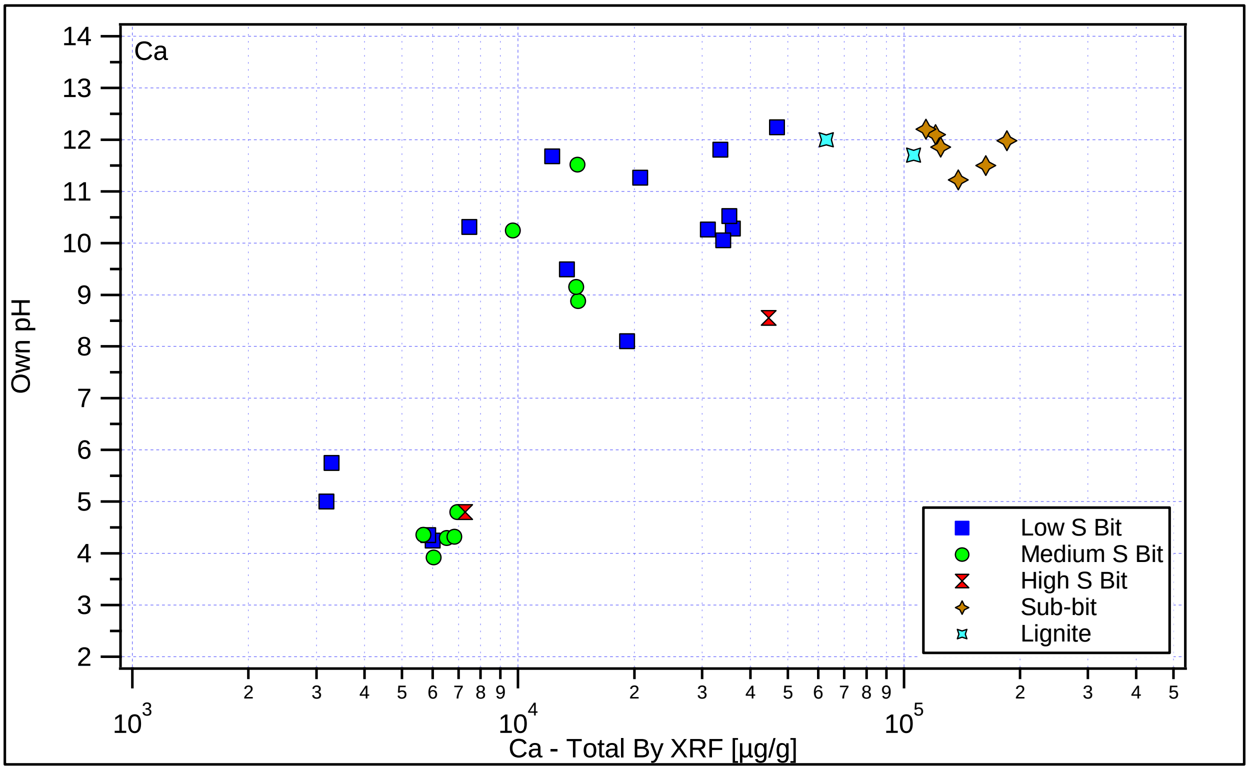

Figure 37. Total calcium content (by XRF) and own pH for fly ash samples.

3.2. LABORATORY LEACHING TEST RESULTS

Appendix F provides graphical presentation of the results of Solubility and Release as a Function of pH (SR002.1) and Solubility and Release as a Function of LS (SR003.1) for the 13 constituents of interest in this report. Results are grouped by facility type and within each facility comparisons are made by CCR type (fly ash without Hg sorbent injection, fly ash without and with Hg sorbent injection pairs, spray dryer, gypsum, scrubber sludge, blended CCRs, and filter cake) and constituent of interest. Appendix G provides graphical presentation of the pH titration curves from test method SR002.1.

Discussed below are:

1. Typical characteristic results for pH and each of the 13 constituents of interest (Section 3.2.1);
2. Comparison of the ranges of observed constituent leaching concentrations from laboratory testing (minimum concentrations, maximum concentrations, and concentrations at the materials' own pH – Section 3.2.2);
3. Comparison of the constituent maximum leaching concentrations and concentrations at the materials' own pH from laboratory testing grouped by material type with measurements reported elsewhere on field leachate and pore water samples for CCR disposal sites and the database used in the EPA Risk Report (EPA, 2007b) (Section 3.2.3); and,
4. pH at the maximum concentration value versus the materials' own pH (Section 3.2.4).

Complete data also have been developed for other constituents (e.g., other ions, DOC, etc.) to facilitate evaluation of geochemical speciation of constituents of concern and provide more thorough evaluation of leaching under alternative management scenarios in the future if warranted.

For each CCR evaluated, results of the leaching tests provide the following information:

- Leachate concentrations for the constituents of interest as a function of pH over the range of reported field management conditions (from test method SR002.1);
- pH titration curves (from test method SR002.1). This information is useful in characterizing the CCR and assessing how it will respond to environmental stresses and material aging (e.g., carbon dioxide uptake, acid precipitation, co-disposal, mixing with other materials); and,
- Leachate concentrations for the constituents of interest and pH as a function of LS ratio when contacted with distilled water (from test method SR003.1). This information provides insight into the initial leachate concentrations expected during land disposal and effects of pH and ionic strength at low LS ratio. Often these concentrations can be either greater than or less than concentrations observed at higher LS ratio (i.e., LS=10 mL/g as used in SR002.1) because of ionic strength and co-constituent concentration effects.

The MCL, DWEL, or AL (for lead) as available is used as a reference value for the constituent of interest. However, laboratory leaching test results presented here are estimates of concentrations potentially leaching from landfills, not the concentrations at potential points of exposure. Any assessment of the environmental impact of these releases needs to consider the dilution and attenuation of these constituents in ground water, and the plausibility of drinking water well contamination resulting from the release. Dilution and attenuation factors for metals (DAFs) have been estimated to be potentially as low as 2 to 10 on a national basis or as high as 8,000 at a particular site with hydrogeology that indicated low transport potential[41]. Therefore, comparison of the laboratory leach test results with thresholds greater than the MCL and developed for specific scenarios may be appropriate.

3.2.1. Typical Characteristic Leaching Behavior as a Function of pH

Comparisons of the leaching behavior as a function of pH for each of the 13 elements of interest are presented in Section 3.2.1.1 for fly ashes without Hg sorbent injection (as a baseline measure), Section 3.2.1.2 for fly ashes without and with Hg sorbent injection pairs, Section 3.2.1.3 for unwashed and washed gypsum, Section 3.2.1.4 for scrubber sludges, Section 3.2.1.5 for spray dryer absorber residues, and Section 3.2.1.6 for blended CCRs (mixed fly ash and scrubber sludge/mixed fly ash and gypsum). These comparisons illustrate on an empirical basis some of the differences in leaching behavior for different CCRs that result from the combination of the coal type combusted and air pollution control configuration used, including particulate control devices (cold-side ESP, hot-side ESP, or fabric filter), NO_x control (none or by passed, SNCR or SCR), and without and with Hg sorbent injection.

These figures illustrate that for a particular constituent, the chemistry controlling release or aqueous-solid equilibrium may be similar within a material type (i.e., mercury behavior for fly ash or scrubber sludge) or across material types (i.e., the same behavior for aluminum in fly ash and blended CCRs) but that there are not necessarily generalized behaviors present for each constituent that are consistent across all samples within a material type or between material types. The most robust groupings of leaching behavior will result from the development of geochemical speciation models of the materials that account for the underlying solid phase speciation (e.g., solid phases, adsorption behavior) and modifying solution characteristics (e.g., dissolved organic matter, pH, ionic strength, co-dissolved constituents). Development of the needed geochemical speciation models, and associated leaching behavior groupings as a function of coal rank, combustion facility design, and CCR type, will be the subject of a subsequent report (Report 4). The resulting models and groupings, in turn, are expected to allow for more detailed constituent release predictions based on limited testing for a broader set of facilities.

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[41] See 60 FR 66372, Dec. 21, 1995, for a discussion of model parameters leading to low DAFs, particularly the assumption of a continuous source landfill. Implied DAFs for the metals of interest here can be found at 60 FR 66432-66438 in Table C-2. Site specific high-end DAFs are discussed in 65 FR 55703, September 14, 2000.

3.2.1.1. Fly Ash without Hg Sorbent Injection

Figure 38 through Figure 40 present comparisons of leaching behavior as a function of pH for fly ash without Hg sorbent injection for each of the 13 elements of interest. Results are organized by coal type: bituminous, low sulfur coal (Figure 38); bituminous, medium and high sulfur coal (Figure 39); and sub-bituminous, sub-bituminous/bituminous mix, and lignite coal (Figure 40).

Figure 41 shows the main characteristic leaching behaviors observed for each element of interest for the different coal types and air pollution control configurations. Figure 42 presents the leaching behavior of calcium, magnesium, iron, strontium, and sulfur, expected to control or have an effect on the chemistry of the materials. Figure 43 illustrates the effect of NO_x controls (none or by-passed, SNCR or SCR) for facilities burning Eastern Bituminous coal and using CS-ESP for particulate control. Figure 44 illustrates the effect of fabric filters versus CS-ESP with and without SNCR for facilities burning Eastern Bituminous coal. Chromium speciation in selected fly ash samples and eluates is shown in Figure 45.

Main characteristics leaching behavior (Figure 41 and Figure 42)

The discussion of the results provided below is solely empirical and intends to show the range of leaching characteristics as a function of pH that were encountered for the fly ash without Hg sorbent injection. Details of speciation are beyond the scope of this report and require development of geochemical speciation models of the materials, which will be part of a subsequent report.

Aluminum (Al). The behavior of Al was generally amphoteric with a broad minimum between $4 < pH < 8.5$ and minima observed at different levels depending upon the ash type. The concentration of the minimum is typically influenced by the amount of DOC complexing aluminum in solution (increased complexation increases dissolved aluminum). Several samples, e.g. UFA, exhibited dramatically decreased leaching at pH > 11.

Arsenic (As). Six different leaching behaviors were observed for As. Sample LAB provides an example of a typical amphoteric behavior with minimum leaching occurring at a pH~5.2. Sample UFA is an example of typical oxyanionic behavior with increasing As concentration as pH decreased from *ca*. 10.5 to less than 3. Sample GAB shows an example where As concentration peaked at pH~8, which was, in this case, most likely a consequence of the presence of the COHPAC. Sample ZFA shows an example where As release was below the MDL for all pHs and was representative of the sub-bituminous and sub-bit/bituminous mix coal, reflecting the relatively high total content of calcium and magnesium of this coal type compared to the other coal types. Sample AaFC also showed amphoteric behavior but was distinctly different from that of sample LAB. Sample AFA also showed oxyanionic behavior but at a lower concentration level than sample UAF. As concentrations were at or above the MCL value for most pHs, except for the sub-bituminous coal, e.g. ZFA, for which arsenic concentrations were below the MDL across the full pH range examined.

In general, As leaching behavior had been reported to be influenced by precipitation/co-precipitation with group II elements (Mg, Ca, Ba, and Sr) and precipitation/adsorption onto iron oxide (Drahota et al., 2009; Mohan et al., 2007). Figure 42 presents the characteristic leaching behavior of these constituents, which shows significant differences between ash types. Sample ZFA had overall the greatest concentrations of group II elements while sample LAB had the lowest concentrations of group II elements. As a general observation, the bituminous coal fly ashes having a low own pH and corresponding to eluate calcium concentrations of less than 120 mg/L, tended to exhibit amphoteric behavior. Detailed mechanistic evaluation is, however, beyond the scope of this report and will be addressed in Report 4.

Boron (B). Most samples showed relatively constant boron concentrations for pH < 10.5 with a few samples, e.g. AFA, showing a decrease in B eluate concentration with increasing pH for pH > 8. In general, samples with decreasing concentration for pH>8 were those with higher own pH and eluate calcium concentration greater than 120 mg/L. B is highly soluble at neutral to acidic pHs and as a result observed B concentrations were most likely controlled by the total B content of the material.

Barium (Ba). All samples showed a similar leaching behavior of Ba with the exceptions of samples ZFA and XFA for which a much greater release of barium was observed, in agreement with a much greater Ba content for these samples (as much as 12 times greater than for the other samples). All own pH results were less than the MCL except for the sub-bituminous and lignite coal samples.

Cadmium (Cd). Typical behavior of increasing eluate concentration with decreasing pH for pH<5 was observed for Cd for most cases except for sample AFA that showed increasing eluate concentration with decreasing pH for pH < 8.

Cobalt (Co). Cobalt leaching behavior was similar for all samples tested with minimum values observed for pH > 11, an increase in eluate concentration with decreasing pH for pH < 11, and a maximum concentration reached for pH less than 5.

Chromium (Cr). Three different leaching behaviors were observed for Cr: (i) amphoteric behavior (e.g., UFA and AaFC), (ii) relatively constant concentration for pH>5 with an increase in concentration for pH < 5 (e.g., AFA and GAB) [Both have fabric filter (one fabric filter and one COHPAC)], and (iii) concentration peaking at 8 < pH < 10 with low concentrations at both low and high pH values (e.g., ZFA, typical for all sub-bituminous coal and sub-bit/bituminous mix samples). The amphoteric behavior was typical for all bituminous coal samples with the exceptions of the samples where SCR or SNCR resulted in elevated ammonia concentrations (e.g., BFA) and the samples where a fabric filter (e.g., CFA) or COHPAC (GAB) was used.

Mercury (Hg). Three different leaching behaviors were observed for Hg: (i) an increasing concentration peaking at pH~8 (e.g., AFA), most likely indicative of ammonium complexation from the use of SNCR (Wang et al., 2007), (ii) an increasing concentration with decreasing pH for pH < 5 with a peak concentration at pH~3.8 and a relatively constant concentration for pH > 5.5 (e.g., GAB, most likely, in this case, a consequence from the use of HS ESP with COHPAC), and (iii) concentrations below the MDL for most pHs (e.g., ZFA and UFA).

Molybdenum (Mo). All bituminous coal and lignite samples, except when SCR or SNCR resulted in elevated ammonia (e.g., AFA), showed relatively constant concentrations with a decrease at pH < 7 (e.g., GAB and LAB) or pH < 4 (UFA) followed by an increase. As with Hg, sample AFA exhibited a Mo concentration peaking at pH~8, most likely indicative of ammonium complexation from the use of SNCR in conjunction with fabric filter. As with Cr, all sub-bit/bituminous mixes showed an increased Mo concentration peaking at pH~8 (e.g., ZAF).

Lead (Pb). Minimal lead leaching was observed. In all cases, lead leaching was below the MDL between pH 4 and 12. For some samples, e.g. AaFC, typical amphoteric behavior was observed with increased concentrations for pHs above 12 and below 4.

Antimony (Sb). Several leaching behaviors were observed for Sb: (i) a decreasing concentration with decreasing pH (e.g., LAB), (ii) an increasing concentration with decreasing pH (e.g., UAF), (iii) concentrations below the MDL over the entire pH range (e.g., ZFA), (iv) a concentration peaking at pH~8 (e.g., AFA), most likely indicative of ammonium complexation from the use of SNCR, and (v) concentrations peaking at $7 < pH < 10$ (e.g., GAB)

Selenium (Se). Four different leaching behaviors were observed for Se. Sample LAB provides an example of typical amphoteric behavior with minimum leaching occurring at $5<pH<6$. Sample GAB illustrates an example of decreasing leaching with decreasing pH while sample ZAF is an example of increasing leaching with decreasing pH. Sample AFA shows an example of increasing concentration peaking at pH~8, most likely indicative of ammonium complexation from the use of SNCR. In most cases, Se concentrations were above the MCL.

Thallium (Tl). Two different leaching behaviors were observed for Tl: (i) increasing concentration with decreasing pH at $pH < 12$ (e.g., UAF and AaFC), $pH < 9$ (e.g., AFA), or $pH < 7$ (e.g, LAB and ZFA) and (ii) relatively constant concentration with an increase at $pH < 7$ (e.g., GAB).

Effect of coal type (Figure 38, Figure 39, and Figure 40)

In general, the bituminous coal samples and the lignite sample (CaFA) behaved similarly with respect to leaching while the sub-bituminous coal and sub-bit/bituminous mix exhibited a significantly different behavior for most elements of interest. A greater release of group II elements (Mg, Ca, Ba, and Sr) was generally observed for the sub-bituminous coal and sub-bit/bituminous mix samples compared to the bituminous coal and lignite samples, in agreement with an overall greater total content of these elements for the sub-bituminous coal and sub-bit/bituminous mix.

Effect of NO_x control (SNCR vs. SCR, Figure 43)

The effect of NO_x control (none or by passed, SNCR or SCR) was examined for the facilities burning Eastern Bituminous coal and using CS-ESP for particulate control. No significant effect on the leaching behavior could be attributed to the presence of SCR or SNCR except one where a pairwise comparison (with and without NO_x control at the same facility) was possible. For Facility B, an increase in Cr and Co with SCR was observed (BFA *vs*. DFA), when NO_x control was in use. This observation and the Cr leaching observed across the set of facilities is likely the result of complex phenomena associated with gas conditioning (addition of ammonia or sulfuric acid) to improve particulate capture, such as for coals with low sulfur and high calcium, and ammonium residual from NO_x control.

Effect of fabric filter vs. CS-ESP (Figure 44)

The effect of fabric filter *vs*. CS-ESP with and without SNCR was examined for the facilities burning Eastern Bituminous coal. An effect was seen only on Cr, Hg, Co, and Mo concentrations with an increase in the release in some cases by a factor much greater than 10 (e.g., Cr from CFA vs. FFA, DFA, TFA, and EFB). The effect of ammonia complexation from the use of SNCR was seen with an increase in Hg and Mo concentrations peaking at pH~8 (AFA).

Chromium speciation in selected fly ash samples and eluates (Figure 45)

Chromium leaching as a function of pH (SR002.1) was analyzed for all samples. Leaching results for samples from selected facilities are provided in Figure 45 to illustrate (i) comparative results from the sample facility operated without and with NO_x controls and bituminous coal (Facility A, SCR-BP and SCR on [samples CFA and AFA, respectively] and Facility B, SNCR-BP and SNCR on [samples DFA and BFA, respectively]), and (ii) for a facility with relatively high chromium leaching but not having NO_x controls and burning sub-bituminous coal (Facility J, sample JAB). Initial review of these results suggested that fly ash samples obtained from facilities with NO_x controls (i.e., SNCR or SCR) resulted in higher chromium concentrations in the leachates as a consequence of the NOx controls. Leaching results as a function of pH also indicated concentration profiles indicative of Cr(VI) leaching. Selected fly ash samples were leached using the SR002.1 procedure at subset of desired endpoint pH values, with the resulting eluates analyzed directly to differentiate between Cr(III) and Cr(VI) in solution. Results of solution phase chromium speciation are provided in a tabular format in Appendix H, and plotted along with the initial SR002.1 results in Figure 45. Chromium speciation in the solid phase of fly ash samples was also confirmed using X-ray absorption fine structure spectroscopy (XAFS; Appendix H). Results of these analyses indicate:

1. Comparison of leaching of the same samples from facilities without and with NO_x controls indicated higher chromium concentrations in eluates when NO_x controls were in use. However, direct comparisons are limited to two facilities and a similar range of leaching results was observed for other facilities that both did and did not have post-combustion NO_x controls.
2. For all of the cases except one examined, the chromium in eluates at pH > 7 was determined to nearly 100 percent Cr(VI), within the uncertainty of the analytical method.
3. The amount of chromium leached under the test conditions and pH > 5 is a small fraction (< 1% up to <10 %) of the total chromium present in the solid phase.
4. The amount of the chromium present in the solid phase as Cr(VI) is on the same order of magnitude as the amount of Cr(VI) leached at neutral to alkaline pH but precise quantification by XAFS is uncertain.

It is hypothesized that residual ammonia injected as part of NO_x controls or to facilitate particulate capture by ESPs may play a role in solubilizing Cr(VI) in the fly ash. If this is the case, it would explain why samples BFA and AFA had relatively less chromium leaching when analyzed after several months of storage in comparison to testing recently sampled fly ash. The expected cause would be loss of ammonia during sample storage. However, although this mechanism is consistent with operations of air pollution control devices (EPRI, 2008) and residual ammonia observed, ammonia content was not measured in CCR samples for this study.

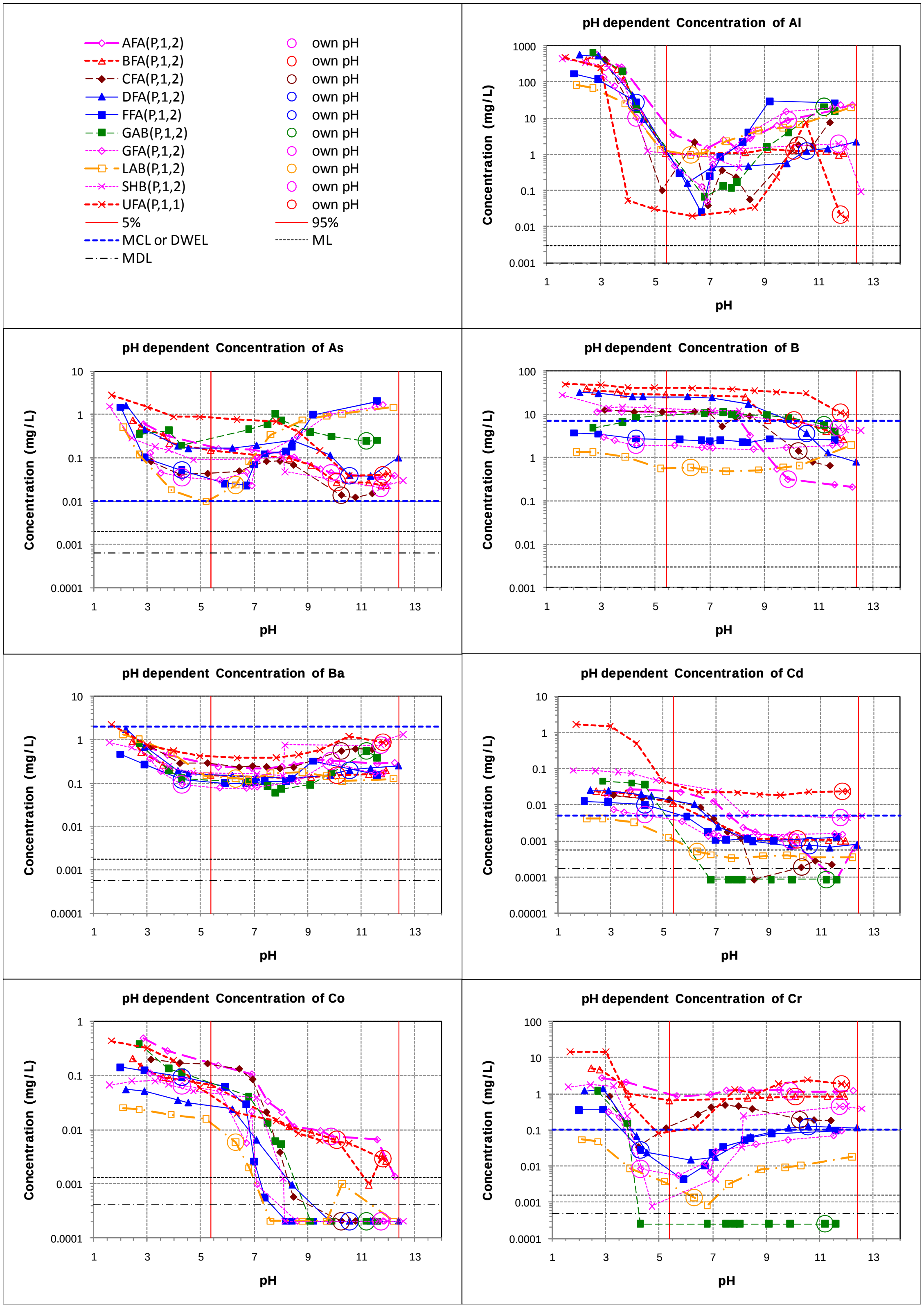


Figure 38. pH dependent leaching results. Fly ash samples from facilities without mercury sorbent injection [bituminous low sulfur coal]. Facility A (AFA, CFA), Facility B (BFA, DFA), Facility C (GAB), Facility G (GFA), Facility L (LAB), Salem Harbor (SHB).

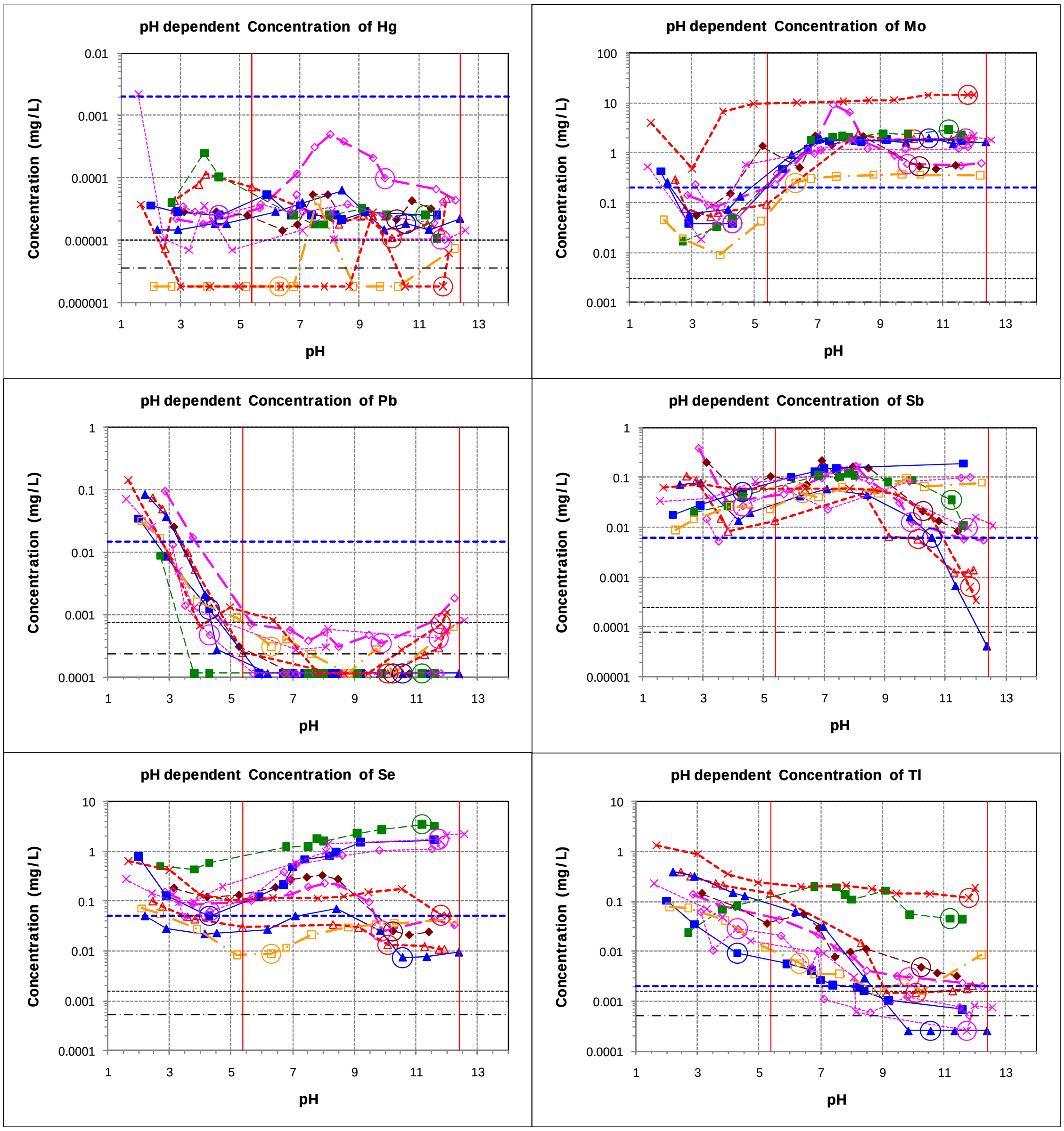


Figure 38 (continued). pH dependent leaching results. Fly ash samples from facilities without mercury sorbent injection [bituminous low sulfur coal]. Facility A (AFA, CFA), Facility B (BFA, DFA), Facility C (GAB), Facility G (GFA), Facility L (LAB), Salem Harbor (SHB).

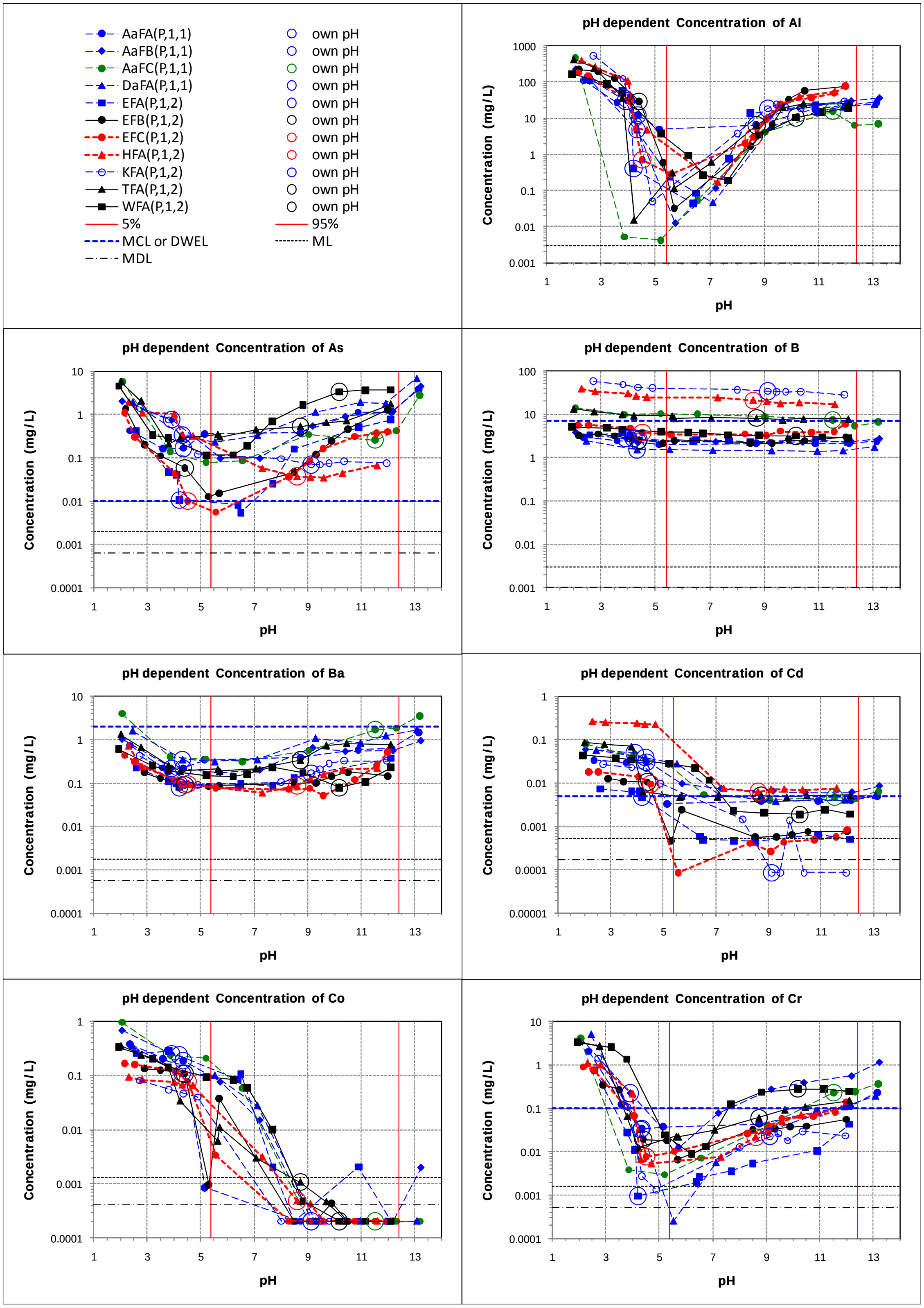


Figure 39. pH dependent leaching results. Fly ash samples from facilities without mercury sorbent injection [bituminous medium and high sulfur coal]. Facility E (EFA, EFB), Facility K (KFA), Facility T (TFA), Facility W (WFA), Facility Aa (AaFA, AaFB, AaFC), Facility Da (DaFA).

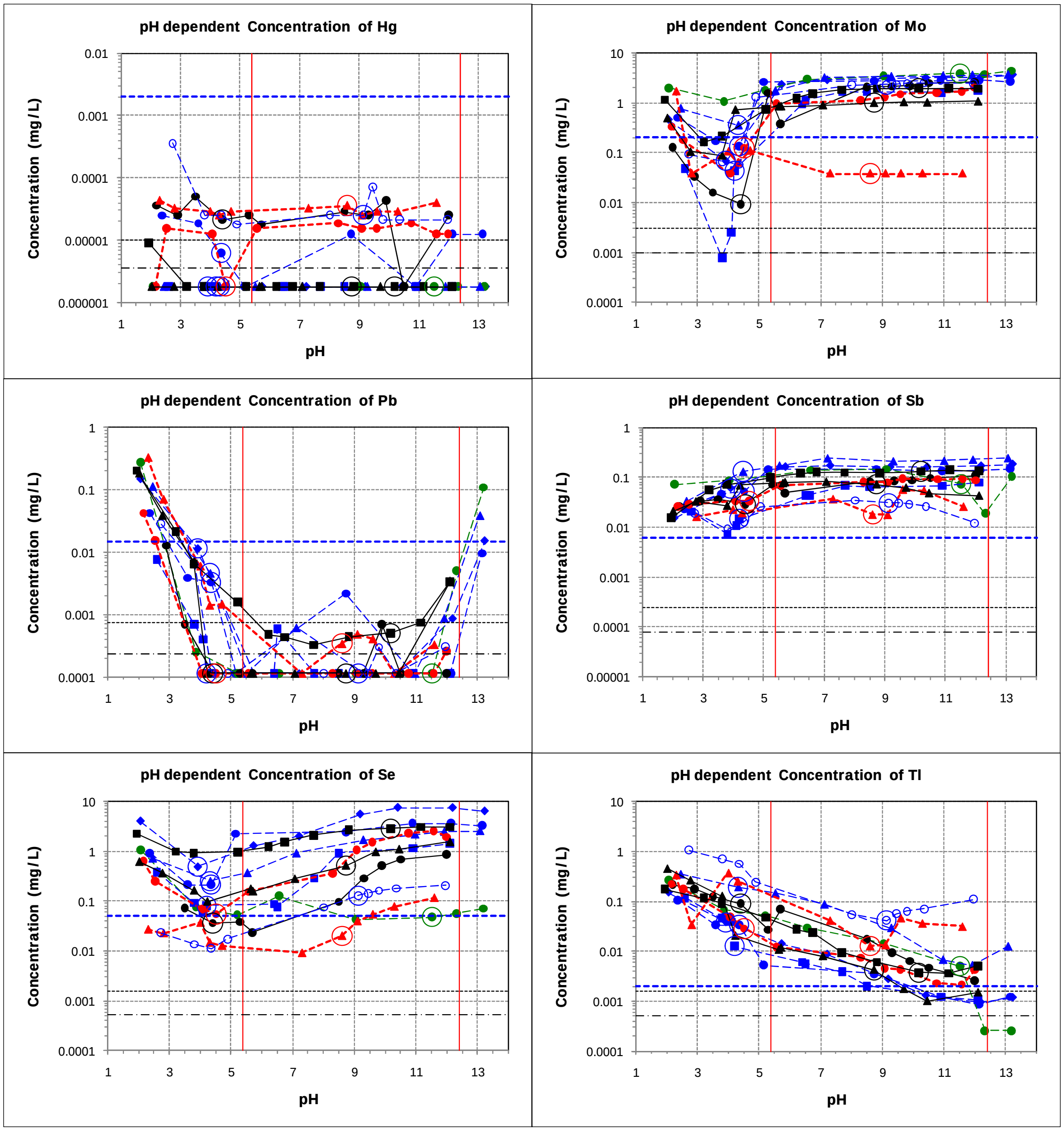


Figure 39 (continued). pH dependent leaching results. Fly ash samples from facilities without mercury sorbent injection [bituminous medium and high sulfur coal]. Facility E (EFA, EFB), Facility K (KFA), Facility T (TFA), Facility W (WFA), Facility Aa (AaFA, AaFB, AaFC), Facility Da (DaFA).

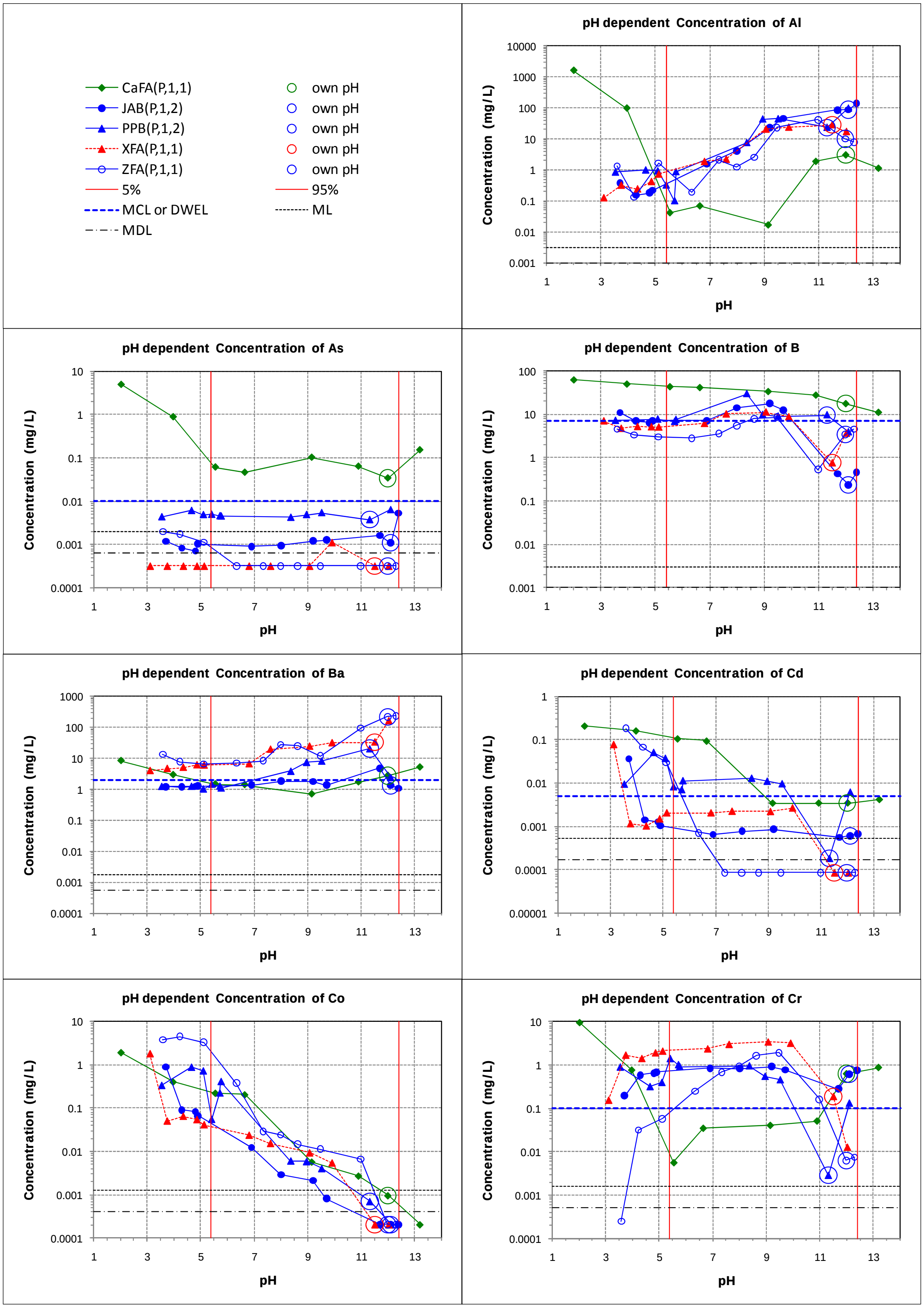


Figure 40. pH dependent leaching results. Fly ash samples from facilities without mercury sorbent injection [sub-bituminous and lignite coal]. Sub-bituminous: Facility J (JAB), Facility X (XFA), Facility Z (ZFA), Pleasant Prairie (PPB). Lignite: Facility Ca (CaFA).

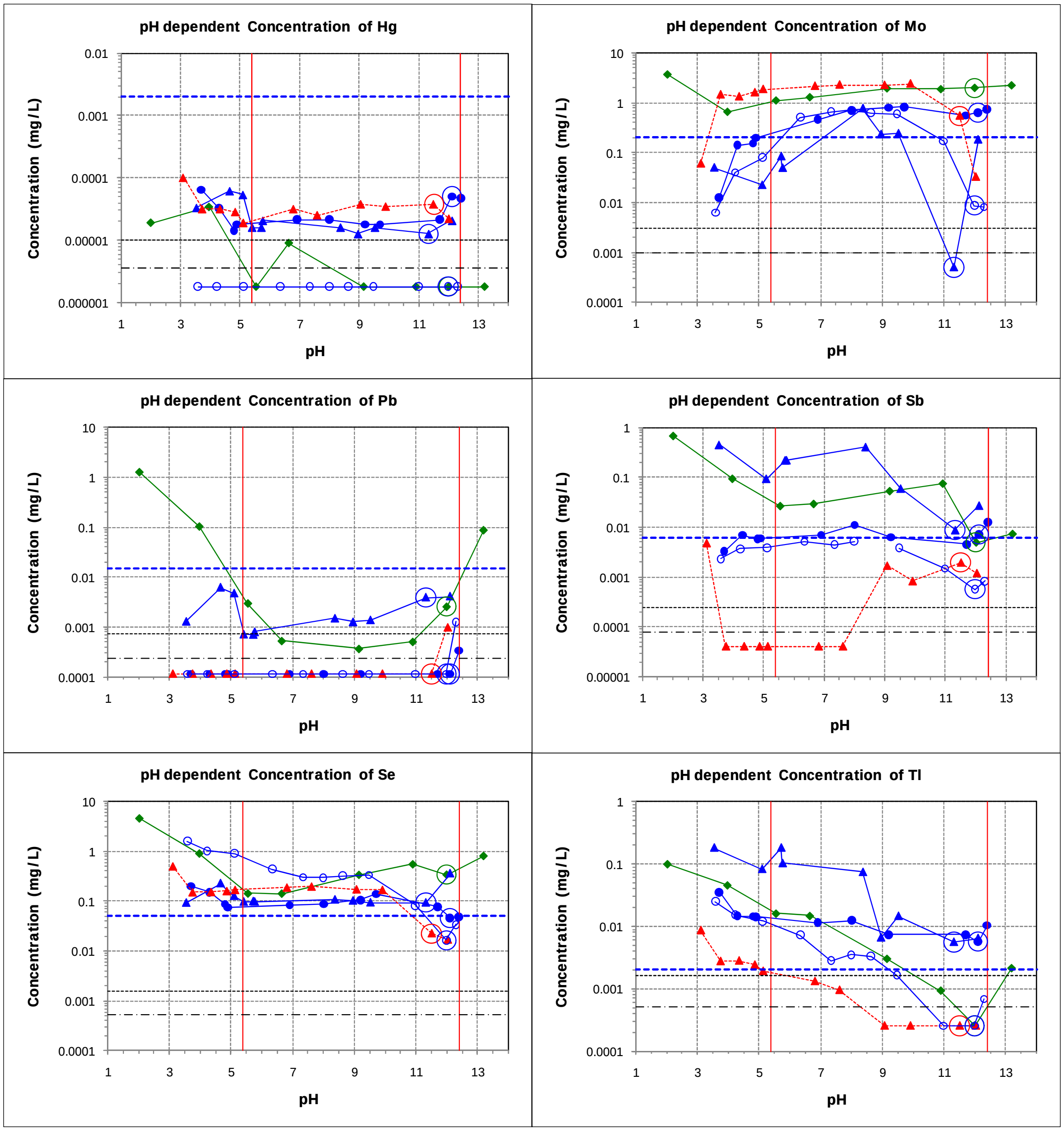


Figure 40 (continued). pH dependent leaching results. Fly ash samples from facilities without mercury sorbent injection [sub-bituminous and lignite coal]. Sub-bituminous: Facility J (JAB), Facility X (XFA), Facility Z (ZFA), Pleasant Prairie (PPB). Lignite: Facility Ca (CaFA).

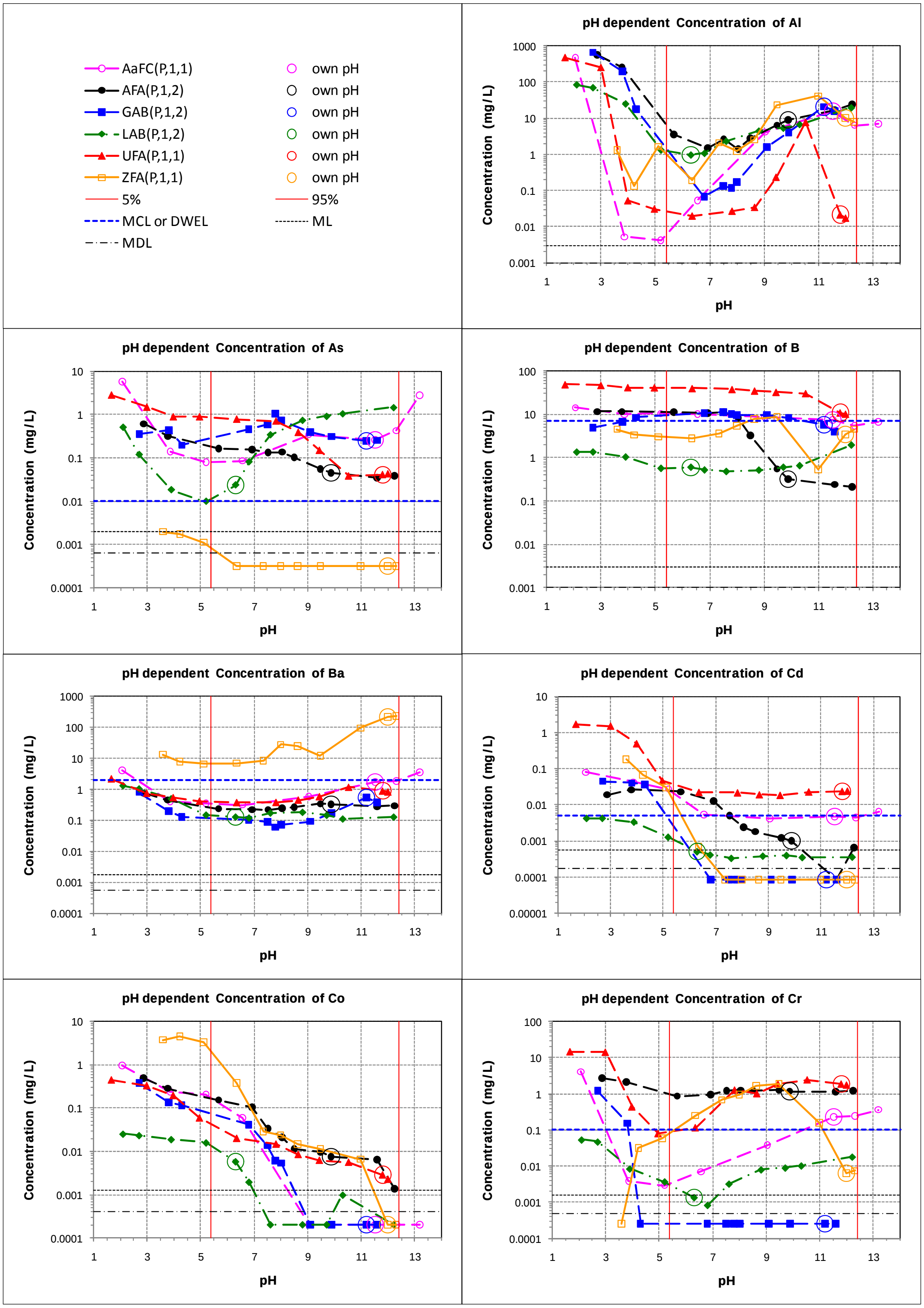


Figure 41. pH dependent leaching results. Selected results to illustrate characteristic leaching behavior.

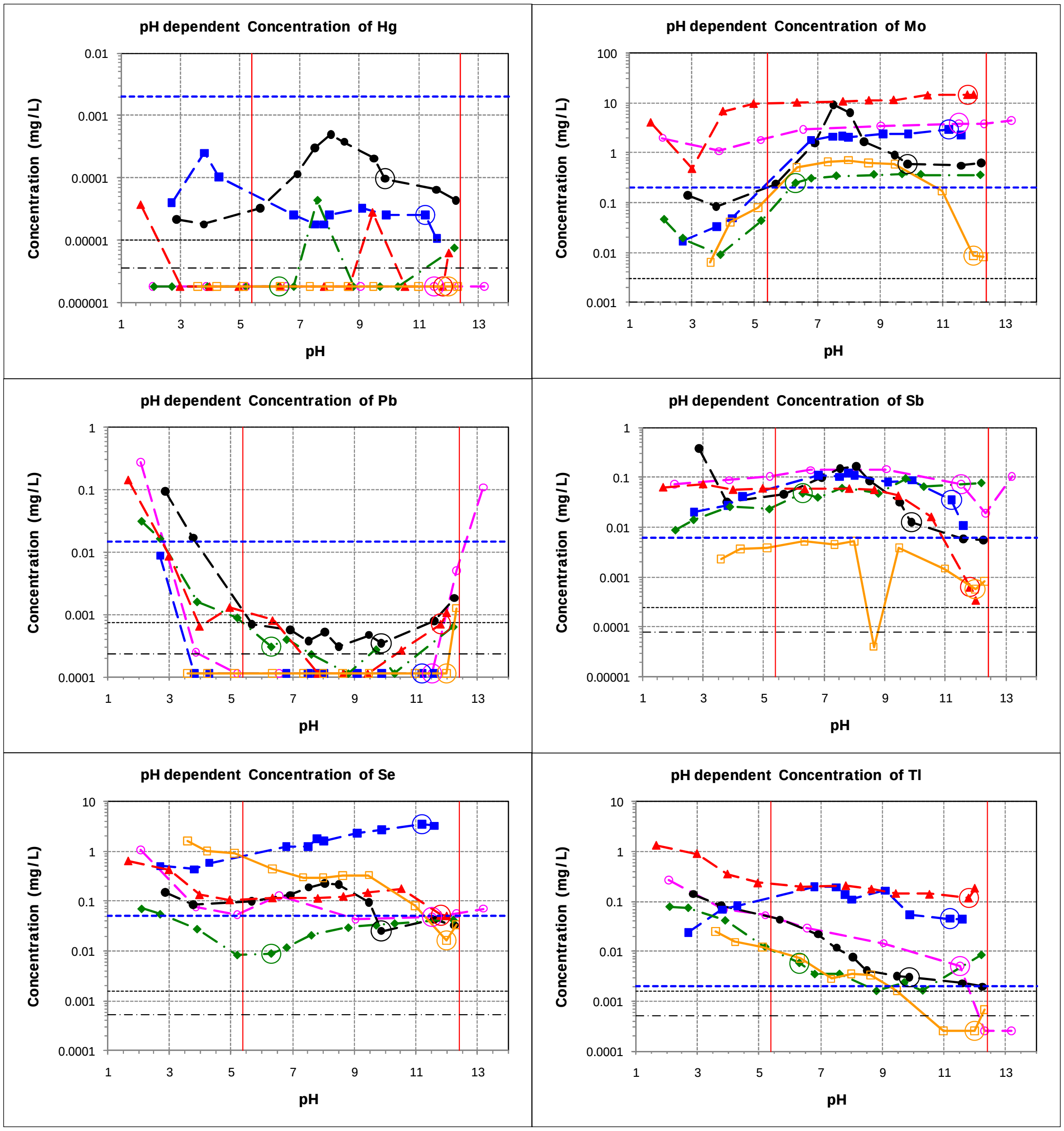


Figure 41 (continued). pH dependent leaching results. Selected results to illustrate characteristic leaching behavior.

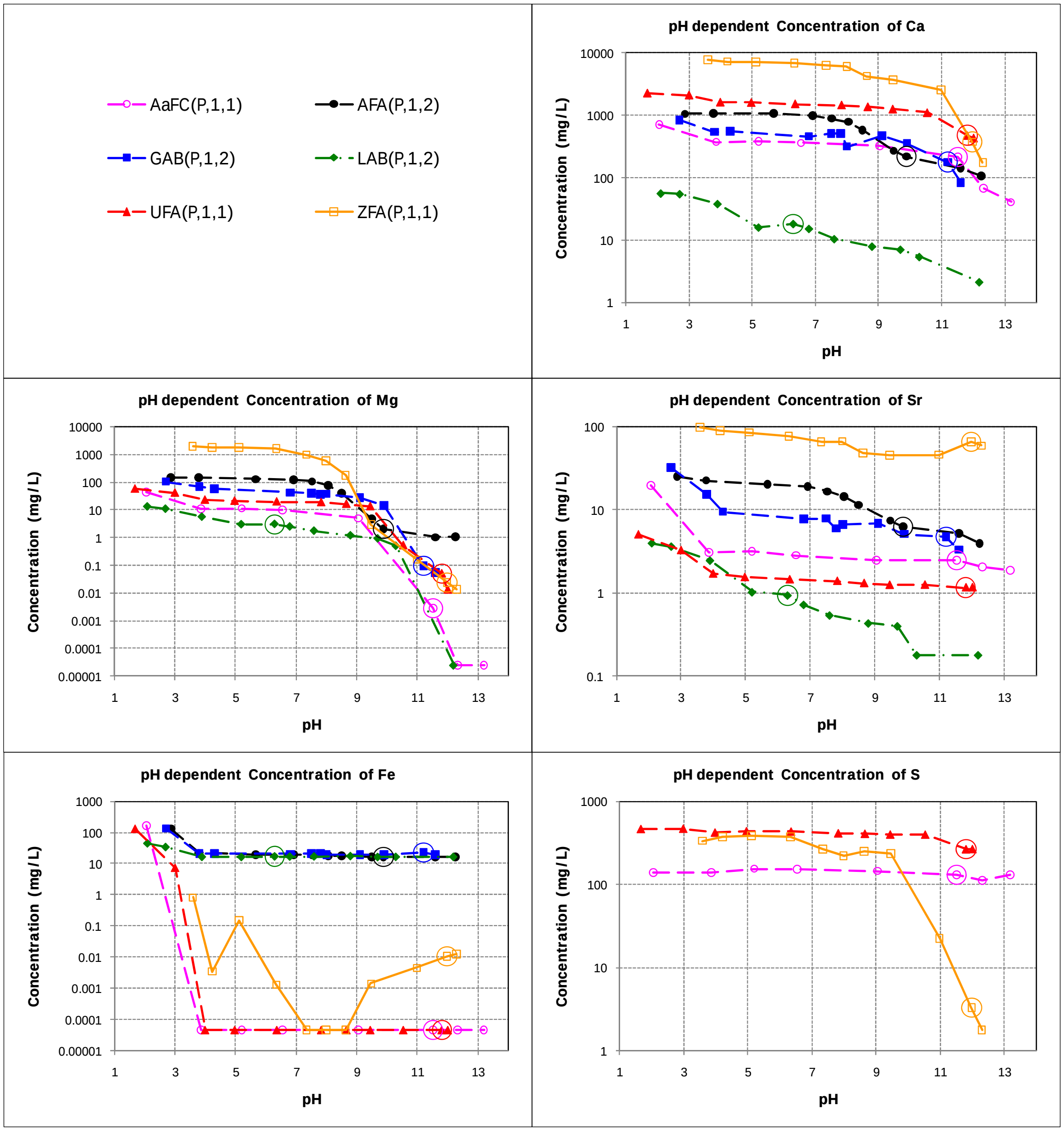


Figure 42. pH dependent leaching results. Selected results to illustrate characteristic leaching behavior of calcium, magnesium, strontium, iron, and sulfur.

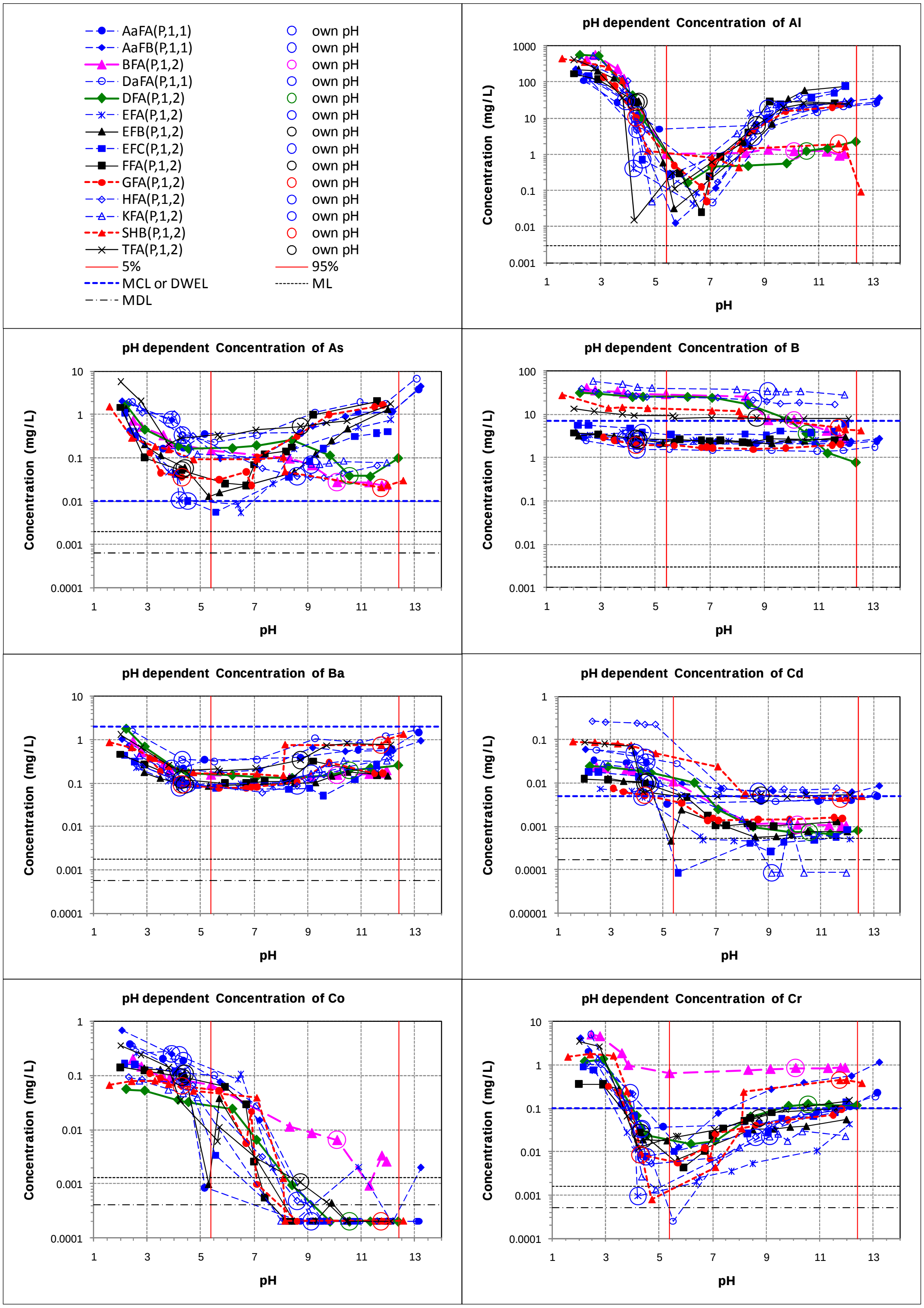


Figure 43. Effect of NO_x controls - none (or by-passed; samples DFA, EFB, FFA, TFA), SNCR (samples GFA, SHB) or SCR (all other samples) for facilities burning Eastern Bituminous coal and using CS-ESP for particulate control.

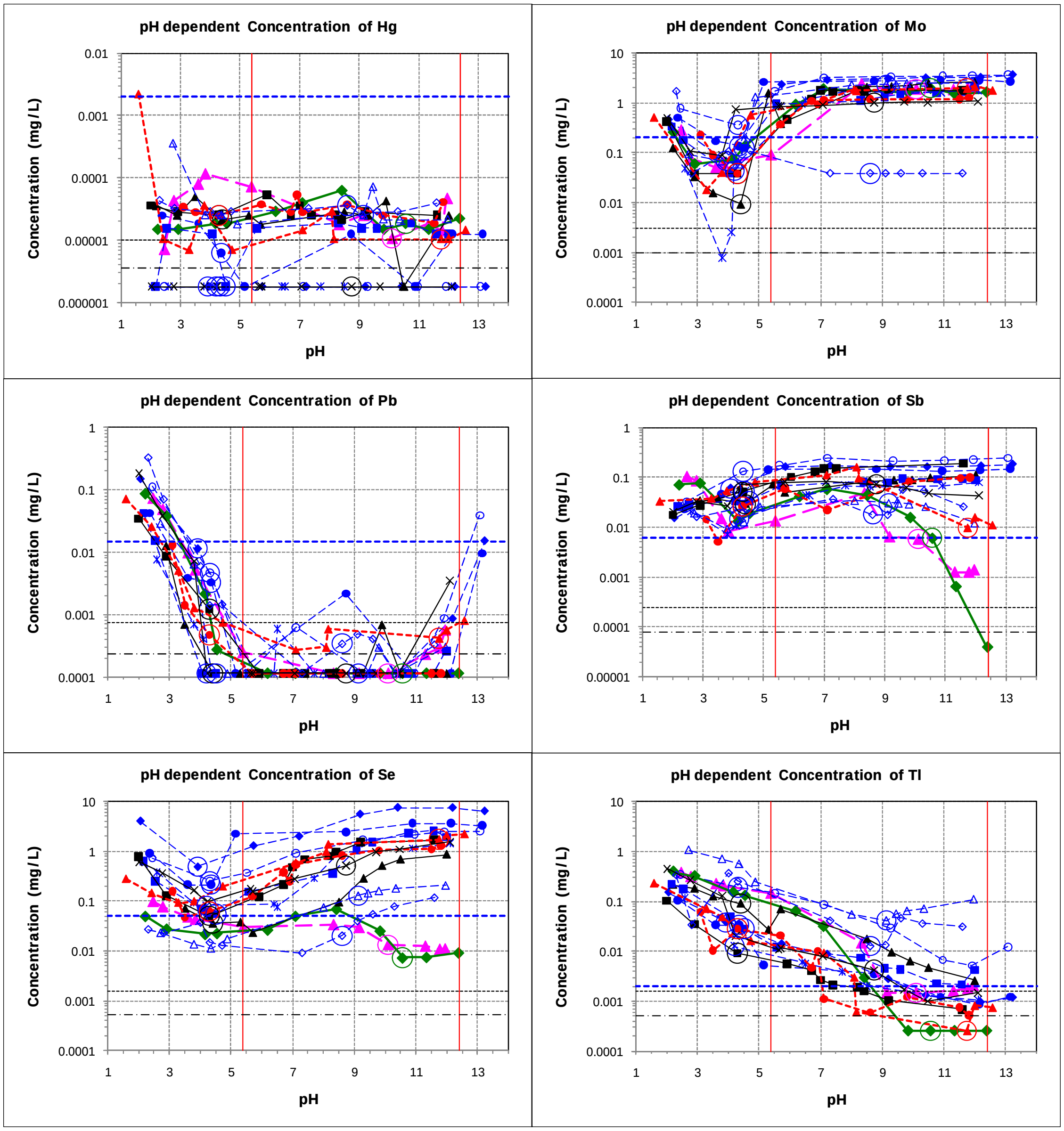


Figure 43 (continued). Effect of NO_x controls - none (or by-passed; samples DFA, EFB, FFA, TFA), SNCR (samples GFA, SHB) or SCR (all other samples) for facilities burning Eastern Bituminous coal and using CS-ESP for particulate control.

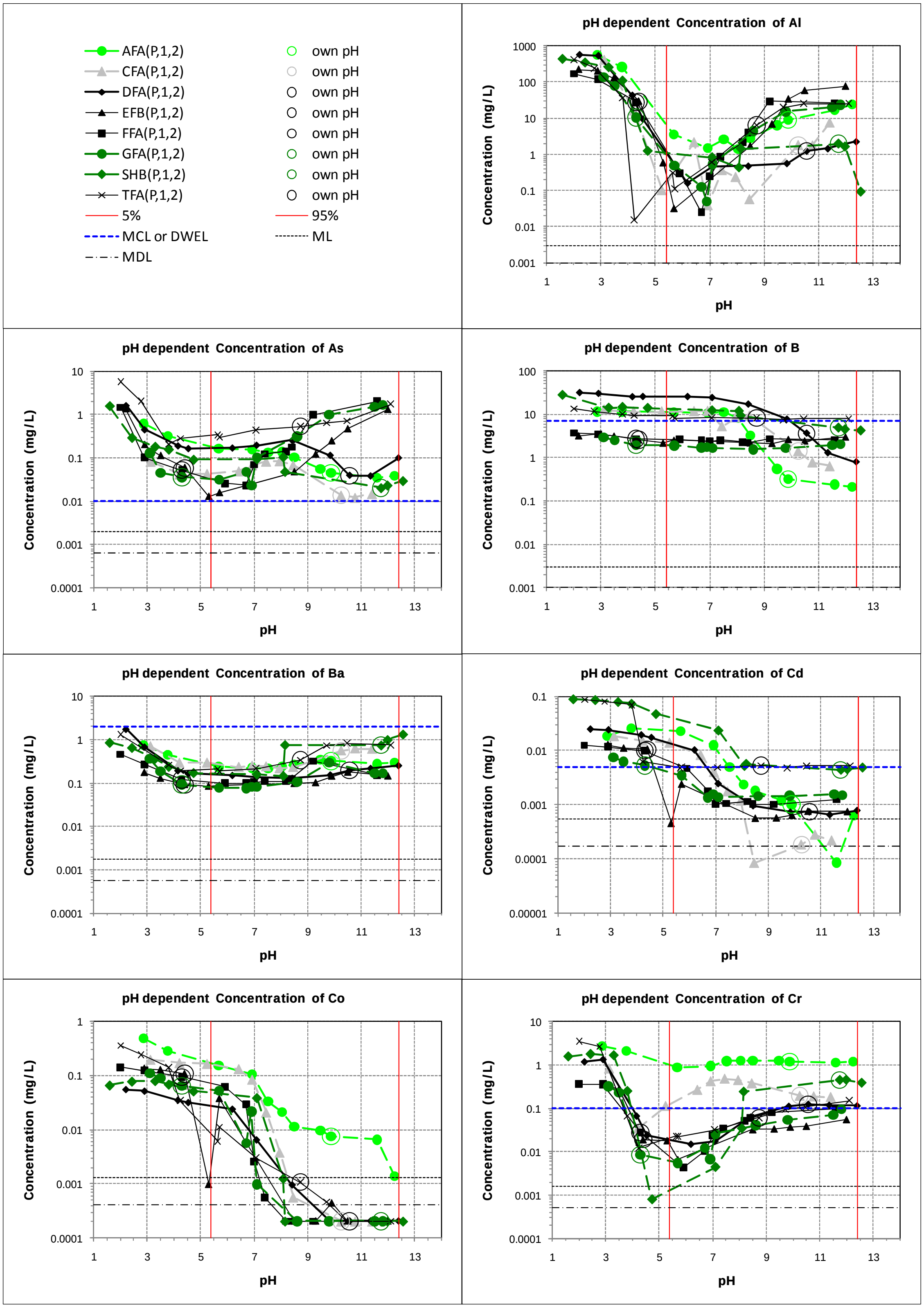


Figure 44. Effect of fabric filter vs. CS-ESP (fabric filter without NO_x control, sample CFA; with SNCR, sample AFA; CS-ESP without NO_x control, samples DFA, EFB, FFA, TFA; with SNCR, samples GFA, SHB) for facilities burning Eastern Bituminous coal.

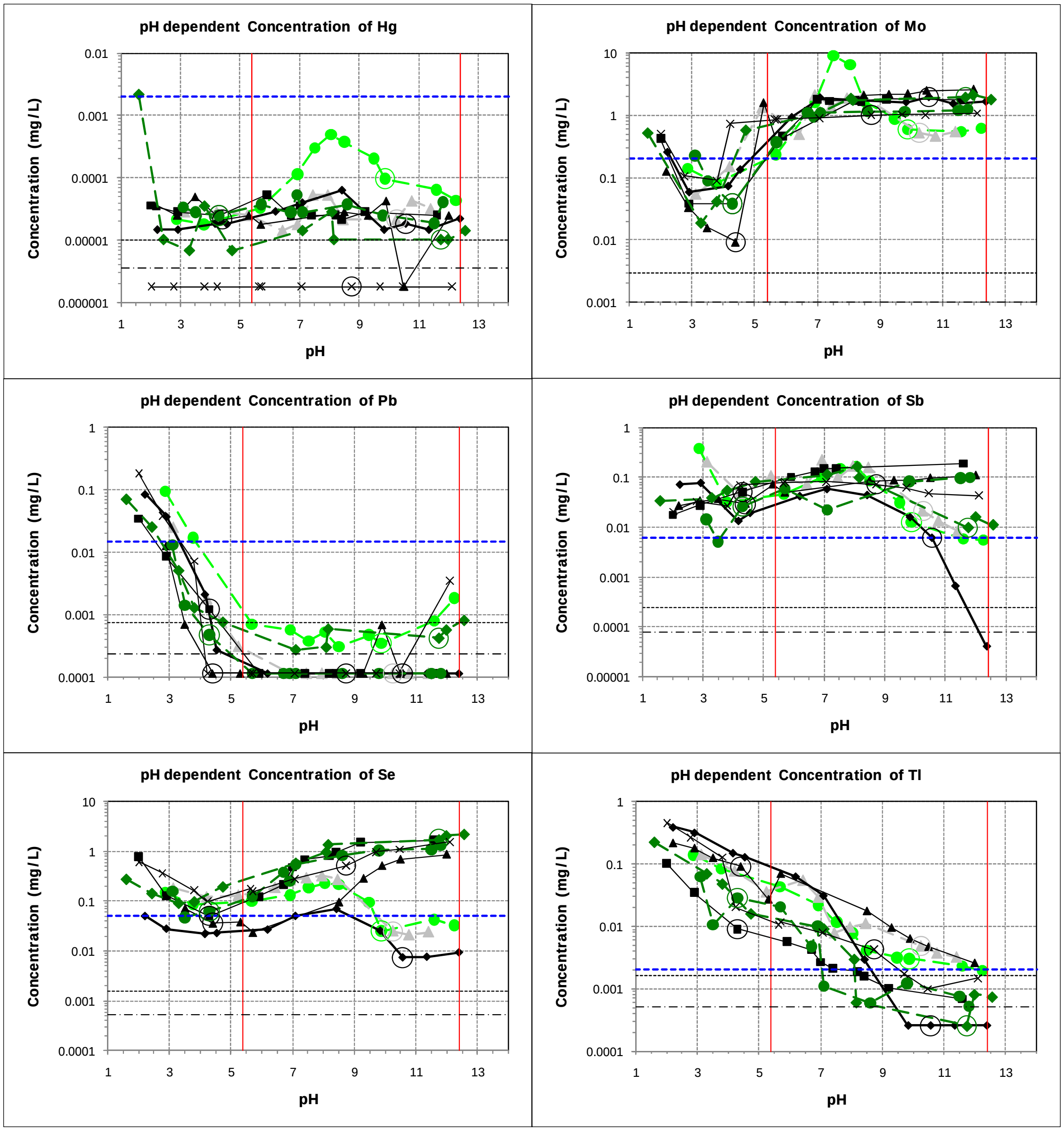


Figure 44 (continued). Effect of fabric filter vs. CS-ESP (fabric filter without NO_x control, sample CFA; with SNCR, sample AFA; CS-ESP without NO_x control, samples DFA, EFB, FFA, TFA; with SNCR, samples GFA, SHB) for facilities burning Eastern Bituminous coal.

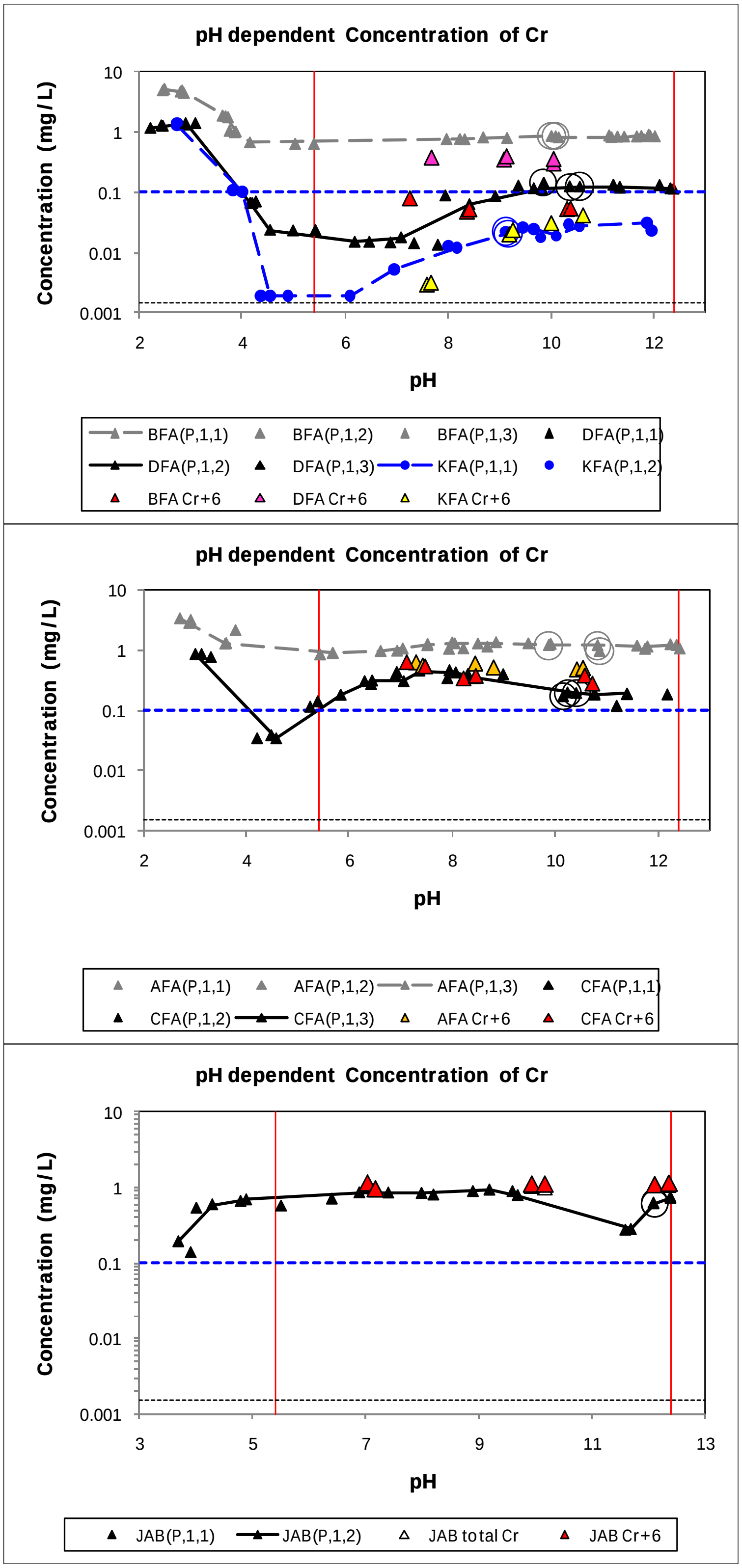


Figure 45. Chromium speciation results. Bituminous coal: Facility B with SCR (BFA), with SCR-BP (DFA); Facility K with SCR (KFA); Facility A with SNCR (AFA), with SNCR-BP (CFA). Sub-bituminous coal: Facility J with SCR (JAB).

3.2.1.2. Fly ash without and with Hg Sorbent Injection Pairs

Figure 46 presents comparisons of leaching behavior as a function of pH for fly ash without and with Hg sorbent injection pairs for each of the 13 elements of interest. For each facility, the baseline case and the treatment case (with Hg sorbent injection), either activated carbon injection or brominated activated carbon injection for facilities J and L, are compared. Also, note that Facilities C and Ba use COHPAC air pollution control configuration. Report 1 (Sanchez *et al.*, 2006) provided results for Hg, As, and Se. The discussion below expands the list to also include Al, B, Ba, Cd, Co, Cr, Mo, Pb, Sb, and Tl.

Considering the results provided in Appendix F and comparisons in Figure 46, the following observations were made.

Aluminum (Al). Al eluate concentrations as a function of pH showed typical amphoteric behavior. For Brayton Point and Facility C, the cases with ACI showed overall an increase in Al concentrations compared to the same facility without. For Facilities J and L, no significant change was observed, while a corresponding decrease was seen for Pleasant Prairie.

Arsenic (As). There was not a consistent pattern with respect to the effect of ACI on the range of laboratory eluate concentrations. For Salem Harbor and slightly for Pleasant Prairie facilities, the cases with ACI had an increase in the upper bound of eluate concentrations compared to the same facility without ACI. For Brayton Point and Facilities C and J, a corresponding decrease was observed.

Very low eluate concentrations were observed for the Facility J without and with brominated PAC, even though the total arsenic content was comparable to several of the other cases. Conversely, relatively high eluate concentrations were observed for Facility L without and with brominated PAC, even though the total arsenic concentration was low compared to the other cases. Thus, the presence of other constituents in the CCRs or the formation conditions appears to have a strong influence on the release of arsenic.

The range of arsenic concentrations observed in the laboratory eluates is consistent with the range of values reported for field leachates from landfills and impoundments. For some cases, both laboratory (Salem Harbor, Facility C, Facility L) and field concentrations exceeded the MCL by greater than a factor of 10. The expected range of arsenic concentrations under field conditions is less than 10 µg/L to approximately 1000 µg/L.

Arsenic leachate concentrations typically are strongly a function of pH over the entire pH range examined and within the pH range observed for field conditions. For some cases (for example, see Facility J, Appendix F), measured concentrations of arsenic are strongly a function of LS ratio at the material's natural pH, with much greater concentrations observed at low LS ratio. Therefore, testing at a single extraction final pH or LS ratio would not provide sufficient information to characterize the range of expected leachate concentrations under field conditions. Furthermore, for some of the CCRs a shift from the CCR's natural pH within the range of anticipated conditions (e.g., Facility L, Brayton Point with ACI, Salem Harbor baseline, Facility C baseline) can result substantial increases in leachate concentrations. Therefore, co-disposal of these CCRs with other materials should be carefully evaluated.

For several cases [Brayton Point, Salem Harbor, Facility C (without ACI), Facility L], arsenic concentrations in laboratory eluates appear to be controlled by solid phase solubility, while adsorption processes appear to play a more important role for other cases [Pleasant Prairie, Facility C (with ACI), Facility J].

Boron (B). No significant effect of ACI on B eluate concentrations as a function of pH was observed, except for Brayton Point that showed an increase in B concentrations for $8 < pH < 12$ with ACI. Facility L showed the lowest B eluate concentrations with and without ACI (by a factor greater than 10). Most samples showed a relatively constant B concentrations over the entire pH range, except for the samples from Facility J showing an increase with decreasing pH for $9.5 < pH < 12$.

Barium (Ba). No significant effect of ACI on Ba eluate concentrations as a function of pH was seen, except for Pleasant Prairie for which a decrease in Ba concentrations was observed with ACI for $6 < pH < 11.5$ and Brayton Point for which a decrease was seen over the entire pH range examined. Sample BaFA (lignite, ACI + COHPAC) had the greatest Ba release for $pH < 7$ and $pH > 12$ (above the MCL).

Cadmium (Cd). For Salem Harbor, the case with ACI had an increase in Cd eluate concentrations for $pH > 4.5$ compared to the same facility without ACI. For Brayton Point a decrease in Cd concentrations was observed with ACI for $pH < 7$. No significant effect of ACI was seen for the other facilities tested.

Cobalt (Co). Sample BaFA (lignite, ACI + COHPAC) showed the greatest Co eluate concentrations for all pHs examined. No significant effect of ACI on Co eluate concentrations was observed, except for Brayton Point that showed a decrease in Co concentration with ACI.

Chromium (Cr). For most cases a decrease in Cr eluate concentrations was observed for the cases with ACI compared to the same facility without ACI. Facility C showed, however, an increase in Cr concentrations for $pH > 7$ for the case with ACI.

Mercury (Hg). Although the use of activated carbon injection substantially increases the total Hg content in the fly ashes, the range of laboratory leaching eluate concentrations in the baseline cases and cases with sorbent injection are either unchanged or the maximum leaching concentration is reduced as a consequence of activated carbon injection. The exceptions are Facility C and Facility L, which have an increased maximum eluate concentration for the case with sorbent injection.

The expected range of Hg leachate concentrations based on these results is from < 0.004 (below MDL) to 0.2 µg/L over the range of pH conditions expected in coal ash landfill leachate.

The range of Hg concentrations observed from laboratory eluates is consistent with the range reported for field leachates from landfills in the EPRI database.

All concentrations observed in laboratory leach test eluates from fly ash over $5.4 \leq pH \leq 12.4$ were at least an order of magnitude less than the MCL.

For all cases of laboratory eluates, Hg concentrations in eluates from fly ash were consistent without any significant effect of total mercury content, pH, or LS ratio observed. Mercury leaching appears to be controlled by adsorption from the aqueous phase with strong interaction between adsorbed mercury molecules, indicating that use of a linear partition coefficient (K_d) approach to model source term mercury leaching would not be appropriate. Variability observed in concentrations observed within individual cases is likely the result of sampling and CCR heterogeneity at the particle scale (i.e., resulting from mercury adsorption specifically onto carbon surfaces and relatively more or less carbon particles in a specific subsample used for extraction).

Molybdenum (Mo). For all cases, there was no significant effect of ACI on Mo eluate concentrations as a function of pH.

Lead (Pb). Minimal Pb leaching was overall observed. In most cases, Pb leaching was at or below the MDL for 4 < pH < 12. For Facility J, the case with ACI showed an increase in Pb eluate concentrations for 4 < pH < 10 compared to the same facility without.

Antimony (Sb). There was no significant effect of ACI on Sb eluate concentrations, except for Salem Harbor that showed an increase in Sb concentrations with ACI over the entire pH range and Brayton Point for which an increase in Sb concentrations for pH > 8 and a decrease for pH < 7.5 was observed with ACI.

Selenium (Se). The range of selenium concentration in laboratory leach test eluates is not correlated with total selenium content in the CCRs. For example, Brayton Point with ACI had much greater total selenium content than the other cases except Facility C with ACI, but had only the fifth highest selenium concentration under the laboratory leaching conditions. Conversely, Facility C baseline had one of the lowest selenium total content (less than MDL) but had second greatest selenium concentration under the laboratory leaching conditions.

The range of selenium concentrations observed in laboratory leach test eluates for Facility C are much greater than the concentrations observed for other cases and for field conditions. This is a COHPAC facility and field leachate composition data for CCRs from this type of facility were not available in the EPA or EPRI databases. For all other facilities, the range of concentrations observed from laboratory testing is consistent with the range reported in the EPRI database for landfills. The concentration range reported in the EPA database for CCR landfills has a much lower upper bound than reported in the EPRI database.

The concentration range for laboratory eluates and field observations exceeded the MCL for all cases except Facility L. For 5 out of 12 of the cases used for laboratory evaluation, and for some field observations, the MCL is exceeded by more than a factor of 10.

Selenium concentrations in laboratory leach test eluates typically are strongly a function of pH over the entire pH range examined and within the pH range observed for field conditions (for example, see leaching test results for Brayton Point, Salem Harbor, Facility C). For some cases (for example, see Brayton Point, Salem Harbor, and Facility J in Appendix F), measured concentrations of selenium are strongly a function of LS ratio at the material’s natural pH, with much greater concentrations observed at low LS ratio. Therefore, testing at a single extraction final pH or LS ratio would not provide sufficient information to characterize the range of expected leachate concentrations under field conditions.

For several cases (Brayton Point, Salem Harbor, Facility C, Facility L) selenium concentrations in laboratory eluates appears to be controlled by solid phase solubility, while adsorption processes appear to play a more important role for other cases (Pleasant Prairie and Facility J).

Thallium (Tl). For Pleasant Prairie, the case with ACI resulted in an increase in Tl concentrations over the entire pH range compared to the same facility without ACI. For Facility J, a decrease in Tl eluate concentrations with ACI was observed for all pHs examined. For Brayton Point, the case with ACI showed an increase in Tl concentrations for pH > 10 and a decrease for pH < 9.

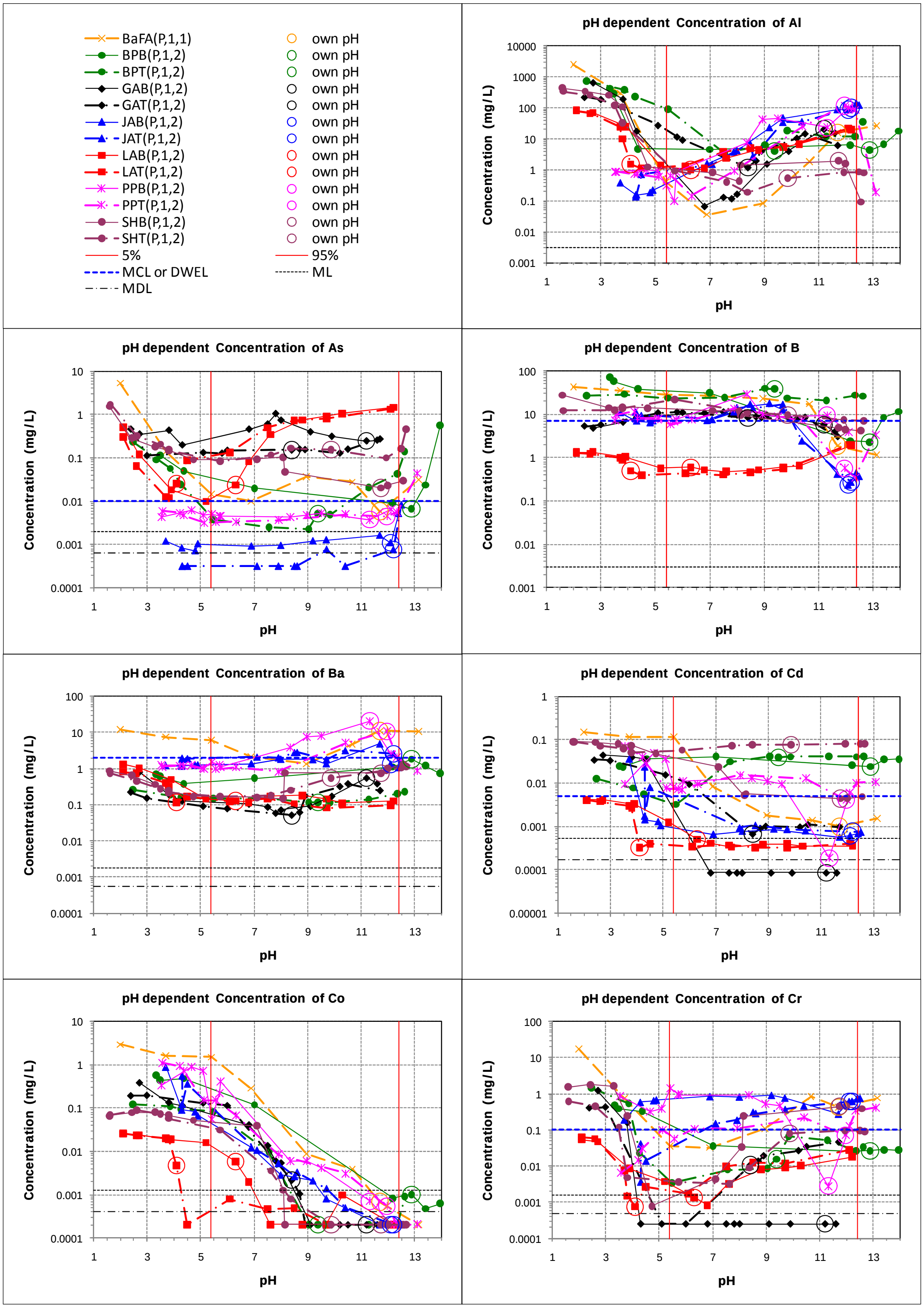


Figure 46. pH dependent leaching results. Fly ash samples from facility pairs with and without mercury sorbent injection. Sample codes ending __B (BPB) indicate without sorbent injection; Sample codes ending __T (BPT) indicate with sorbent injection for the corresponding facility.

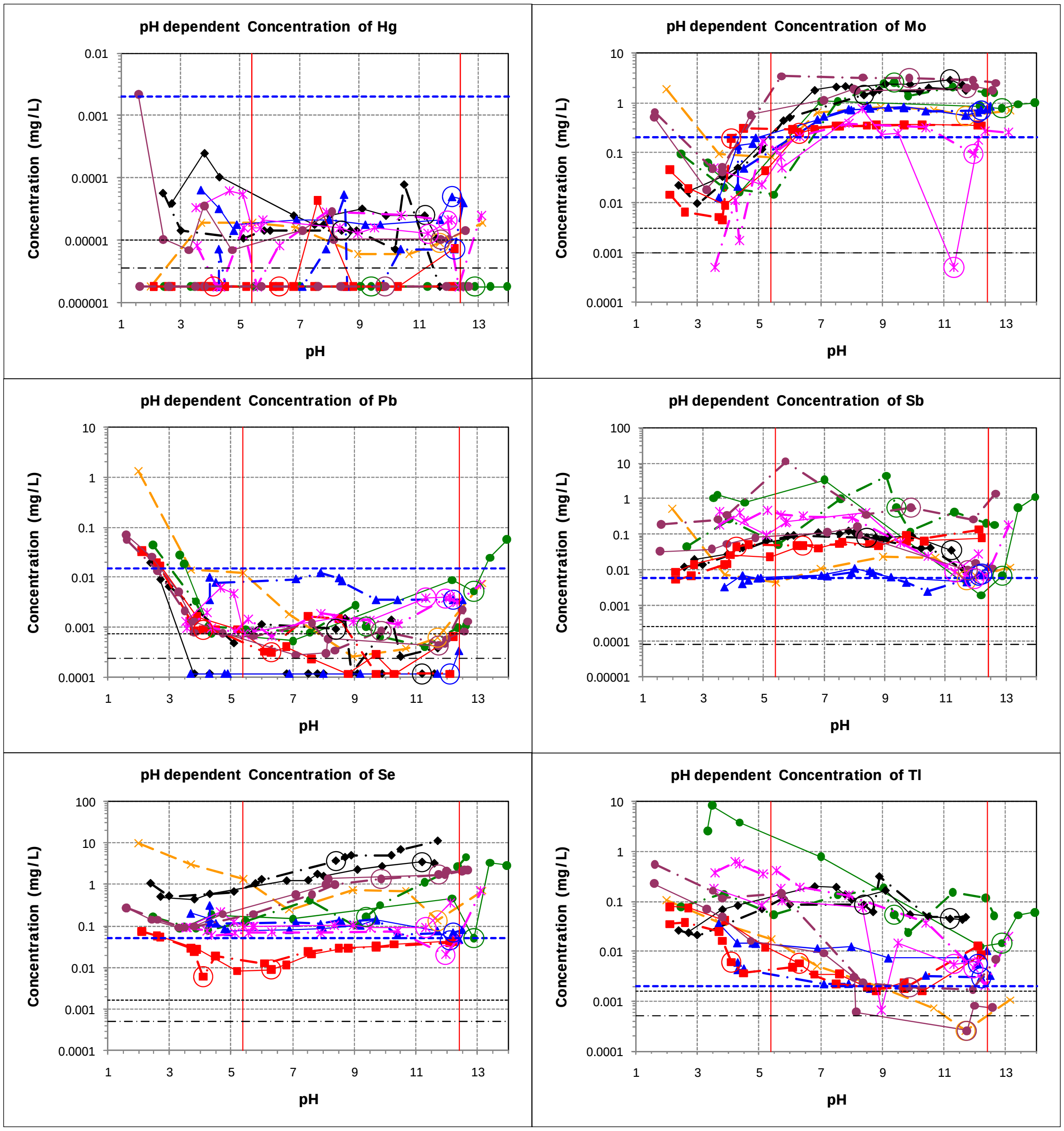


Figure 46 (continued). pH dependent leaching results. Fly ash samples from facility pairs with and without mercury sorbent injection. Fly ash samples from facility pairs with and without mercury sorbent injection. Sample codes ending __B (BPB) indicate without sorbent injection; Sample codes ending __T (BPT) indicate with sorbent injection for the corresponding facility.

3.2.1.3. Gypsum, Unwashed and Washed

The effect of the washing step on the leaching behavior of gypsum as a function of pH for each of the 13 elements of interest is illustrated in Figure 47, Figure 48, and Figure 49. Typically, washing resulted in at least an order of magnitude reduction in the observed leached concentrations for the soluble species (e.g., B, Tl) and the oxyanions (e.g., Se). B and Tl release from both unwashed and washed gypsum were generally relatively constant as a function of pH for most facilities. Se release was either relatively constant as a function of pH (Facilities O, P) or amphoteric (Facilities N, Q).

The washing step resulted, however, in greater leaching concentrations of Hg ($7 < pH < 10$) and Cr ($4 < pH < 12$) for Facility X. Also, the washed gypsum sample from lignite (CaAW) showed a greater release for Pb and Se compared to washed and unwashed gypsum samples from facilities using high sulfur bituminous or sub-bituminous coal.

The unwashed sample from Facility W (WAU) showed greater concentrations of As, Pb, and Tl, which was most likely a consequence of the Trona injection used for SO_3 control by this facility.

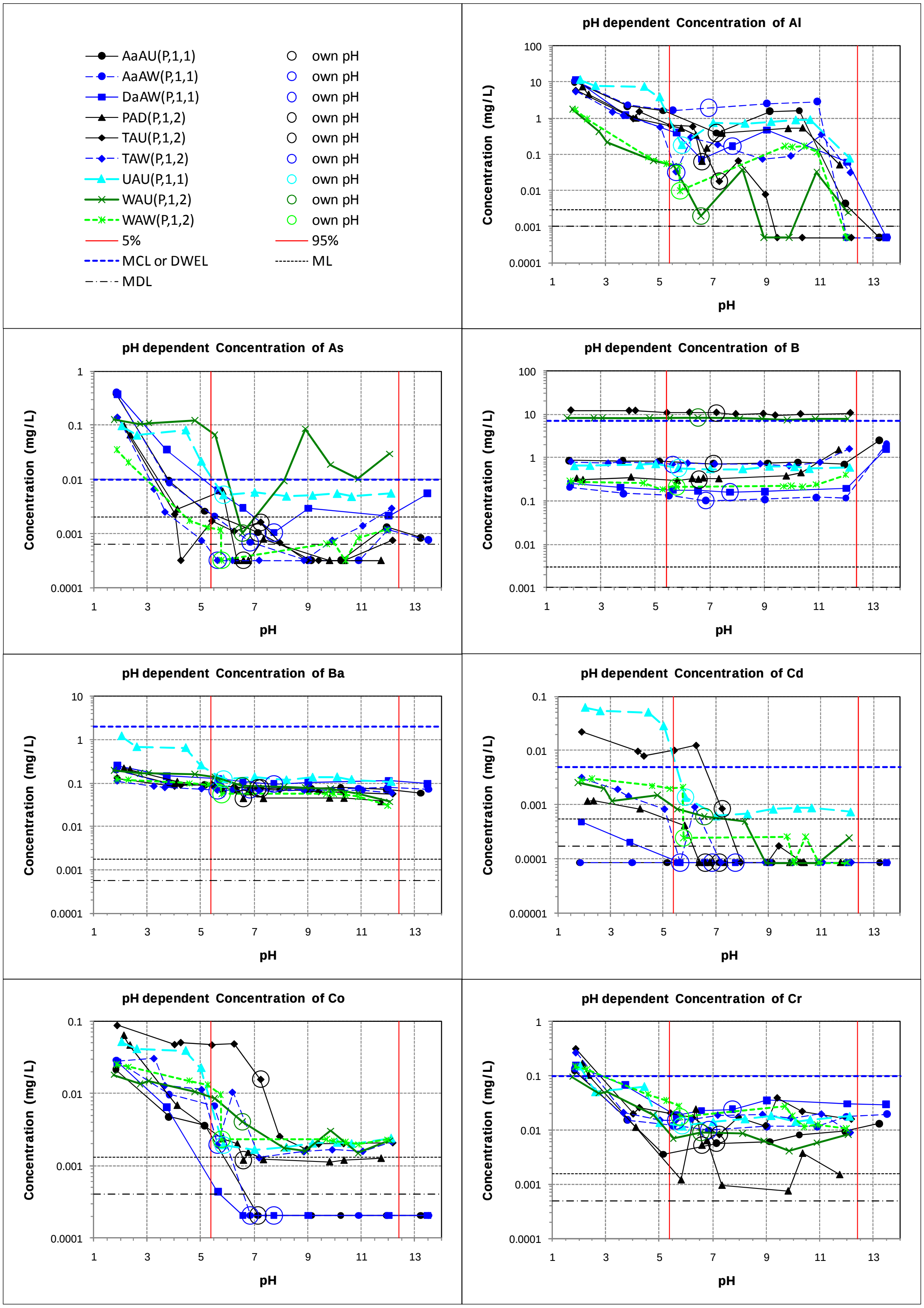


Figure 47. pH dependent leaching results. Gypsum samples unwashed (sample codes __U) and washed (sample codes __W) from facilities using low and medium sulfur bituminous coals.

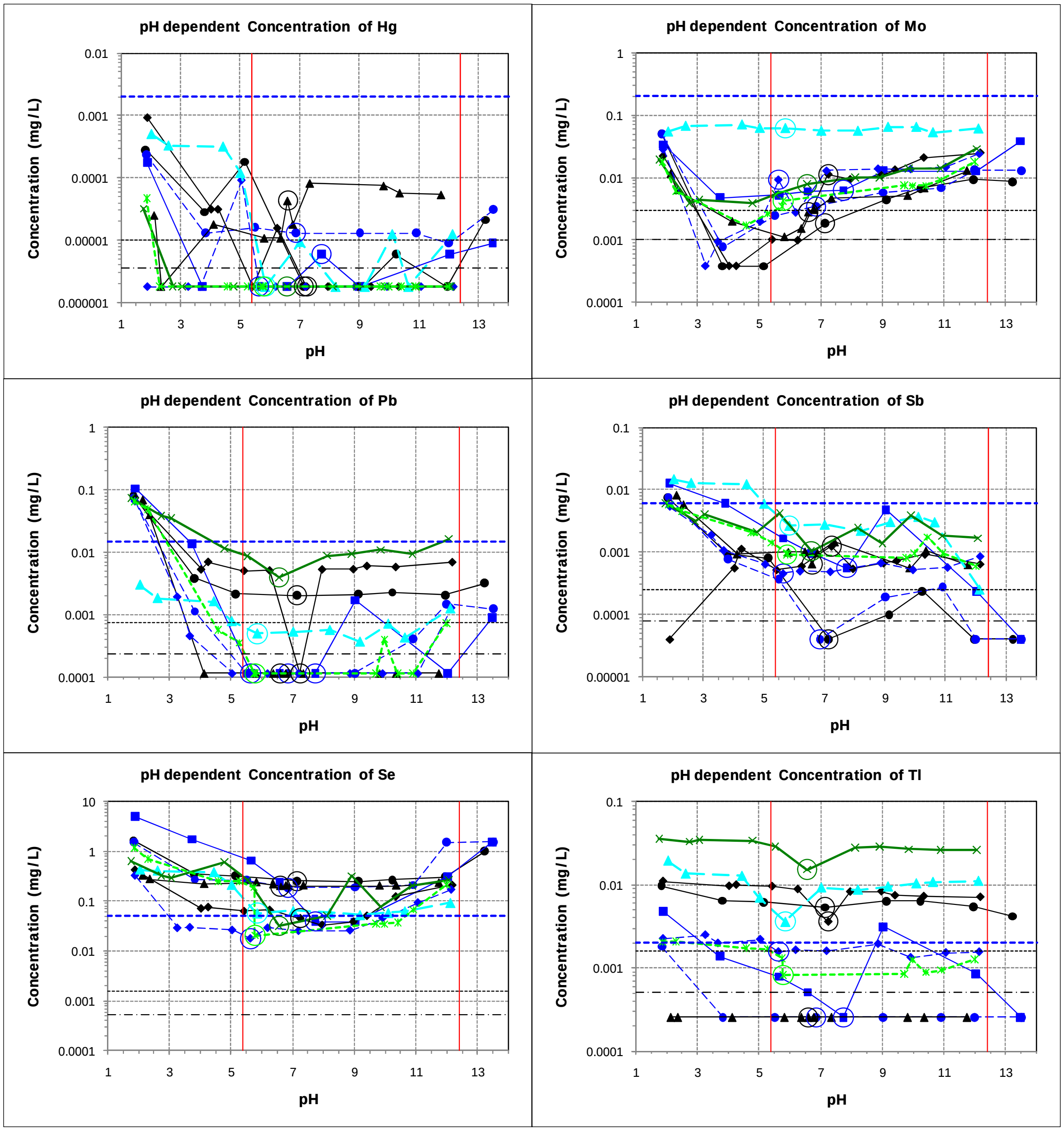


Figure 47 (continued). pH dependent leaching results. Gypsum samples unwashed (sample codes __U) and washed (sample codes __W) from facilities using low and medium sulfur bituminous coals.

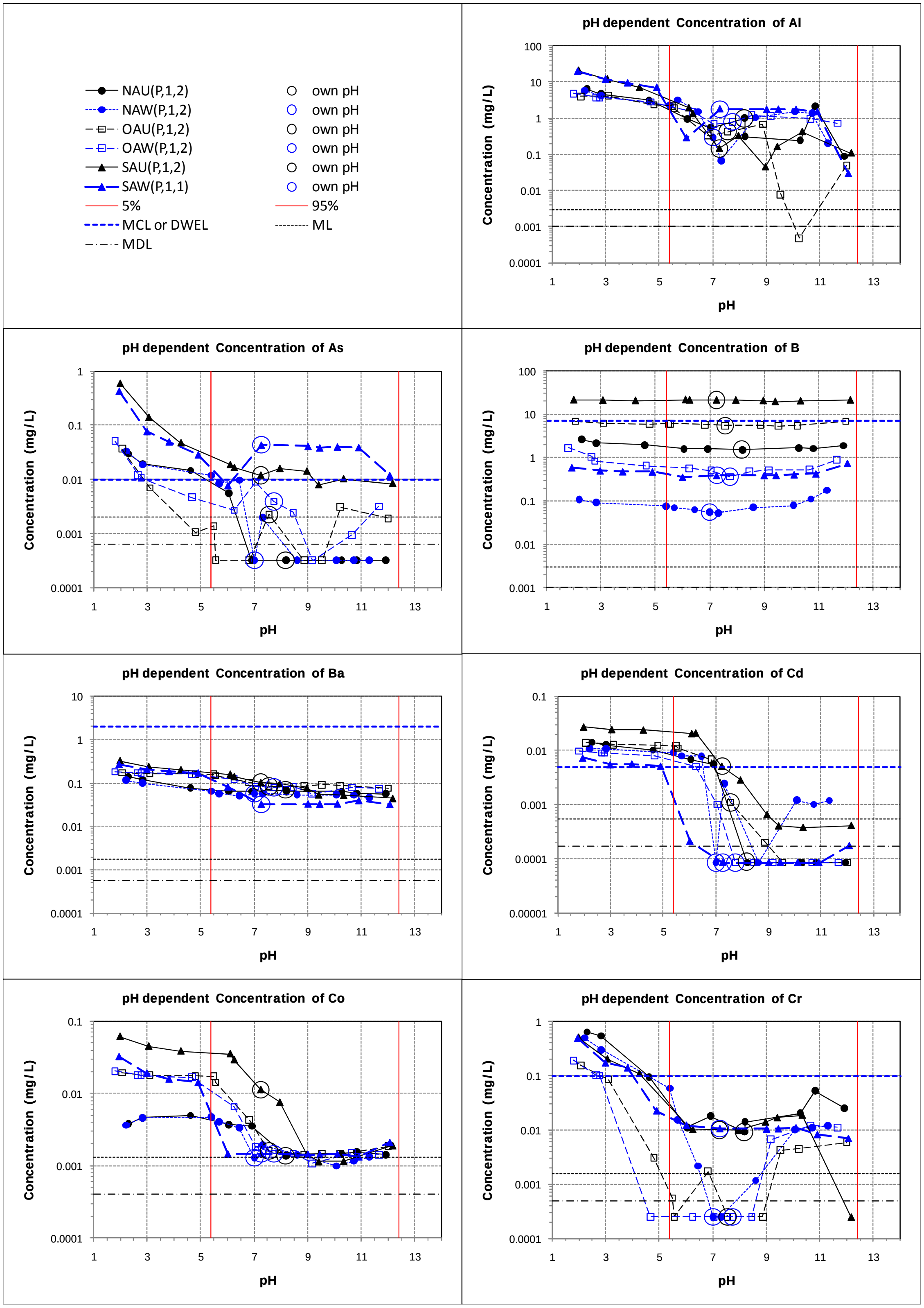


Figure 48. pH dependent leaching results. Gypsum samples unwashed (sample codes __U) and washed (sample codes __W) from facilities using high sulfur bituminous coal.

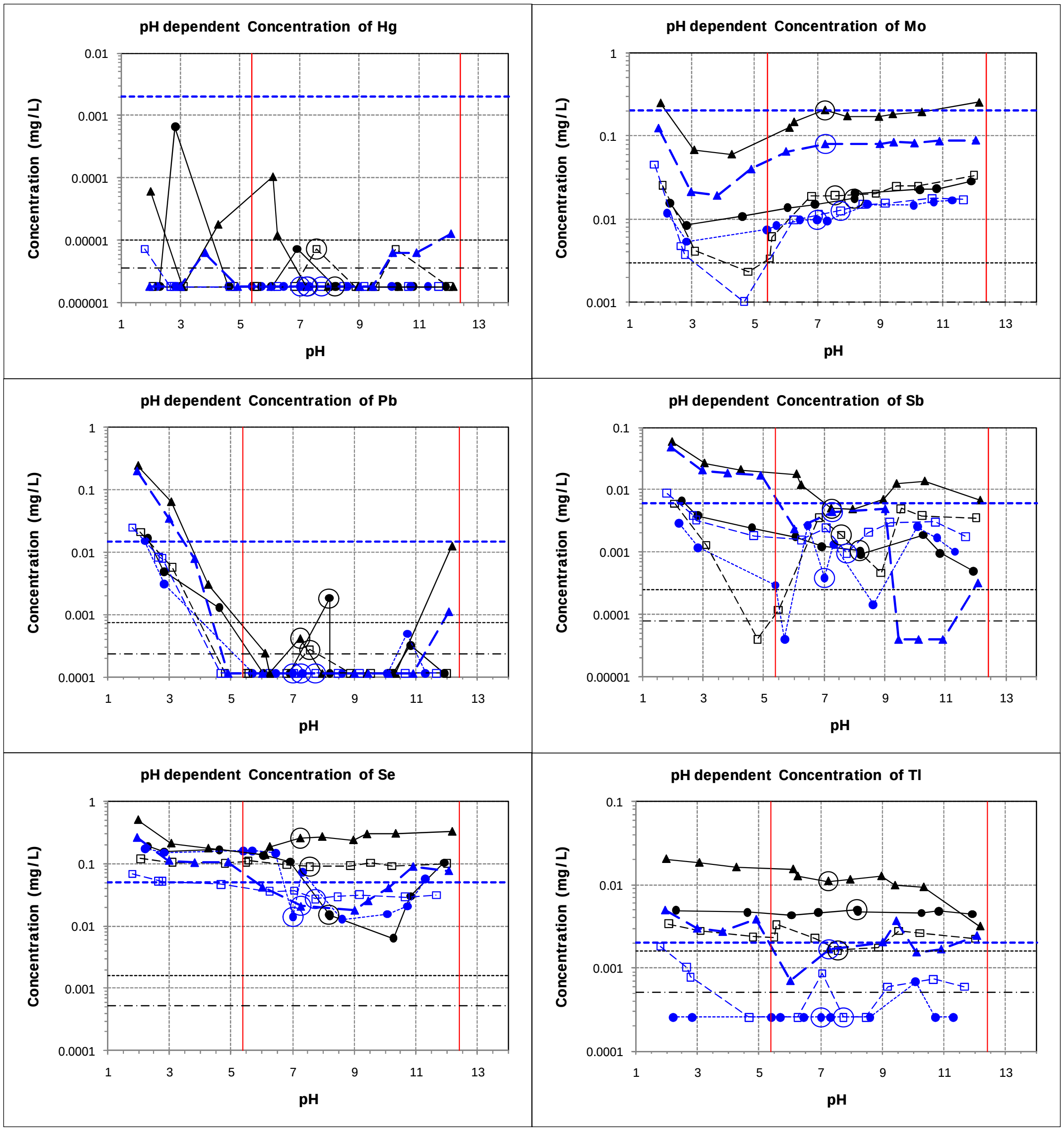


Figure 48 (continued). pH dependent leaching results. Gypsum samples unwashed (sample codes __U) and washed (sample codes __W) from facilities using high sulfur bituminous coal.

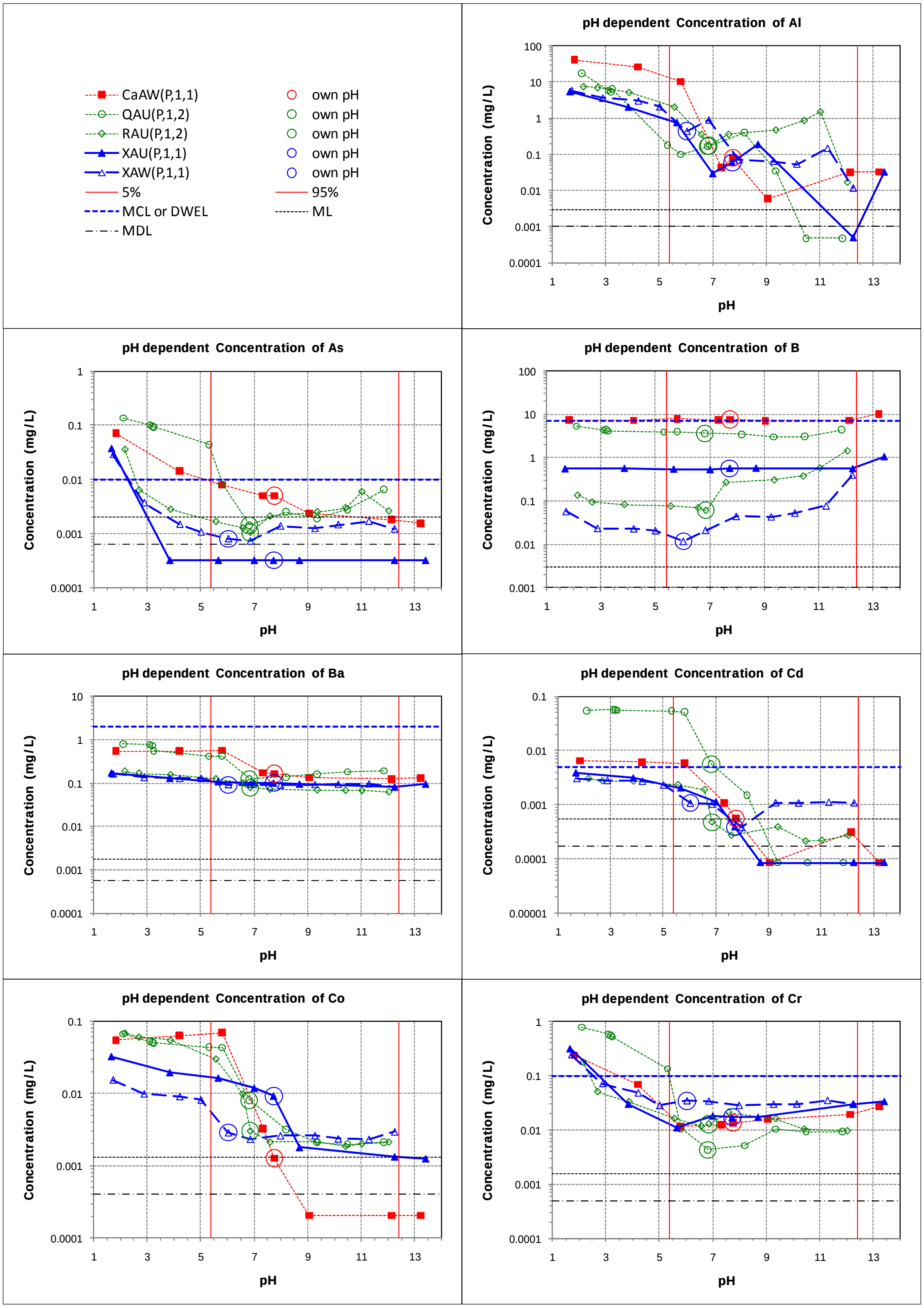


Figure 49. pH dependent leaching results. Gypsum samples unwashed (sample codes __U) and washed (sample codes __W) from facilities using sub-bituminous and lignite bituminous coals.

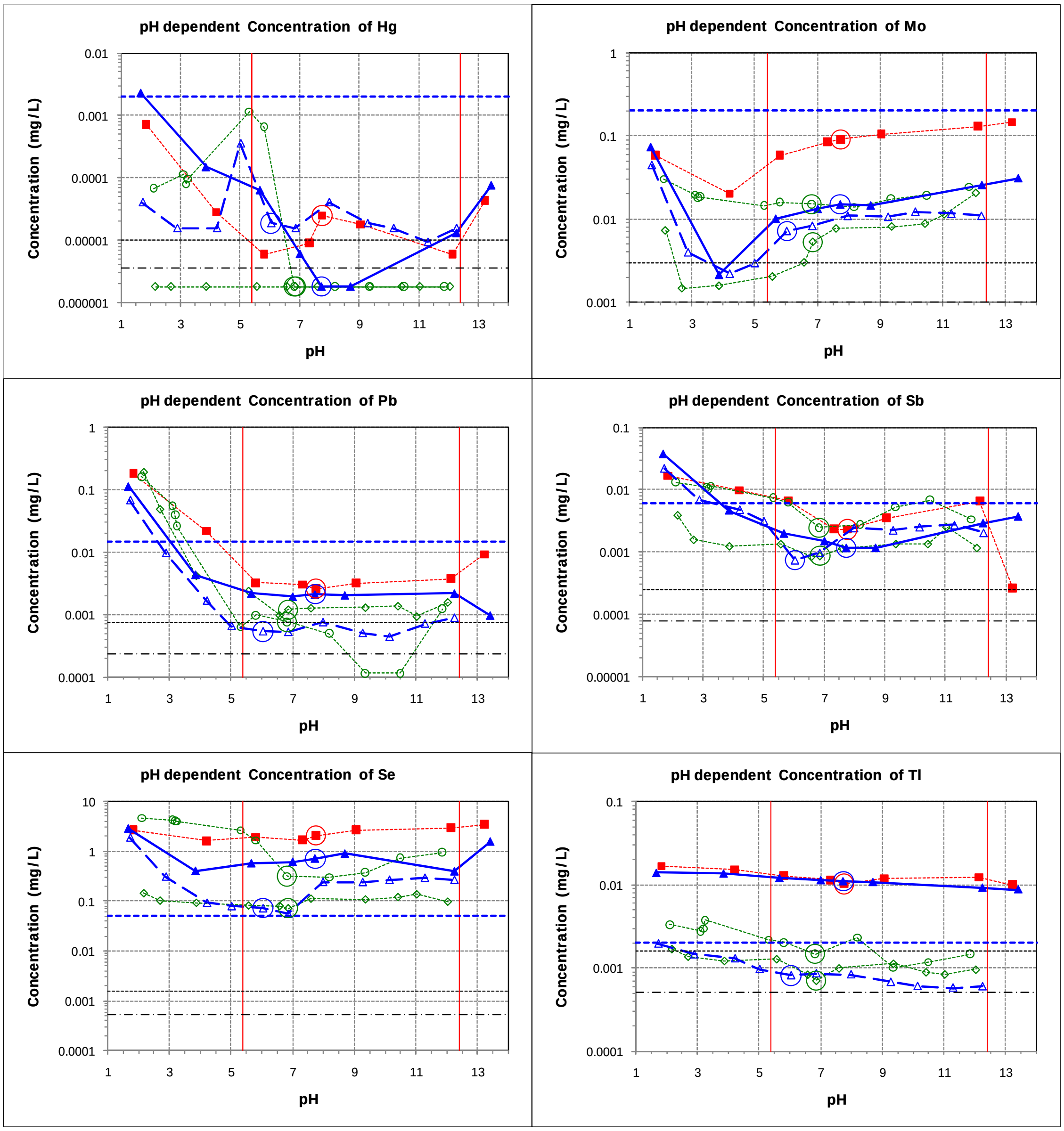


Figure 49 (continued). pH dependent leaching results. Gypsum samples unwashed (sample codes __U) and washed (sample codes __W) from facilities using sub-bituminous and lignite bituminous coals.

3.2.1.4. Scrubber Sludge

Figure 50 presents results of the leaching behavior as a function of pH for the scrubber sludge samples. The effect of SNCR in combination with a fabric filter (AGD *vs*. CGD) was manifested by (i) a significant increase in the leaching concentrations of Cr over the entire pH range examined, (ii) a slight reduction in Hg, and (iii) an increase in Tl. An effect of SCR (BGD *vs*. DGD) was seen for As (slight increase with SCR), Ba (increase with SCR), Co (increase with SCR), and Cr (significant increase with SCR). Sample KGD exhibited the highest leaching concentrations for Ba, Cd, Co, Mo, Se, and Tl.

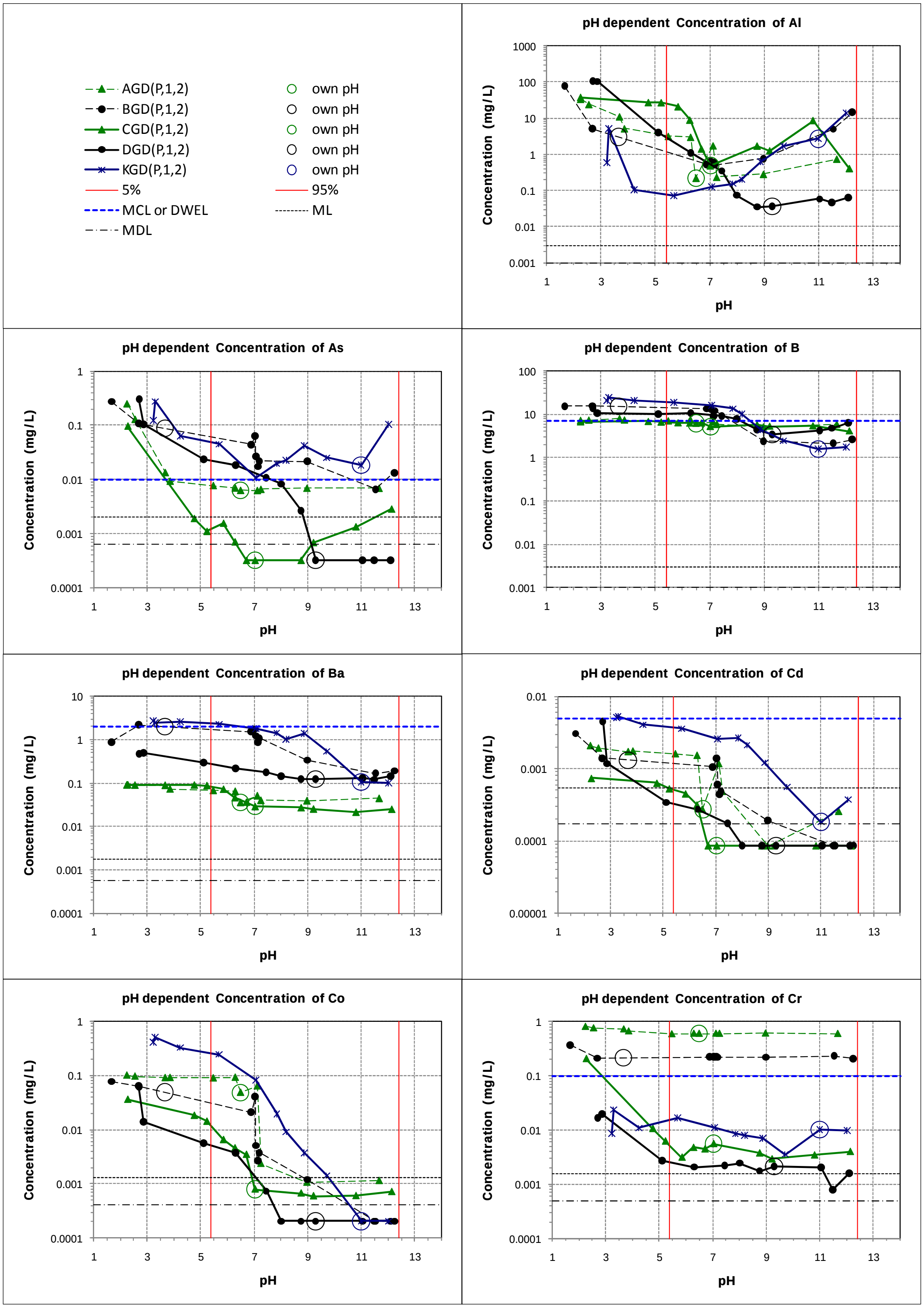
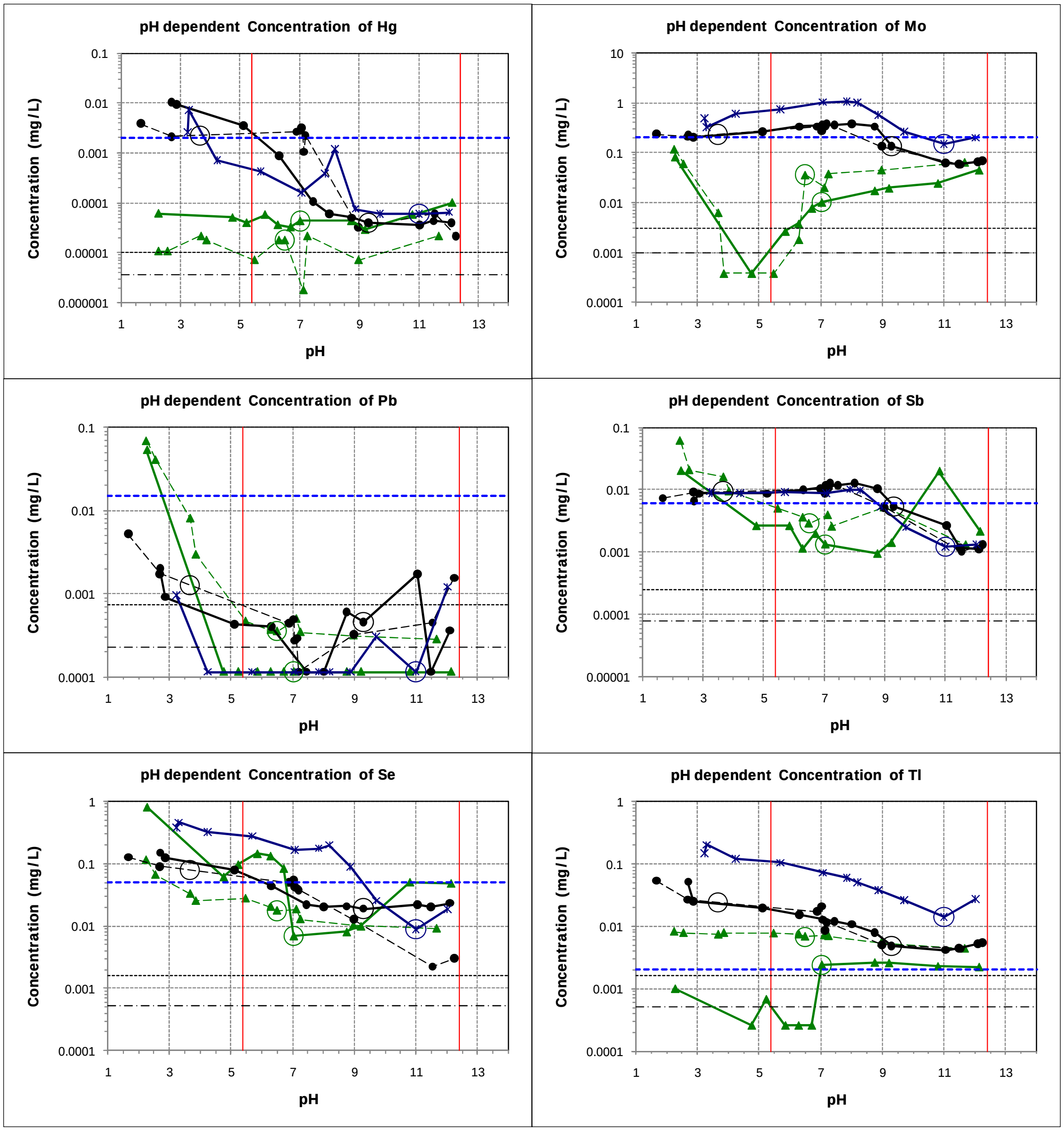


Figure 50. pH dependent leaching results. Scrubber sludges. Facility A (AGD, CGD), Facility B (BGD, DGD), Facility K (KGD). Samples DGD and KGD with SCR, Samples BGD with SNCR. Samples CGD and DGD without post-combustion NO_x controls.


pH dependent Concentration of Hg

pH dependent Concentration of Mo

pH dependent Concentration of Pb

pH dependent Concentration of Sb

pH dependent Concentration of Se

pH dependent Concentration of Tl

Figure 50 (continued). pH dependent leaching results. Scrubber sludges. Facility A (AGD, CGD), Facility B (BGD, DGD), Facility K (KGD). Samples DGD and KGD with SCR, Samples BGD with SNCR. Samples CGD and DGD without post-combustion NO_x controls.

3.2.1.5. Spray Dryer Absorber Residues

Figure 51 presents results of leaching behavior as a function of pH for spray dryer residue samples. Sample VSD showed a greater release of Al ($9 < pH < 12$), Ba ($8 < pH < 12$), Cr ($pH < 6$), and Tl ($pH < 6$) and a lower release of Co and Pb ($4 < pH < 12$) than sample YSD, though the two samples are from the same coal type and air pollution control configurations. The observed differences between the two samples could be due to differences in the lime used.

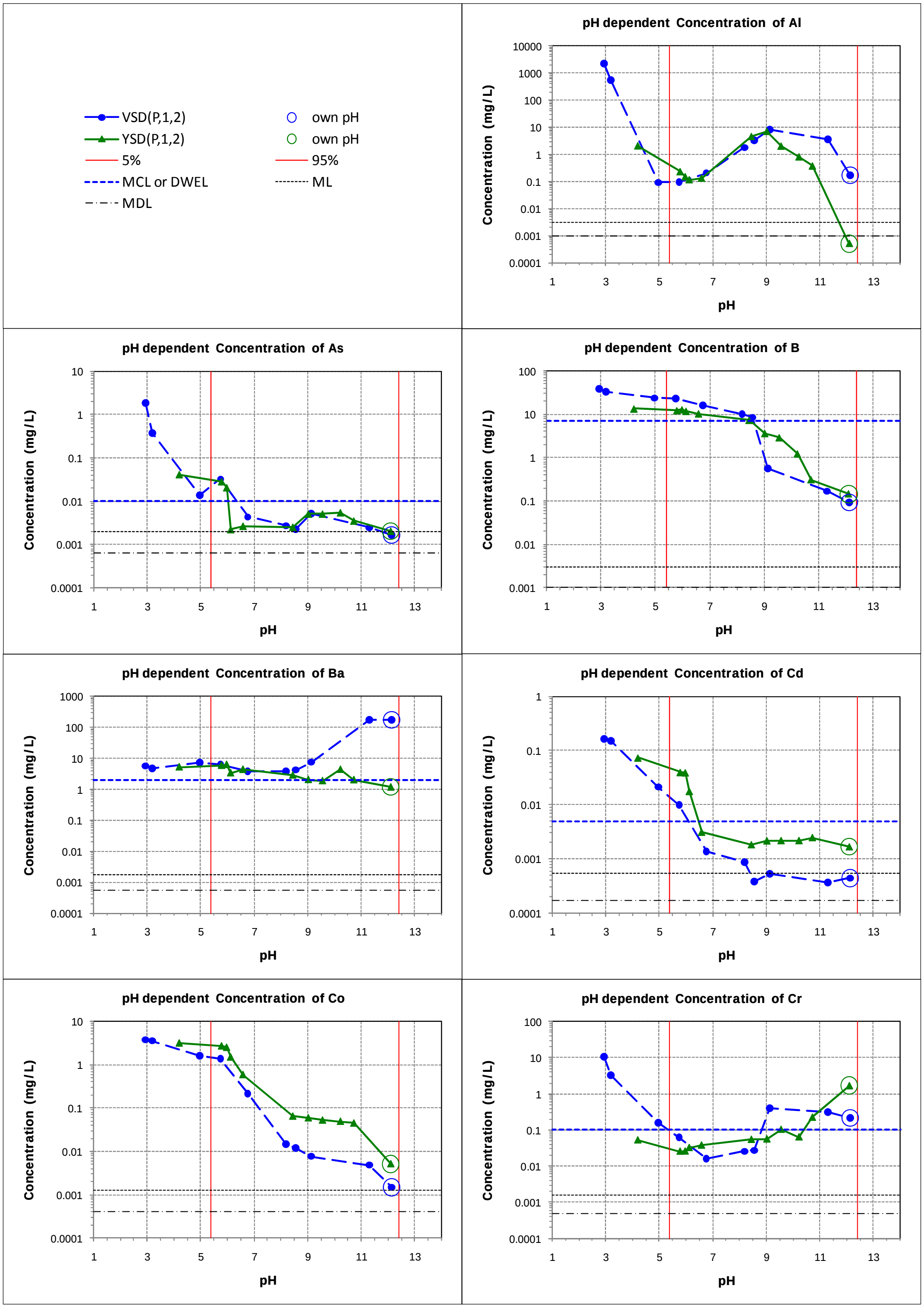


Figure 51. pH dependent leaching results. Spray dryer residue samples (sub-bituminous coal).

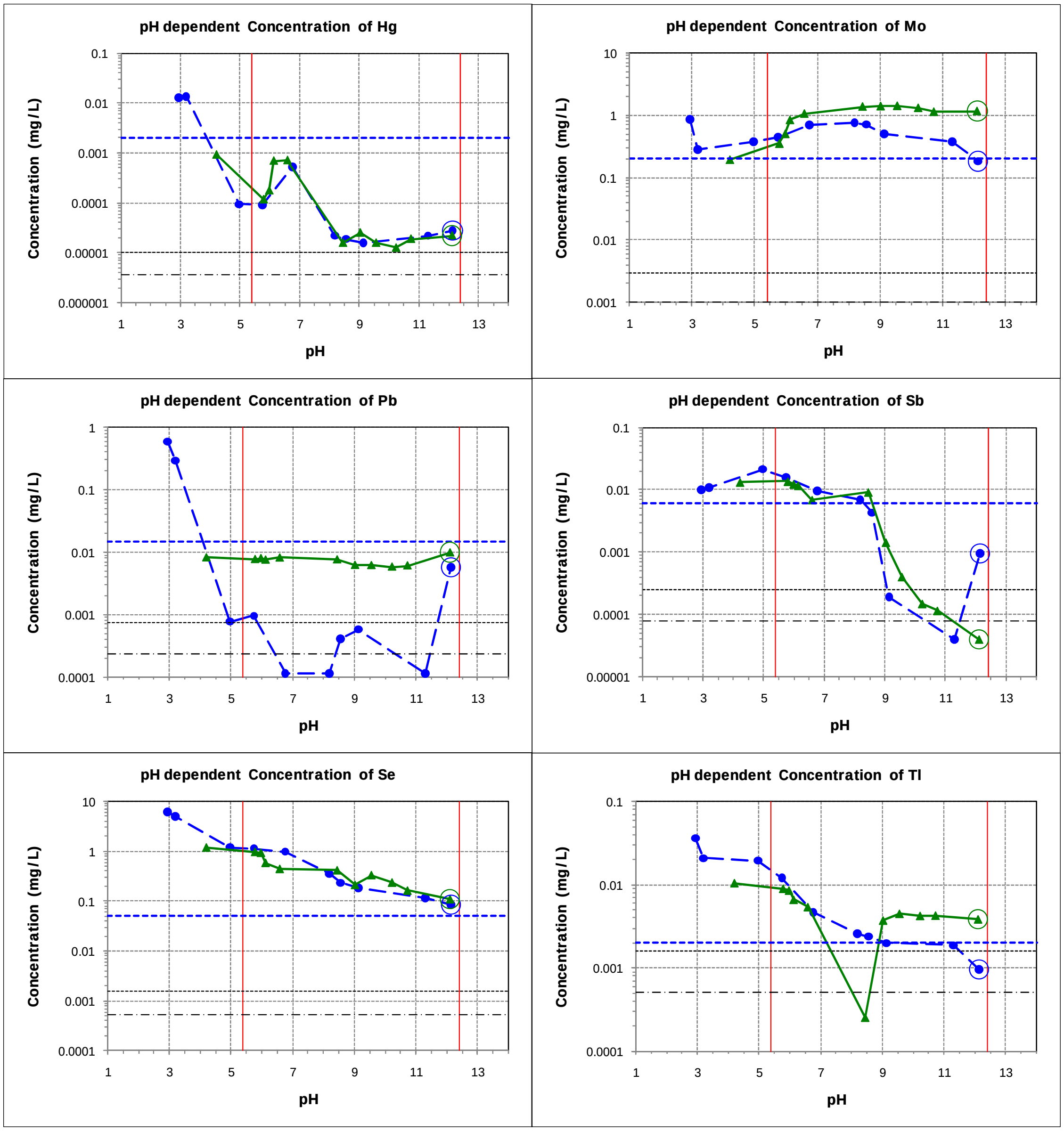


Figure 51 (continued). pH dependent leaching results. Spray dryer residue samples (sub-bituminous coal).

3.2.1.6. Blended CCRs (Mixed Fly Ash and Scrubber Sludge/Mixed Fly Ash and Gypsum)

The leaching behavior of the blended CCRs (mixed fly ash and scrubber sludge/mixed fly ash and gypsum) was mainly controlled by the behavior of the fly ash. This behavior is illustrated in Figure 52 (Facility A, SNCR-BP) that shows comparisons of pH dependent leaching results for fly ash (CFA), scrubber sludge (CGD), and blended fly ash and scrubber sludge (CCC). Results for the blended fly ash and gypsum can be found in Appendix F (UGF).

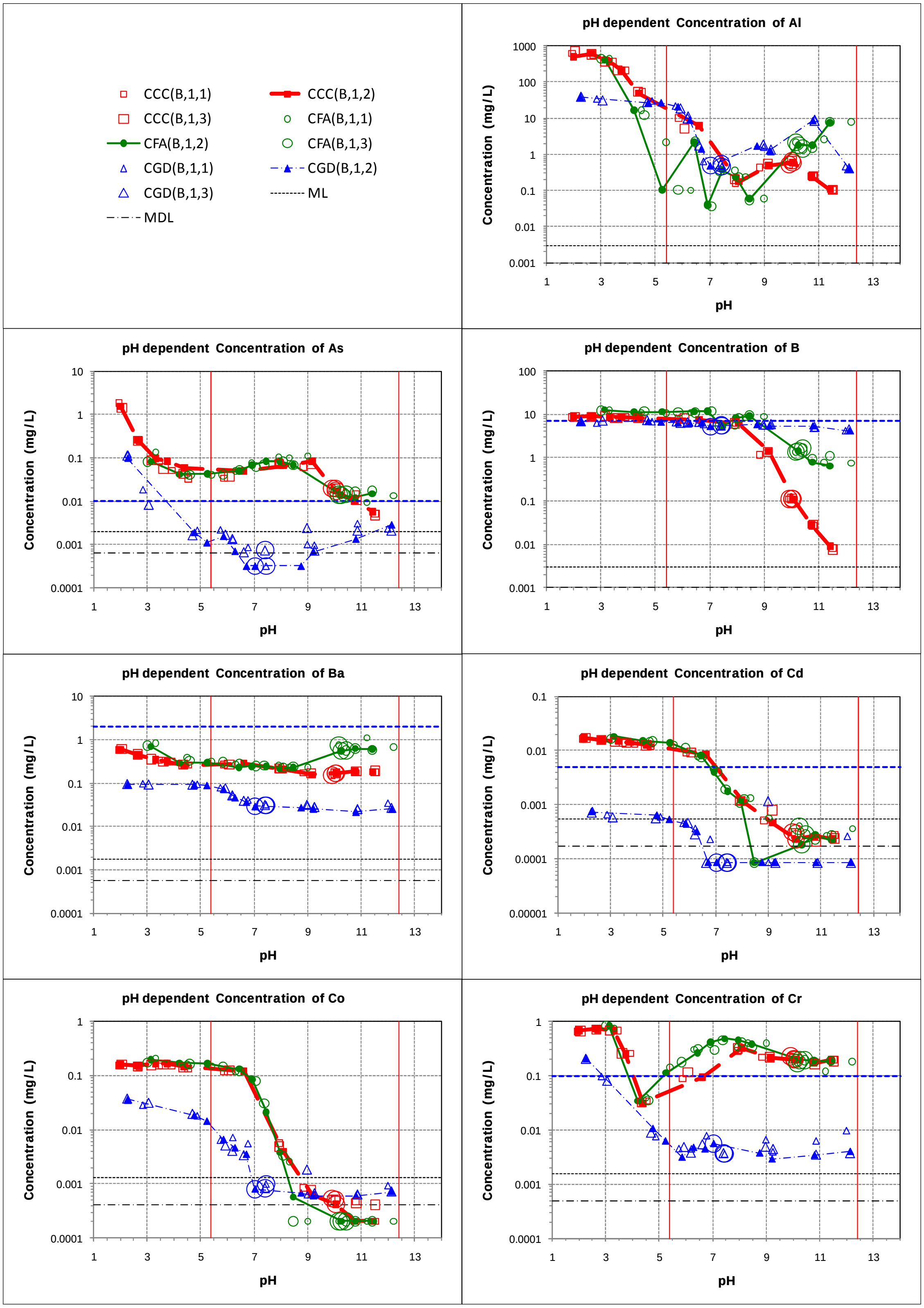


Figure 52. pH dependent leaching results. Facility A samples (low S east-bit., fabric filter, limestone, natural oxidation). SNCR-BP. Fly ash (CFA); scrubber sludge (CGD); blended fly ash and scrubber sludge (“as managed,” CCC).

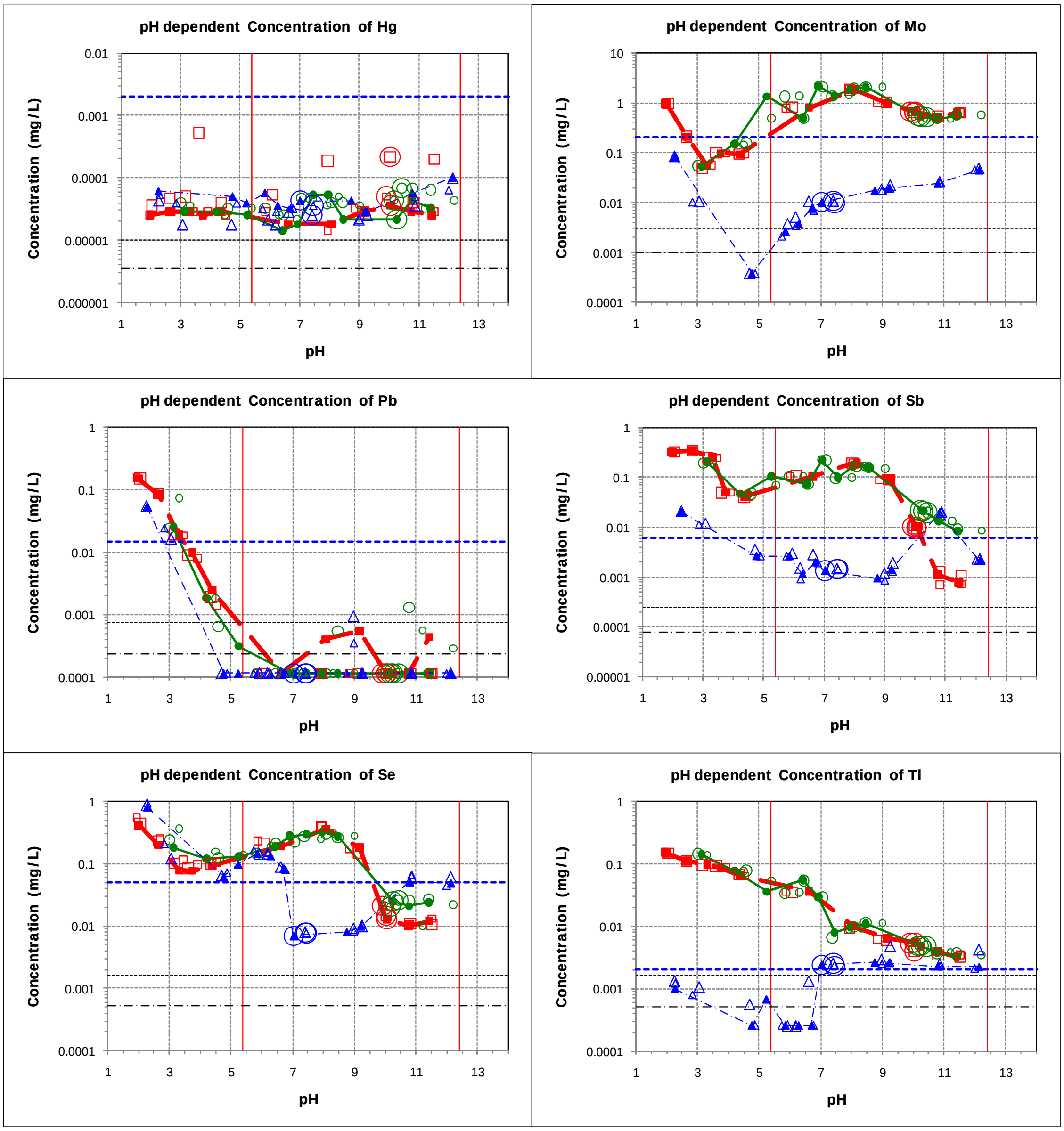


Figure 52 (continued). pH dependent leaching results. Facility A samples (Low S East-Bit., Fabric F., Limestone, Natural Oxidation). SNCR-BP. Fly ash (CFA); Scrubber sludge (CGD); Blended fly ash and scrubber sludge ("as managed," CCC).

3.2.1.7. Waste Water Filter Cake

Figure 53 presents results of leaching behavior as a function of pH for waste water filter cake for each of the 13 elements of interest. These are samples with waste water treatment process associated with management of CCRs and are not a direct product of the air pollution control systems. Overall similar results were observed for all samples tested except for sample XFC that showed a greater release for Hg, Mo, Pb, and Se.

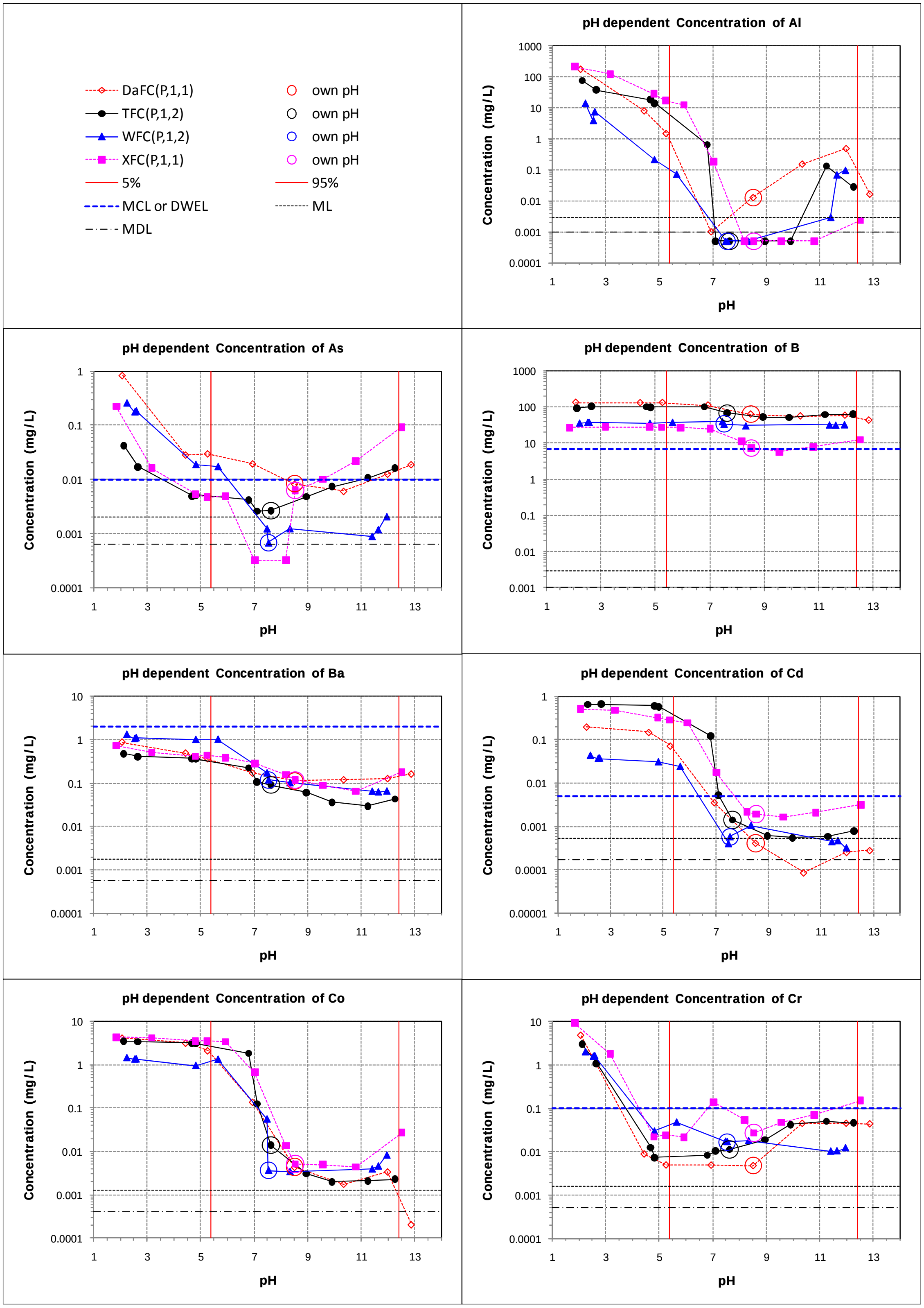


Figure 53. pH dependent leaching results. Filter cake samples.

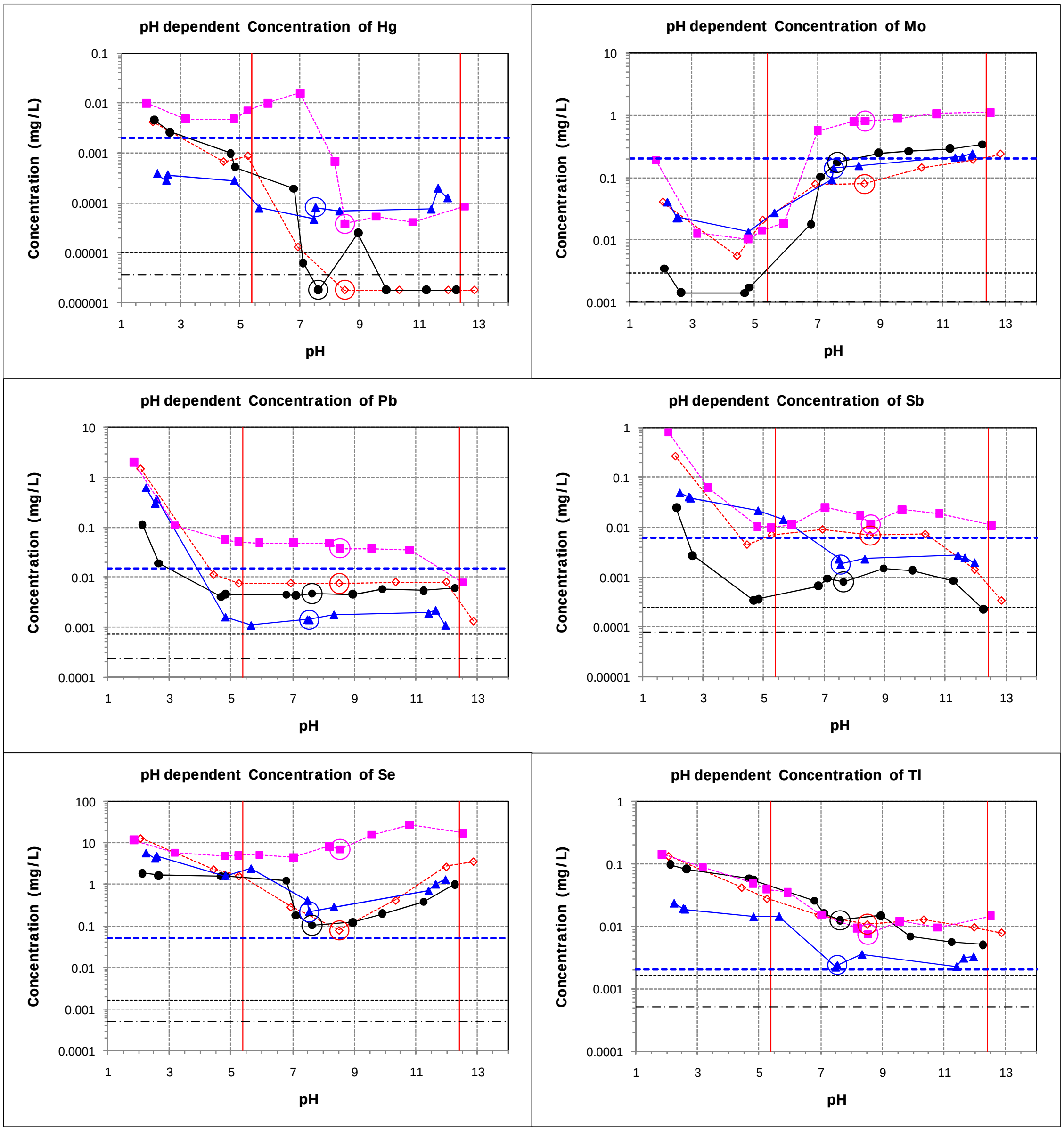


Figure 53 (continued). pH dependent leaching results. Filter cake samples.

3.2.2. Comparisons of the Ranges of Constituent Concentrations from Laboratory Testing (Minimum Concentrations, Maximum Concentrations, and Concentrations at the Materials' Own pH)

Figure 54 through Figure 66 present comparisons of the range of constituent concentrations observed in laboratory eluates from testing as a function of pH and LS (SR002.1 and SR003.1) over the pH range from 5.4 to 12.4 and LS ratios from 0.5 to 10. This pH range represents the 5th and 95th percentiles of pH observed in field samples from CCR landfills and surface impoundments, as discussed in Section 2.5.2. For laboratory leaching test eluates, the presented data represent the observed maximum and minimum concentrations within the pH range from 5.4 to 12.4 from both test methods (upper and lower whiskers) and the concentration at the materials' own pH (closed circles or asterisks), which may be outside the pH range criteria. Including results from testing as a function of LS allows consideration of potentially higher concentrations observed for initial releases that may occur at low LS ratios in the field. The TC and MCL, DWEL, or AL (as available) is included in each figure as a dashed horizontal line to provide a reference value. The concentration ranges indicated in the figures as results of this study are direct measurements of laboratory eluates of the CCRs and do not consider attenuation that may occur in the field. Tabular results are provided in Appendix I.

Important observations from these figures are summarized as follows.

Aluminum (Al). Gypsum generally had lower eluate concentration ranges than the other CCR types. No trend was readily discernable with respect to coal type or facility configuration.

Arsenic (As). Lower eluate concentration ranges were associated with fly ash produced from sub-bituminous coal than other coal types. Many of the values for eluates from fly ash exceeded the MCL but results only for one fly ash sample (WFA) exceeded the TC. Results for five of the gypsum samples exceeded the MCL. For scrubber sludges, results suggest that use of post-combustion NO_x controls may increase As leachability.

Boron (B). Washed gypsum samples all had lower eluate concentrations for B than unwashed gypsum samples, indicating the effectiveness of the washing process in reducing leachable B. All of the CCR types had a significant fraction of the samples that exceeded the DWEL.

Barium (Ba). The greatest Ba concentrations in eluates was from fly ash and SDA sample produced from sub-bituminous coal. All gypsum samples had barium eluate concentrations less than the MCL. Use of post-combustion NO_x controls appears to have reduced Ba leachability in blended CCRs.

Cadmium (Cd). All CCR types had a significant fraction of samples from which eluate concentrations exceeded the MCL. For many samples of all CCR types, the own pH concentration was less than the method detection limit.

Cobalt (Co). All CCR types had samples with cobalt eluate concentrations from less than the method detection limit up to three orders of magnitude greater. SDA residues had the greatest range in Co eluate concentrations.

Chromium (Cr). Use of post-combustion NO_x controls appeared to increase the eluate concentrations for fly ash, scrubber sludges, and blended CCRs when samples were collected from the same facility. All gypsum samples except one unwashed gypsum, had eluate concentrations less than the MCL. All other CCR types had multiple samples with eluates that exceeded the MCL.

Mercury (Hg). The greatest Hg concentrations in eluates were from scrubber sludges and blended CCRs, including all of those that exceeded the MCL.

Molybdenum (Mo). Higher eluate concentration ranges were associated with fly ash, SDA residues and blended CCRs (which include fly ash) than associated with gypsum and scrubber sludge samples. All CCR types had multiple samples with eluates that exceeded the DWEL.

Lead (Pb). Eluate concentrations were below the AL for eluates from all samples except for 8 samples. There was no clear trend with respect to coal type, facility configuration or CCR type.

Antimony (Sb). Higher eluate concentration ranges were associated with fly ash samples than with gypsum samples although there were exceptions to this trend. All CCR types had samples for which eluate concentrations exceeded the MCL.

Selenium (Se). All CCR types had similar ranges in Se eluate concentrations with several fly ash and gypsum samples having notably higher Se eluate concentrations without any clear dependence on coal type or facility configuration.

Thallium (Tl). Most CCR samples had eluate concentrations that exceeded the MCL with no apparent trend with respect to coal type or facility configuration.

pH. Figure 67 presents the pH ranges (minimum and maximum) of actual samples observed in SR002.1 and SR003.1 over the pH domain $5.4 \leq pH \leq 12.4$. The closed circles represent the material’s own pH. When the closed circle is outside the range $5.4 \leq pH \leq 12.4$, this means that the material’s own pH was more acidic than pH 5.4. Fly ash samples exhibited own pH values ranging from acidic ($4 \leq pH \leq 6$) to moderately alkaline ($8 \leq pH \leq 11$) to highly alkaline ($11 < pH$) with a high degree of correlation with total calcium content. The own pH range for gypsum samples was between 5.5 and 8, while the range was much larger for scrubber sludges and blended CCRs.

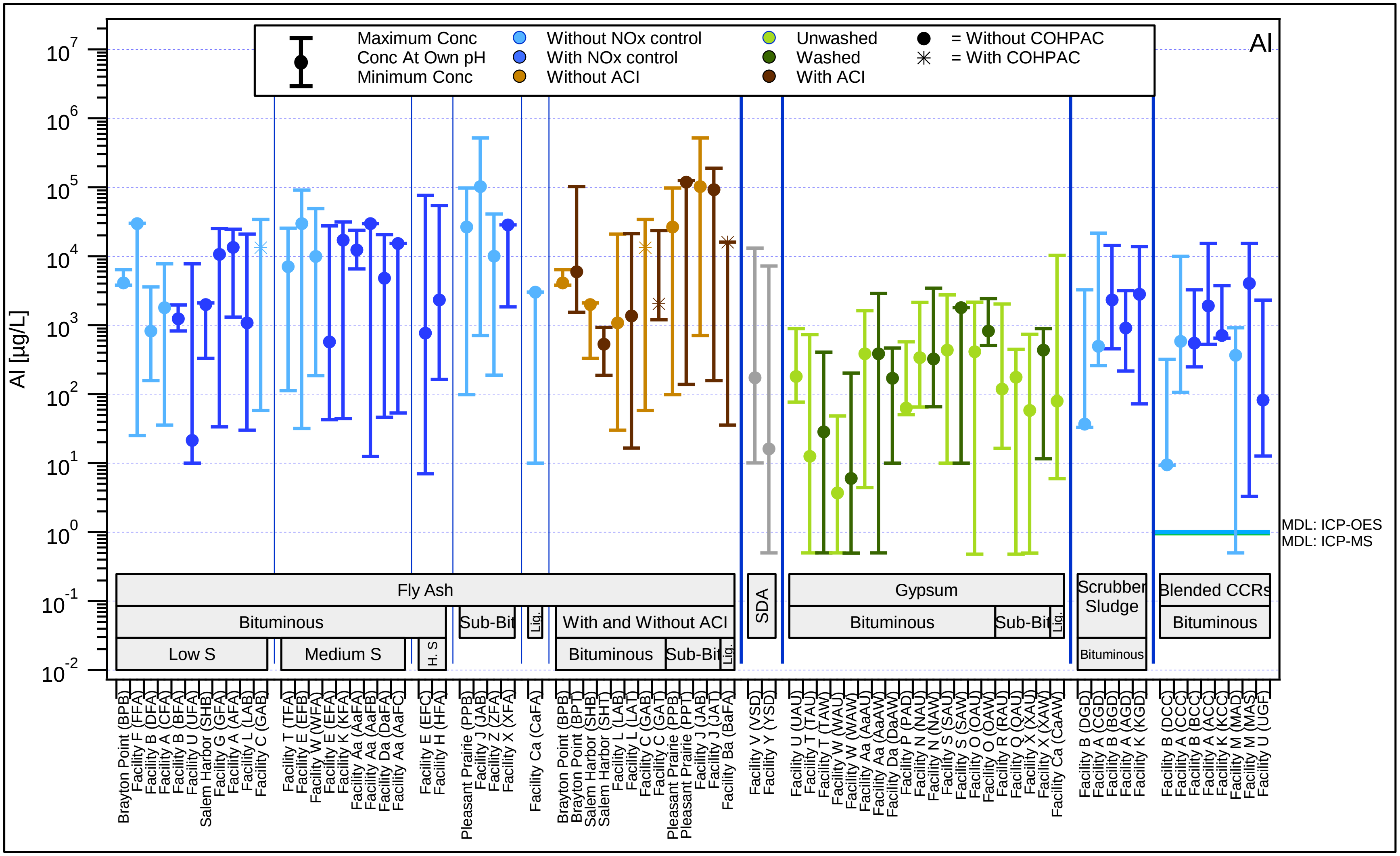


Figure 54. Aluminum. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

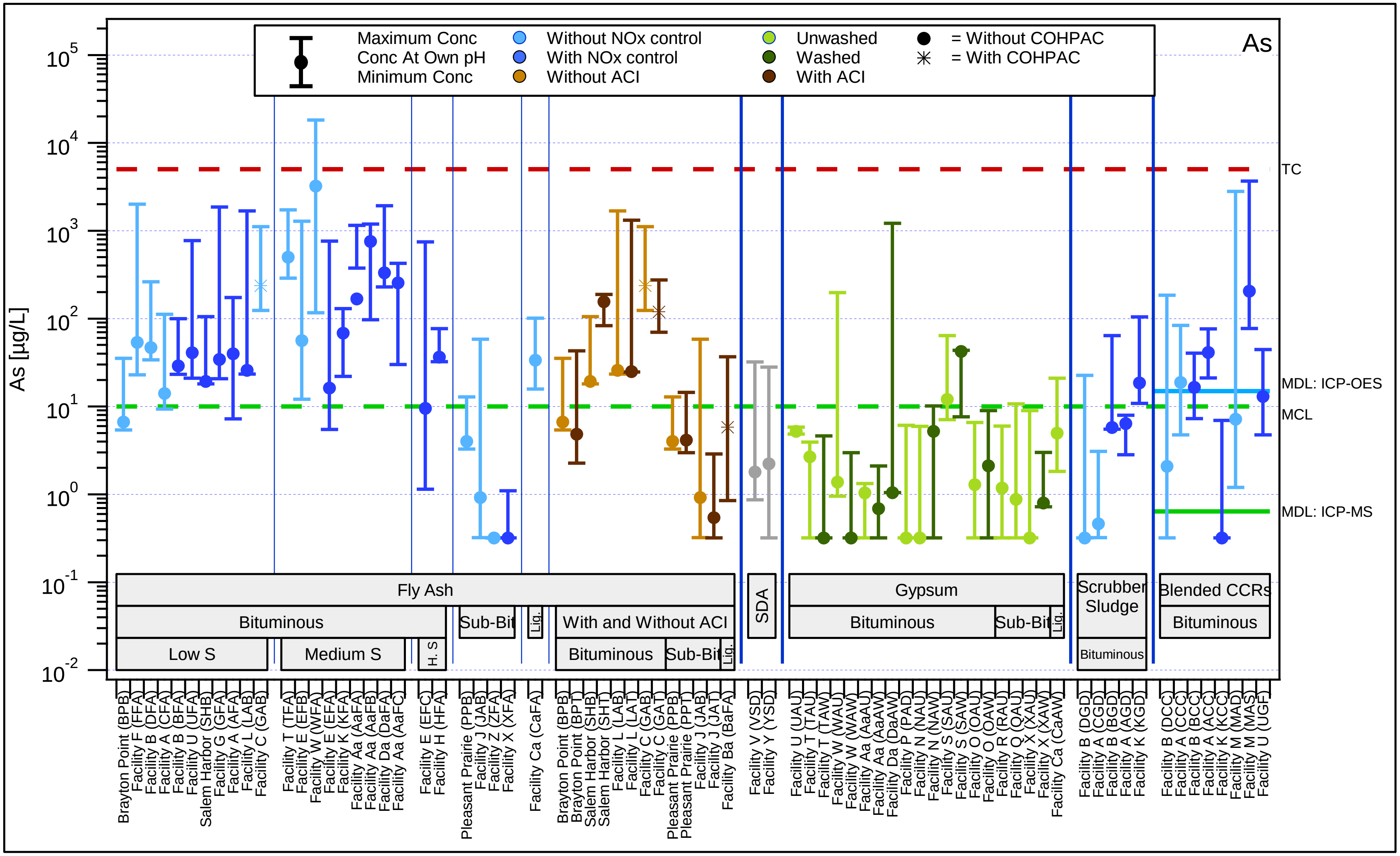


Figure 55. Arsenic. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

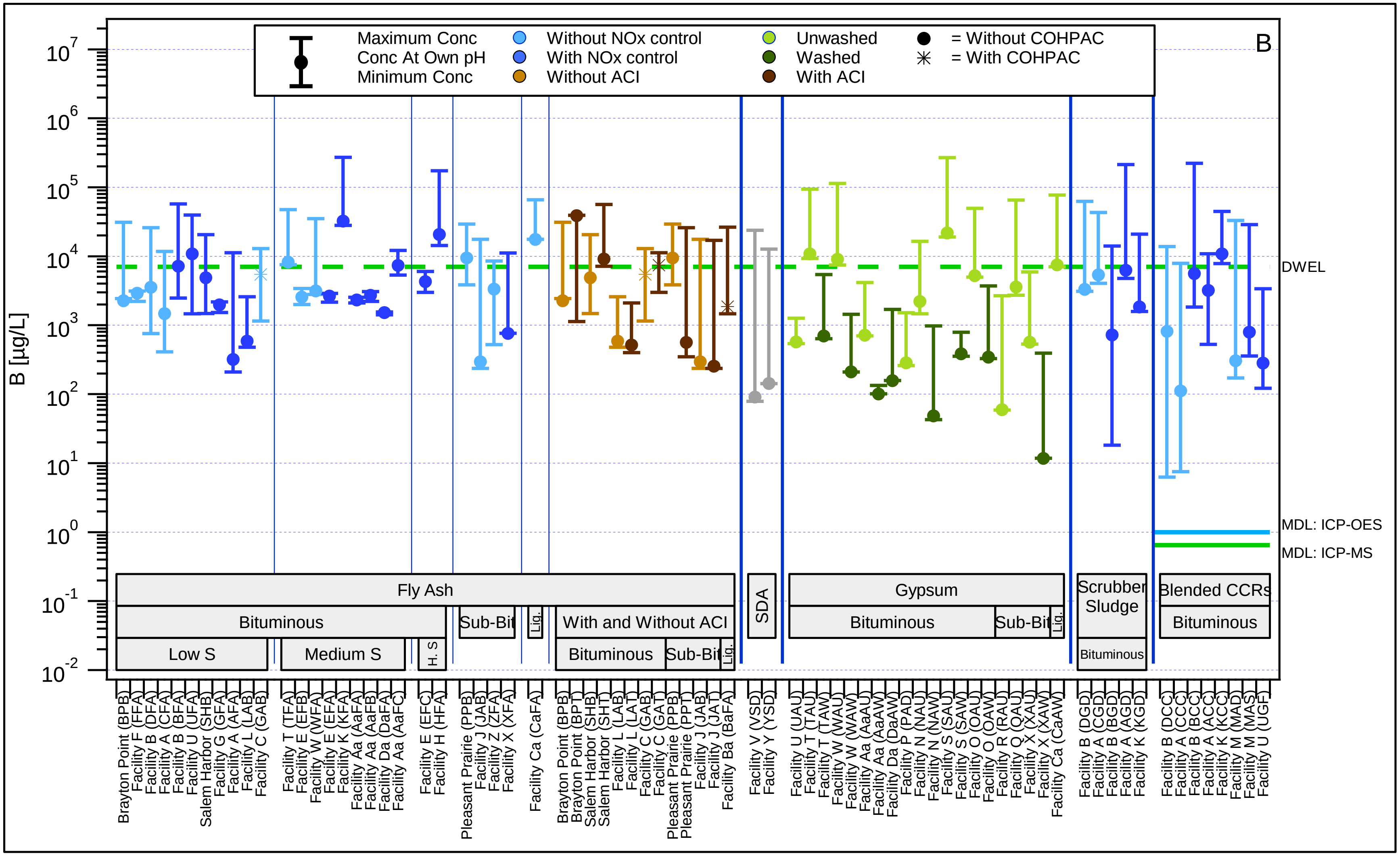


Figure 56. Boron. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤pH≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

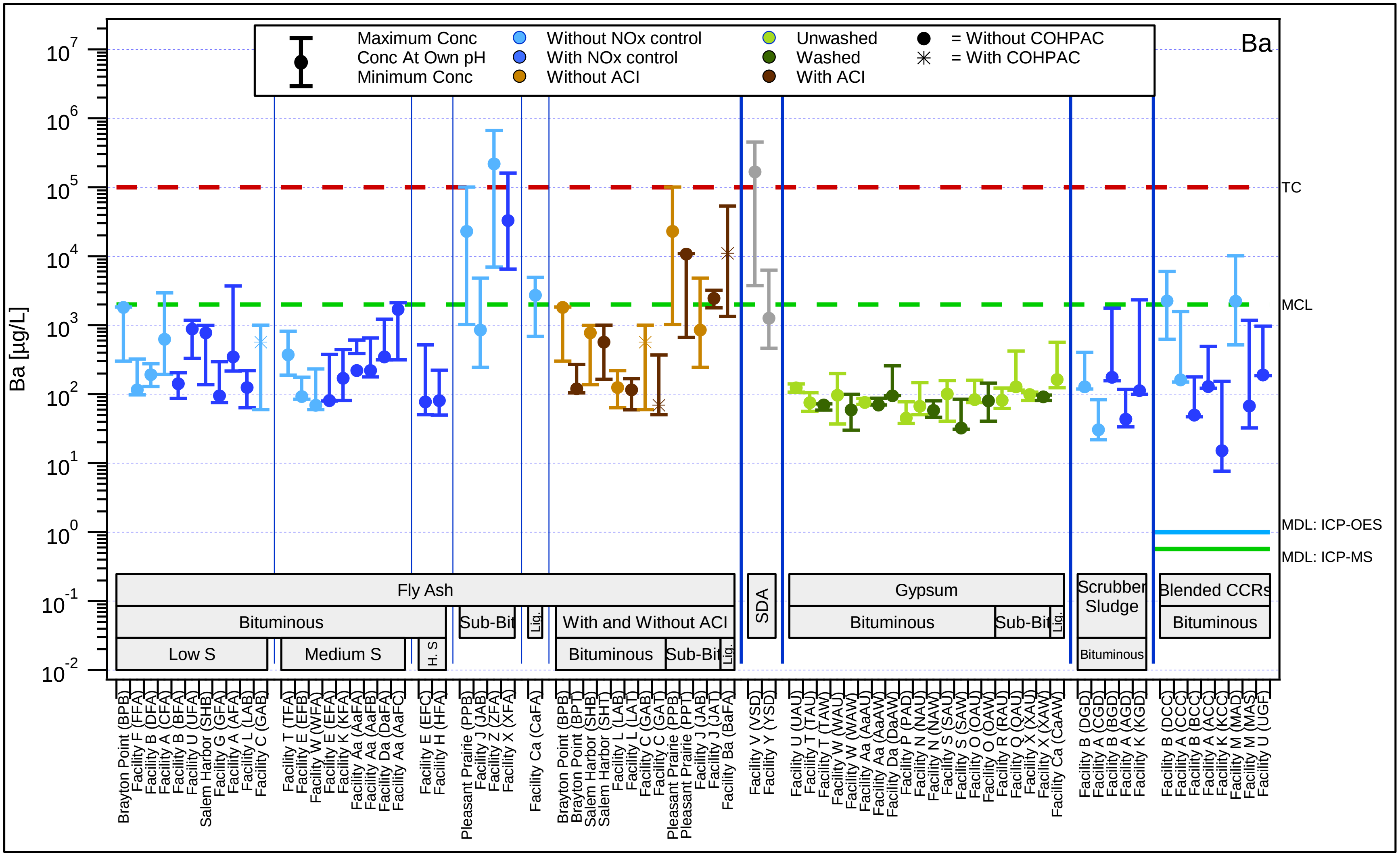


Figure 57. Barium. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

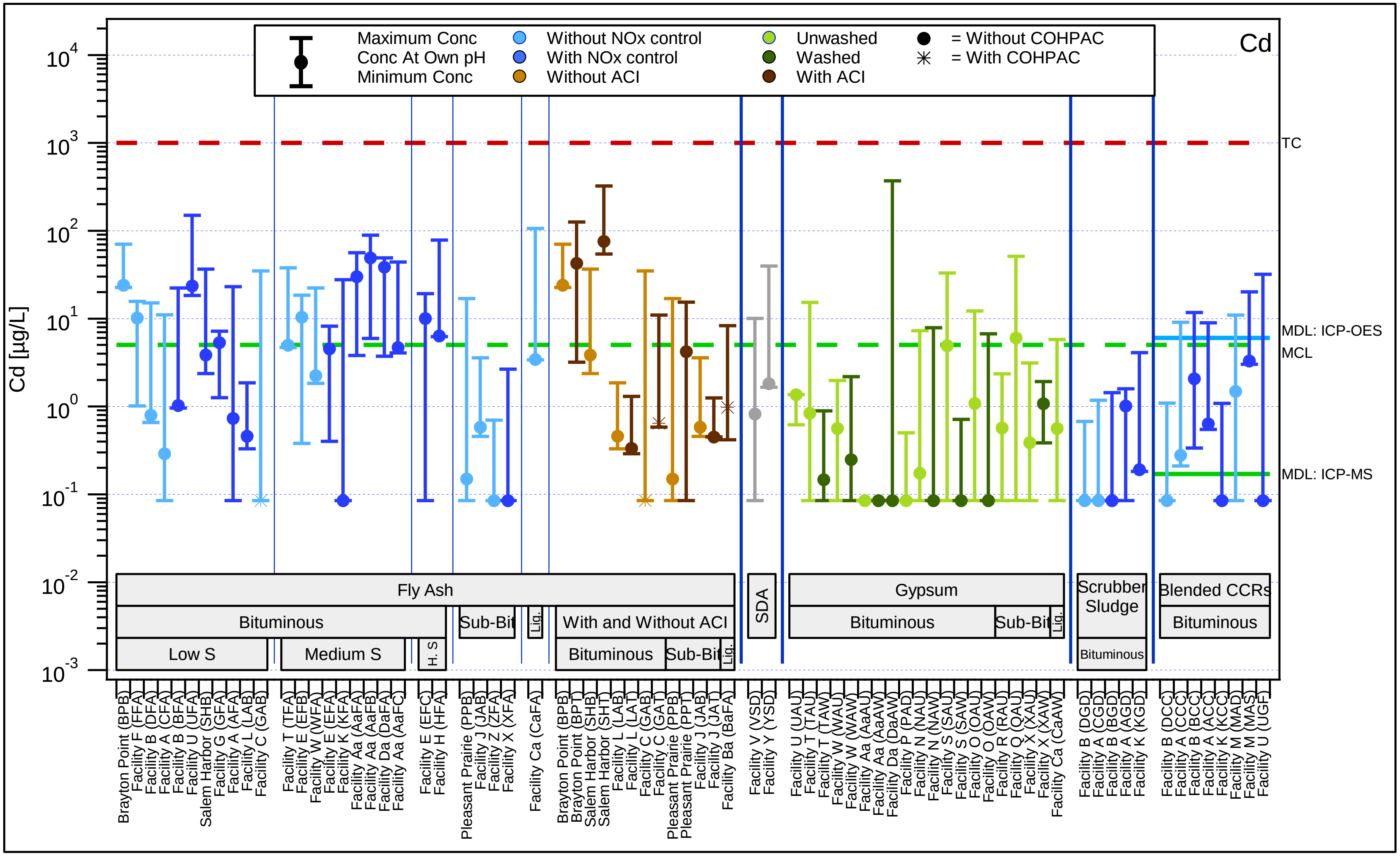


Figure 58. Cadmium. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

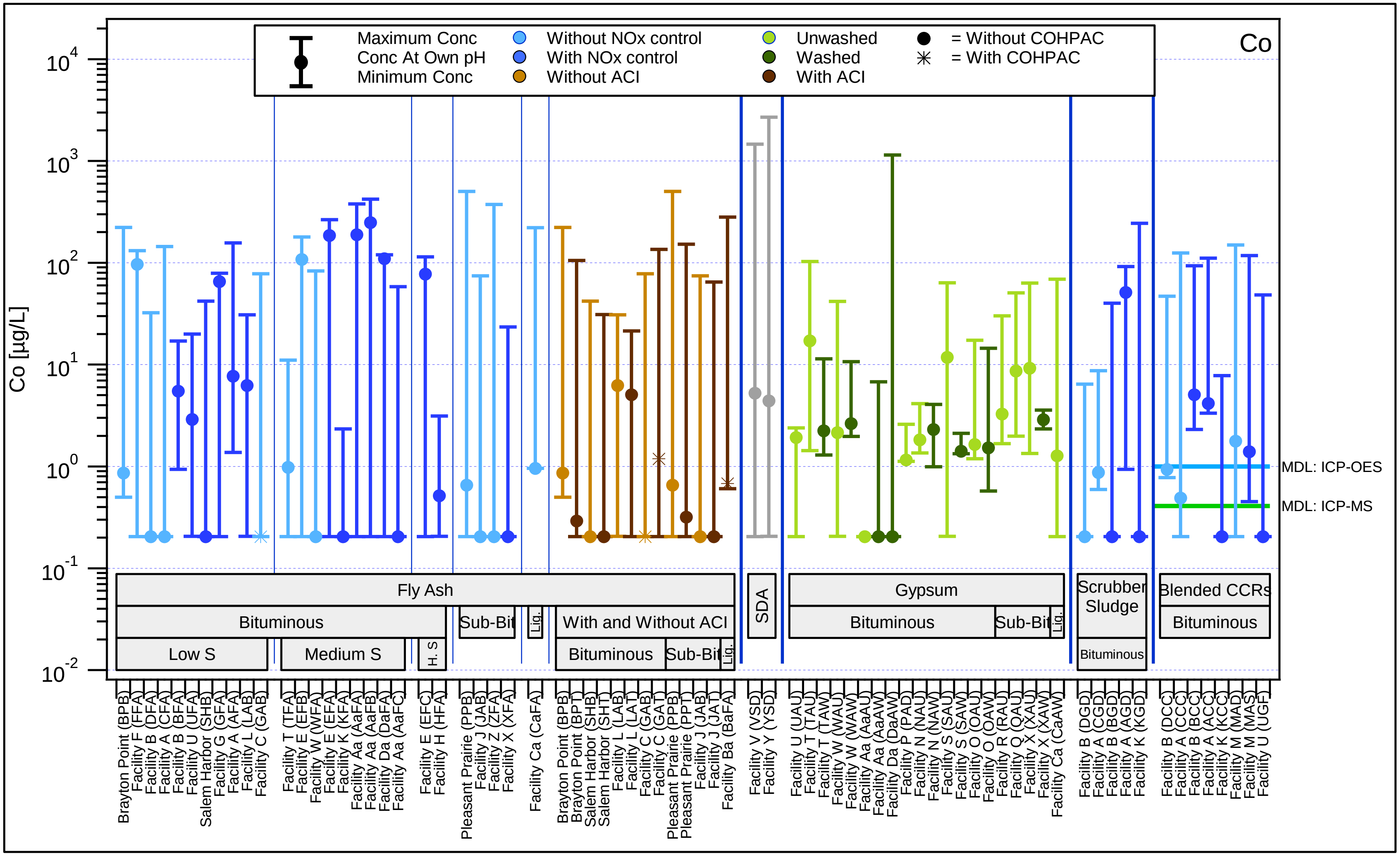


Figure 59. Cobalt. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

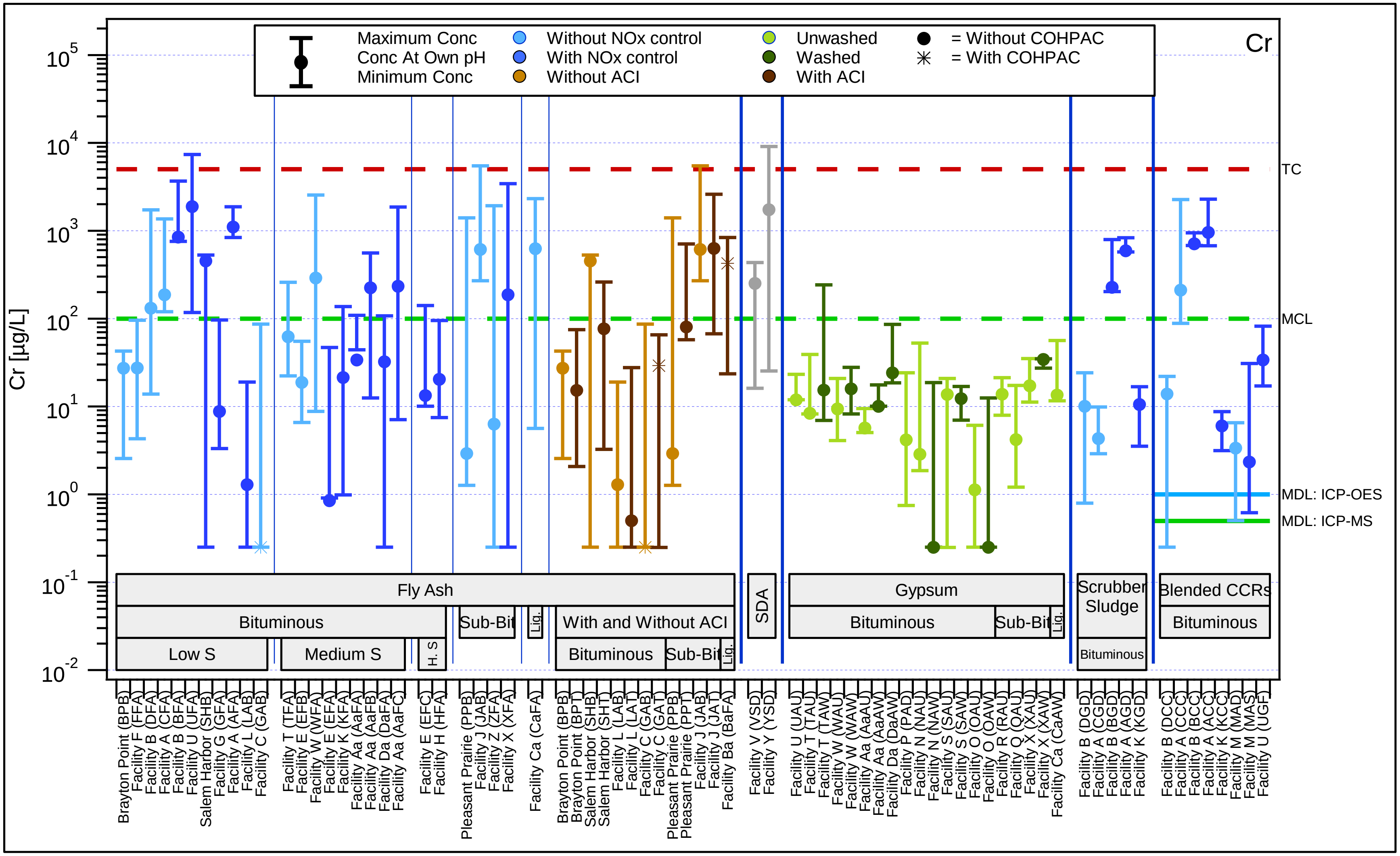


Figure 60. Chromium. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

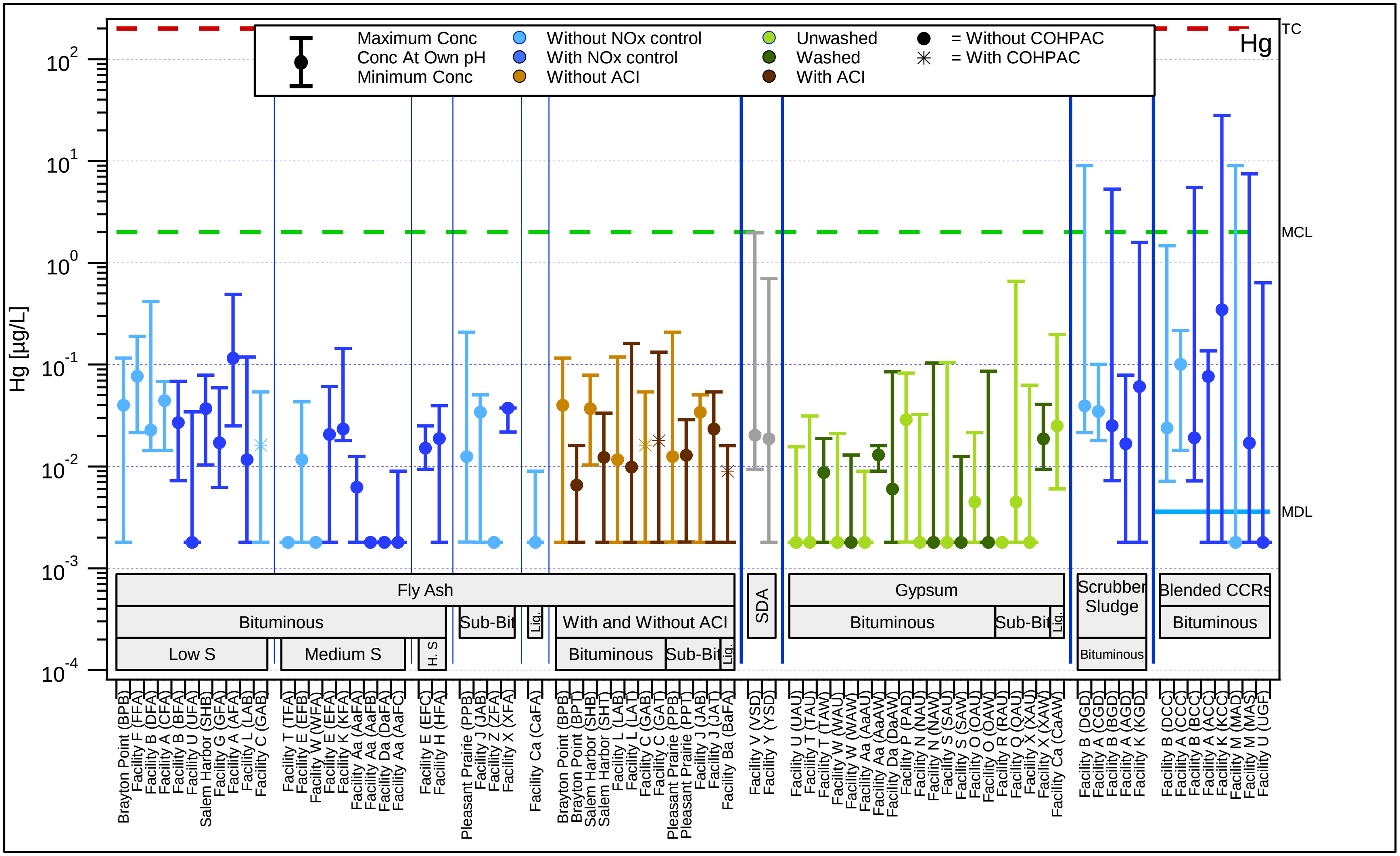


Figure 61. Mercury. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

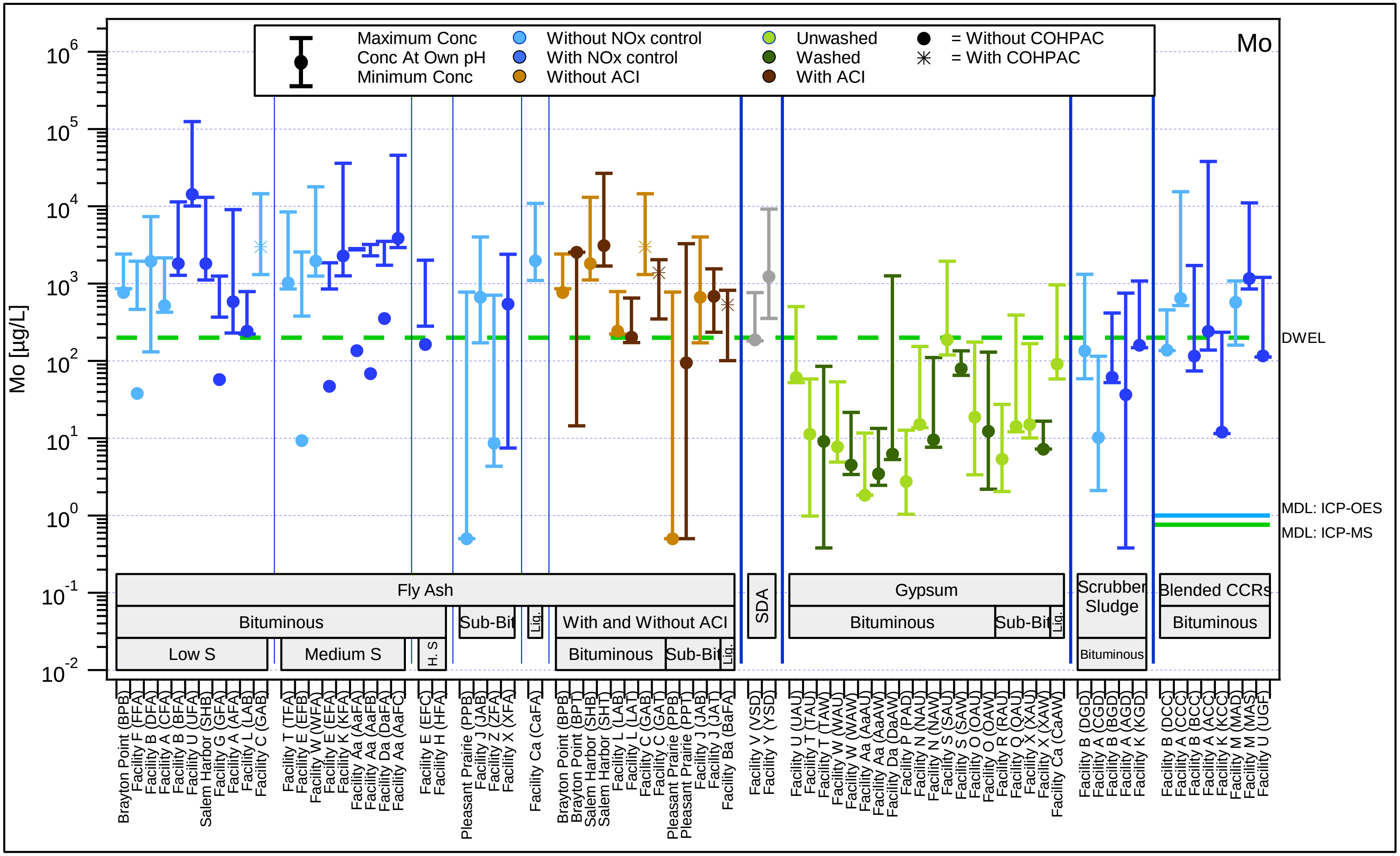


Figure 62. Molybdenum. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

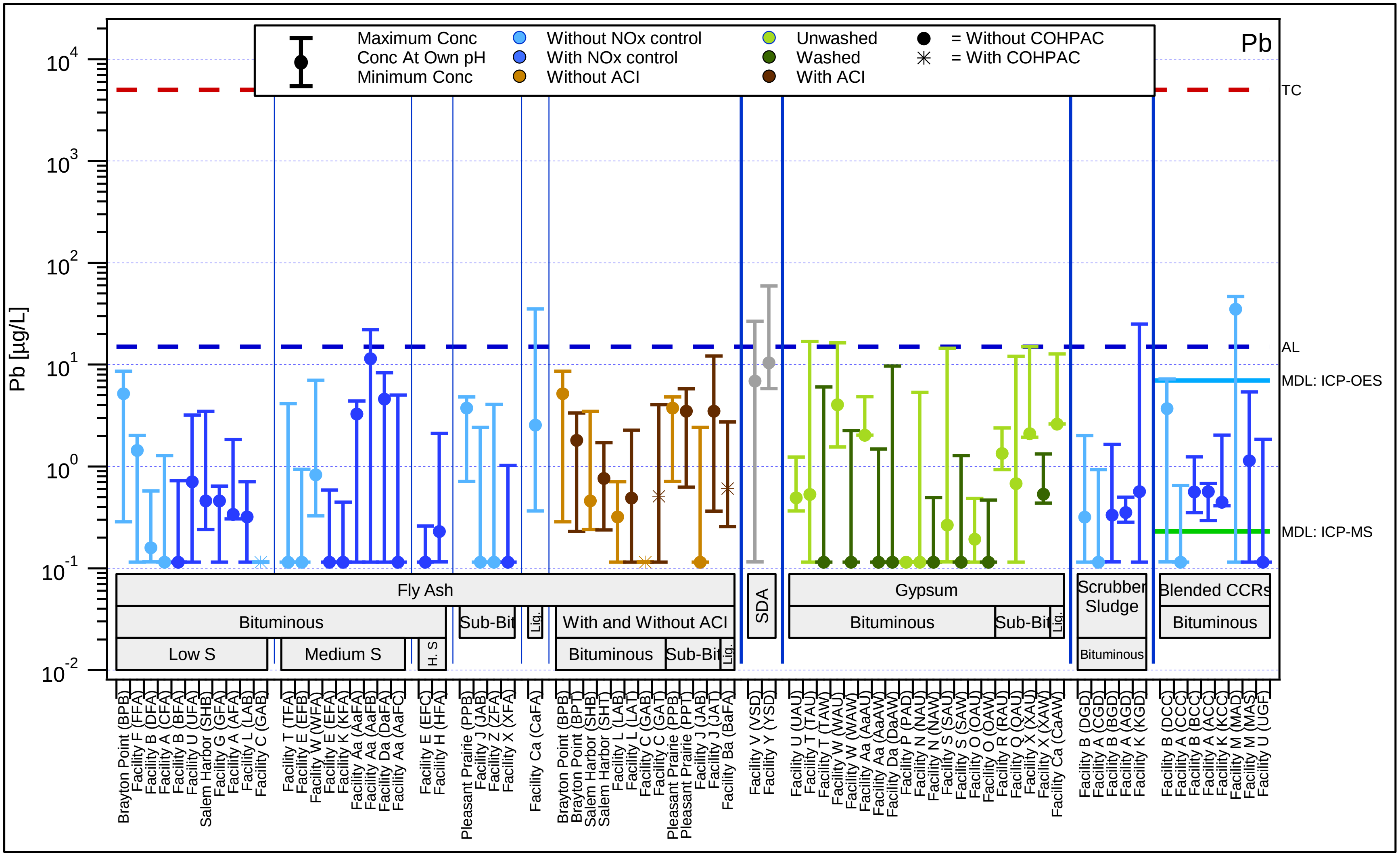


Figure 63. Lead. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

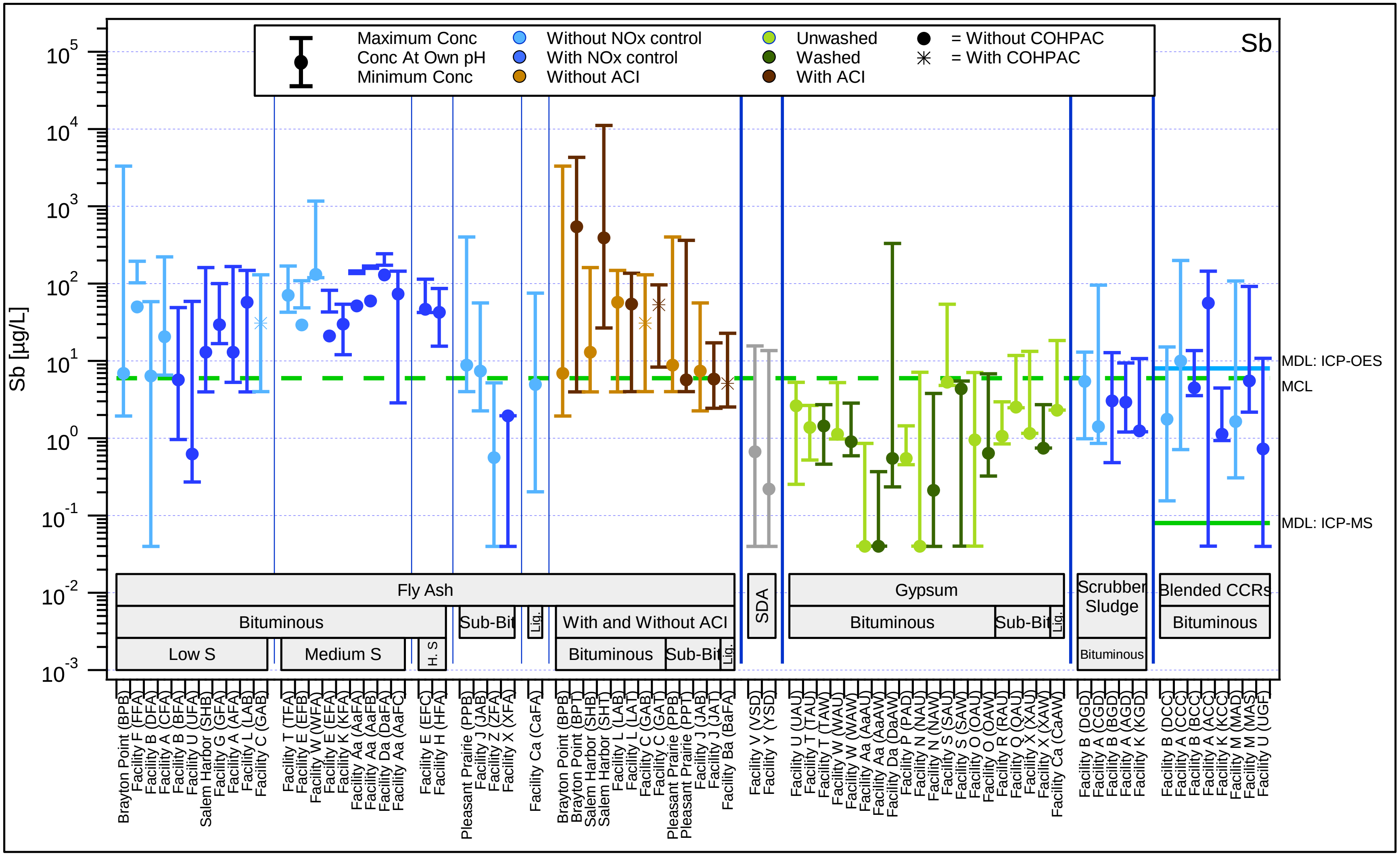


Figure 64. Antimony. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

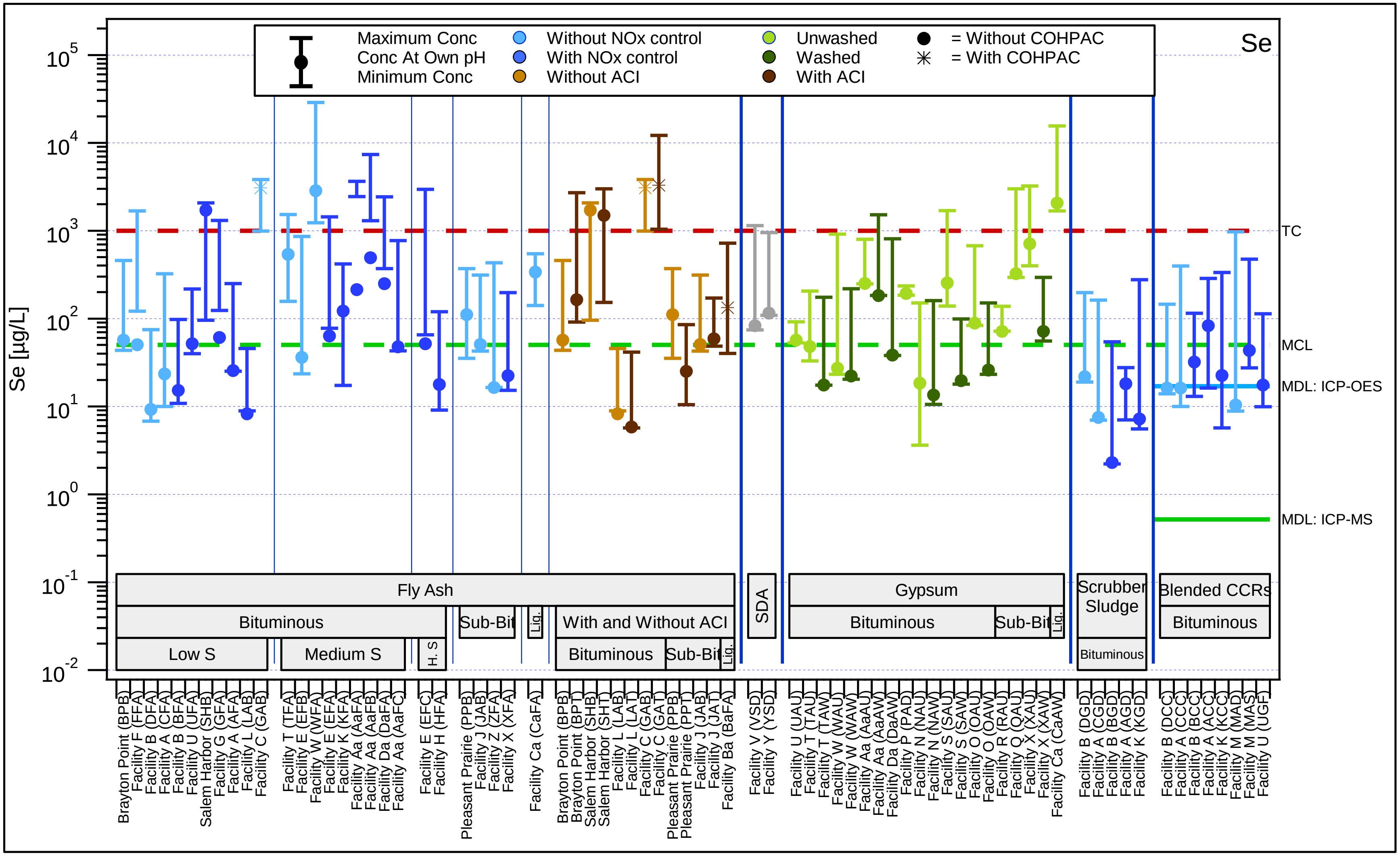


Figure 65. Selenium. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

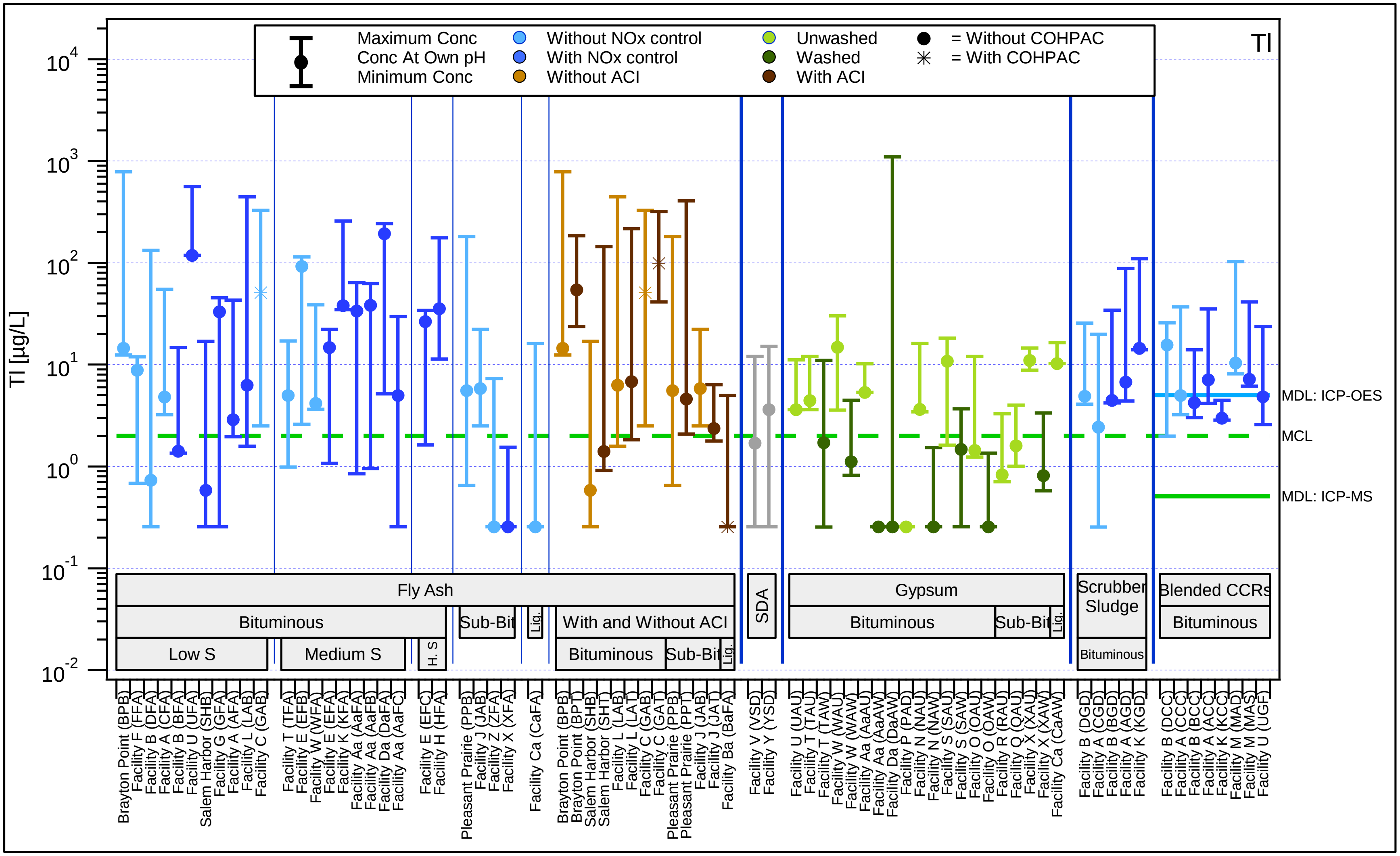


Figure 66. Thallium. Comparison of maximum, minimum and own pH concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

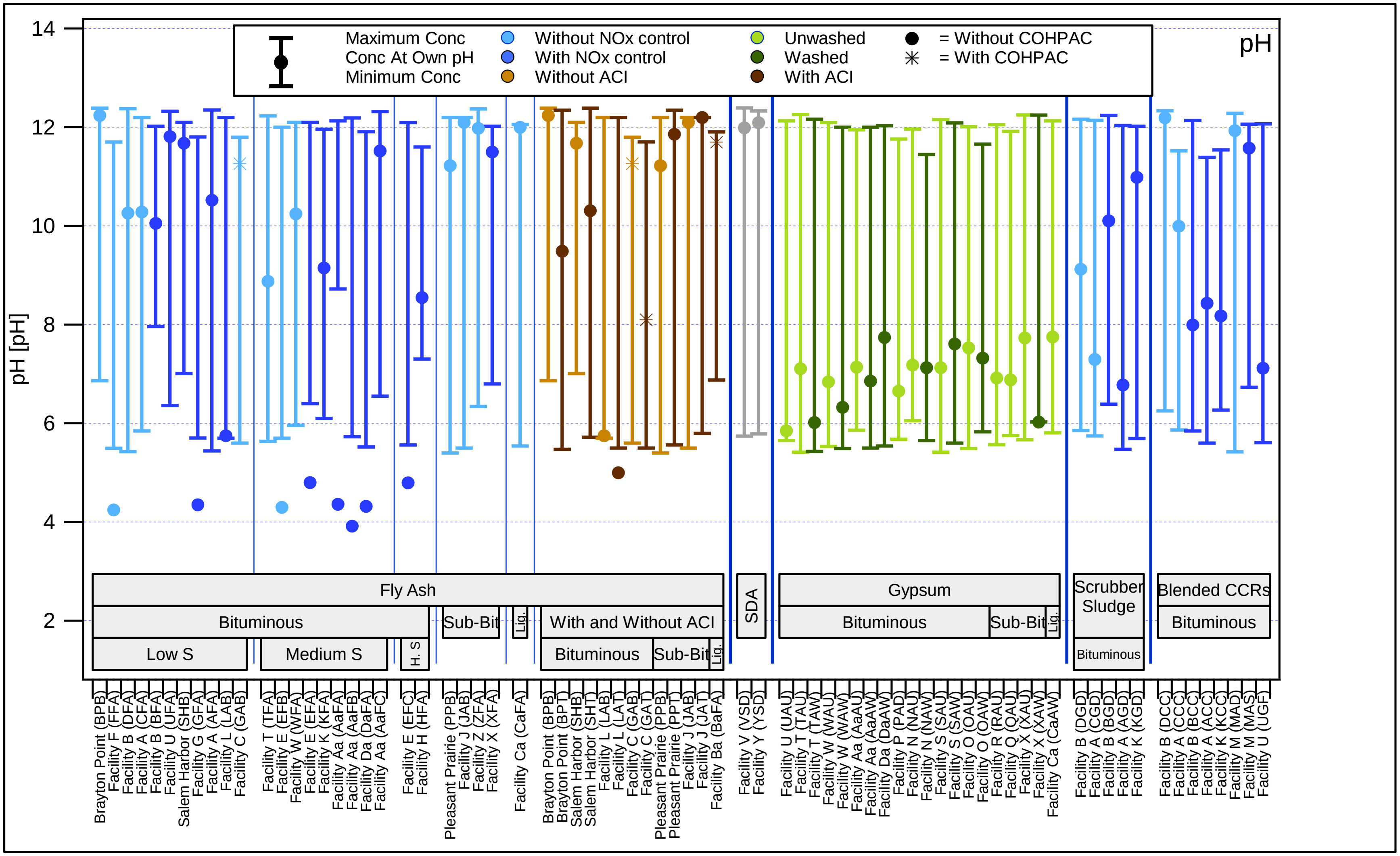


Figure 67. pH. Comparison of maximum, minimum and own pH observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4. SDA samples were from facilities burning sub-bituminous coal.

3.2.3. Leaching Dependency on Total Content

An on-going question has been whether or not total content of an element in a CCR sample is a useful indicator of potential environmental impact by leaching. This question was evaluated by comparing for the COPCs (i) the maximum eluate concentration over the pH domain $5.4 \leq pH \leq 12.4$ with the total content by digestion (Figure 68 to Figure 79), and (ii) the eluate concentration at own pH with the total content by digestion (results not shown). The maximum eluate concentration as a function of total content is presented in Figure 68 to Figure 79 because in understanding the meaning of research results, the focus is often on the potential for exceedance of a particular threshold value. However, results of own pH eluate concentration as a function of total content were similar. Results are annotated on Figure 69 (arsenic) for illustration purposes.

Each of these figures show (i) there is a poor correlation between leachate concentration and total content of any of the elements considered, (ii) a wide range of total content values (over more than one order of magnitude) can result in the same or very similar eluate concentrations, and (iii) a wide range of eluate concentrations (over more than one order of magnitude) can be observed for CCRs with similar total content values. If leaching correlated closely with total concentration, the data on these figures would be expected to show strong linearity, and relatively less scatter. Thus, it is clear that leaching phenomena is controlled by complex solid-liquid partitioning chemistry and that total content is not a good indicator of leaching. Furthermore, the absence of a linear or unique monotonic relationship between total content and eluate concentrations indicates that representation of leaching as a linear partitioning phenomenon (i.e., the linear distribution coefficient, K_d, approach) is not appropriate.

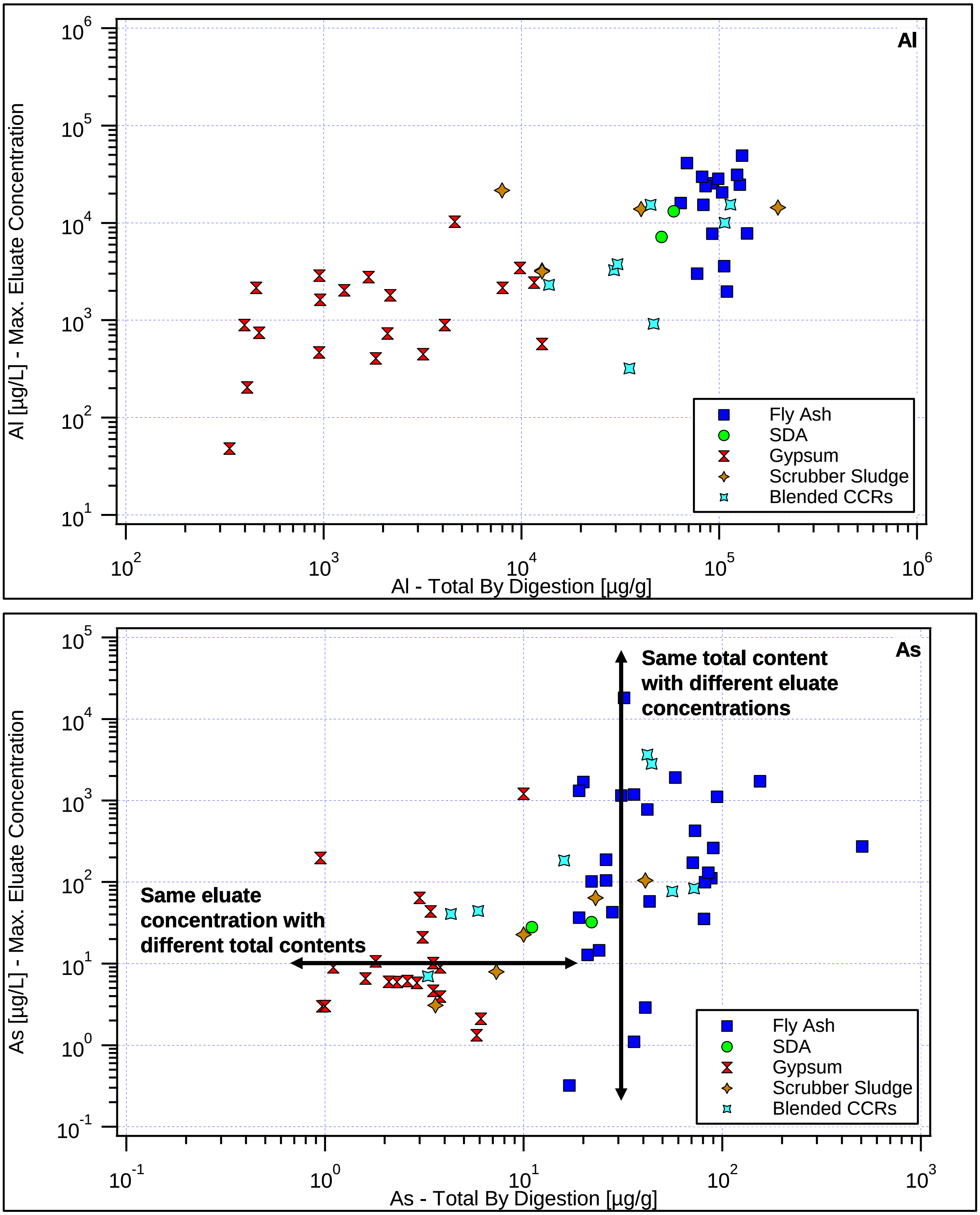
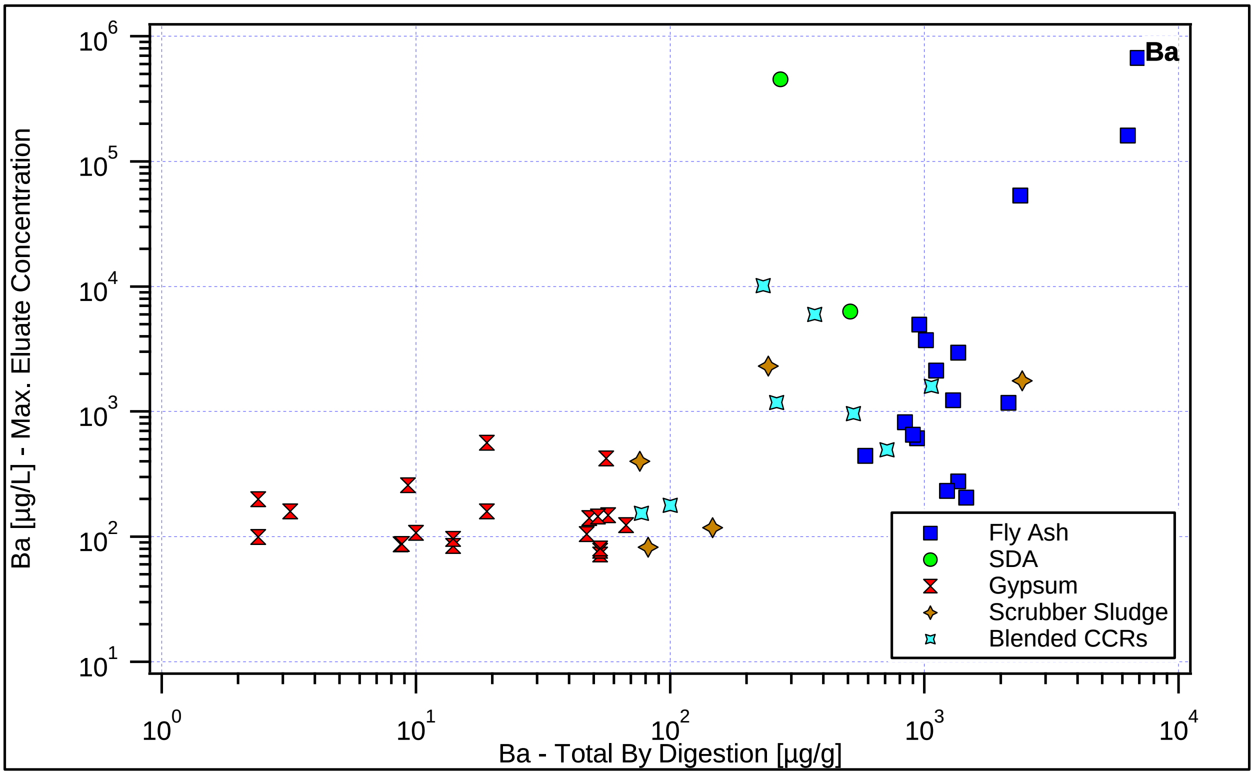


Figure 68 and Figure 69. Aluminum and Arsenic. Maximum eluate concentration ($5.4 \leq pH \leq 12.4$) as a function of total content by digestion.



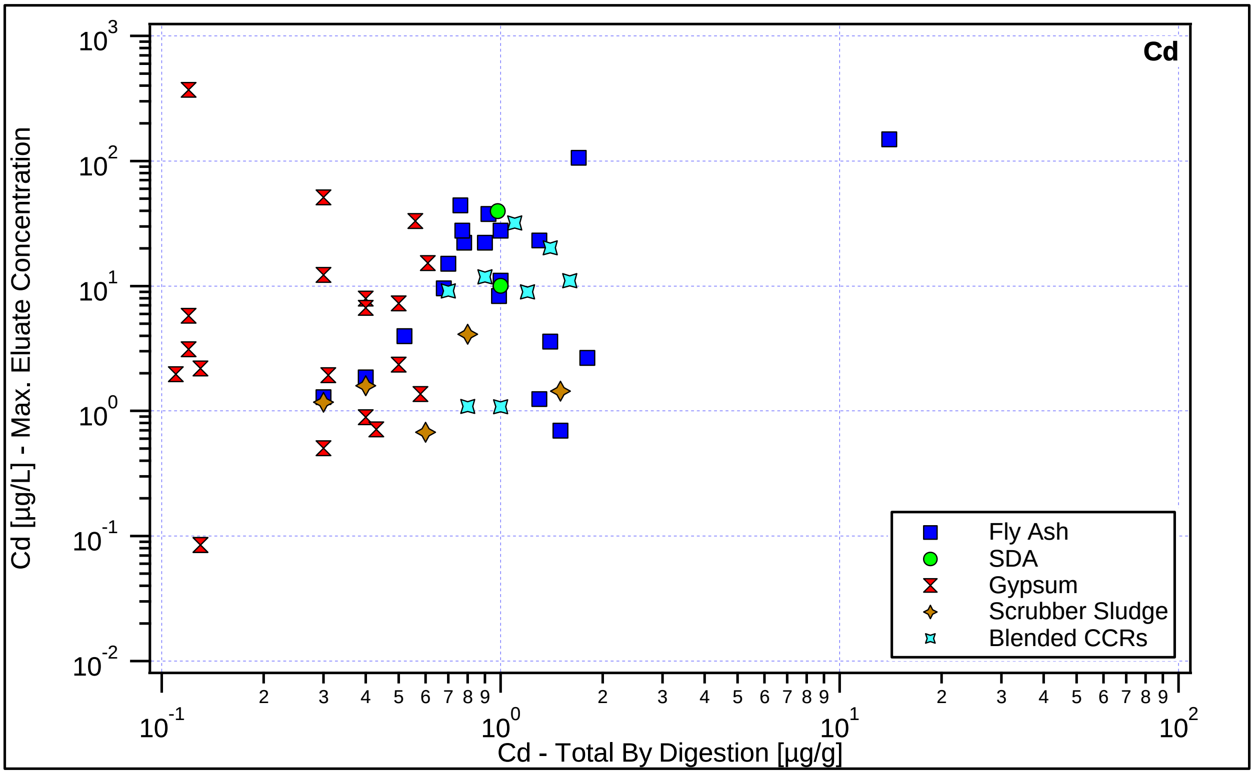
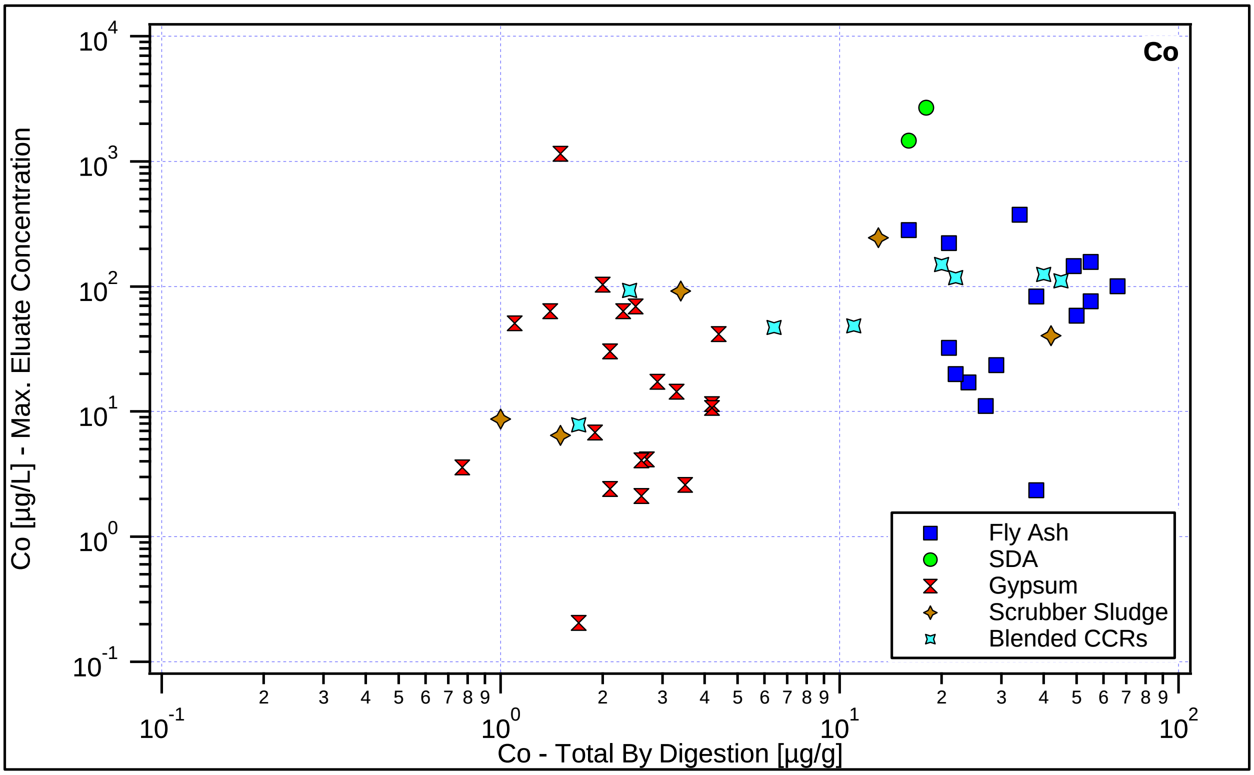


Figure 70 and Figure 71. Barium and Cadmium. Maximum eluate concentration (5.4 ≤ pH ≤ 12.4) as a function of total content by digestion.



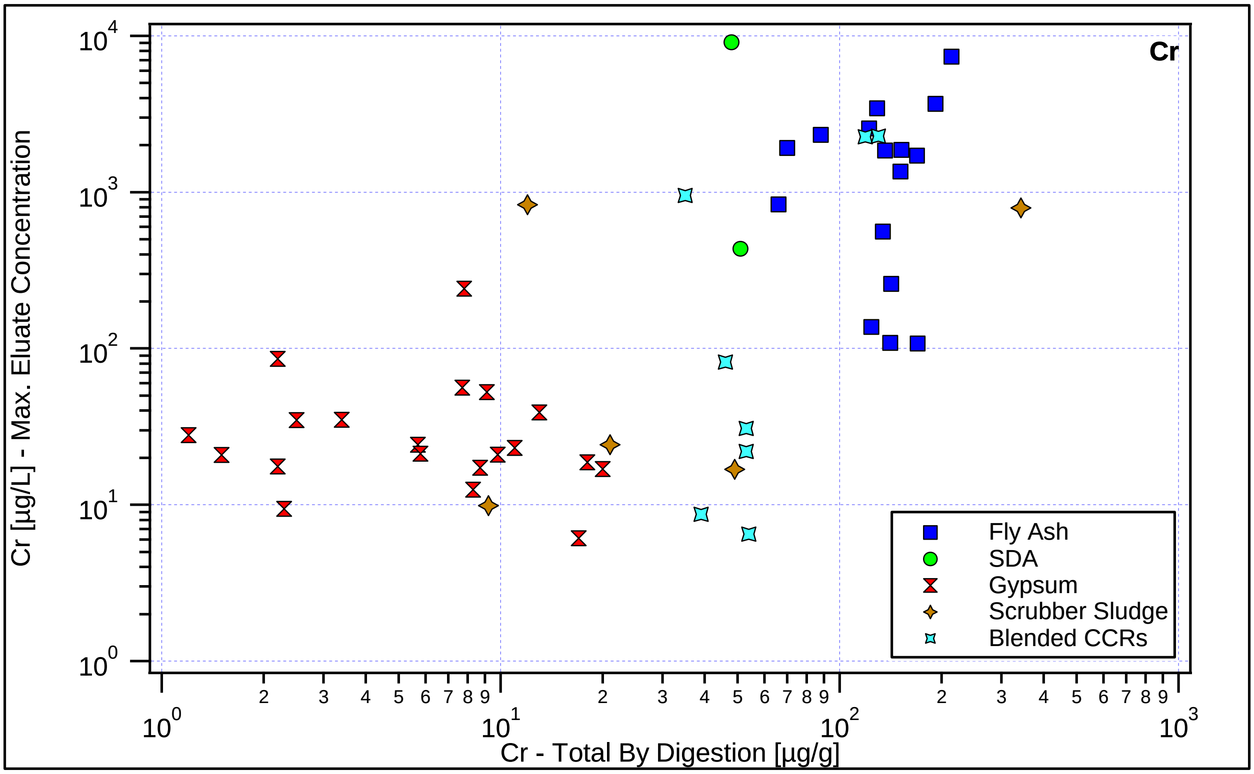


Figure 72 and Figure 73. Cobalt and Chromium. Maximum eluate concentration (5.4 ≤ pH ≤ 12.4) as a function of total content by digestion.

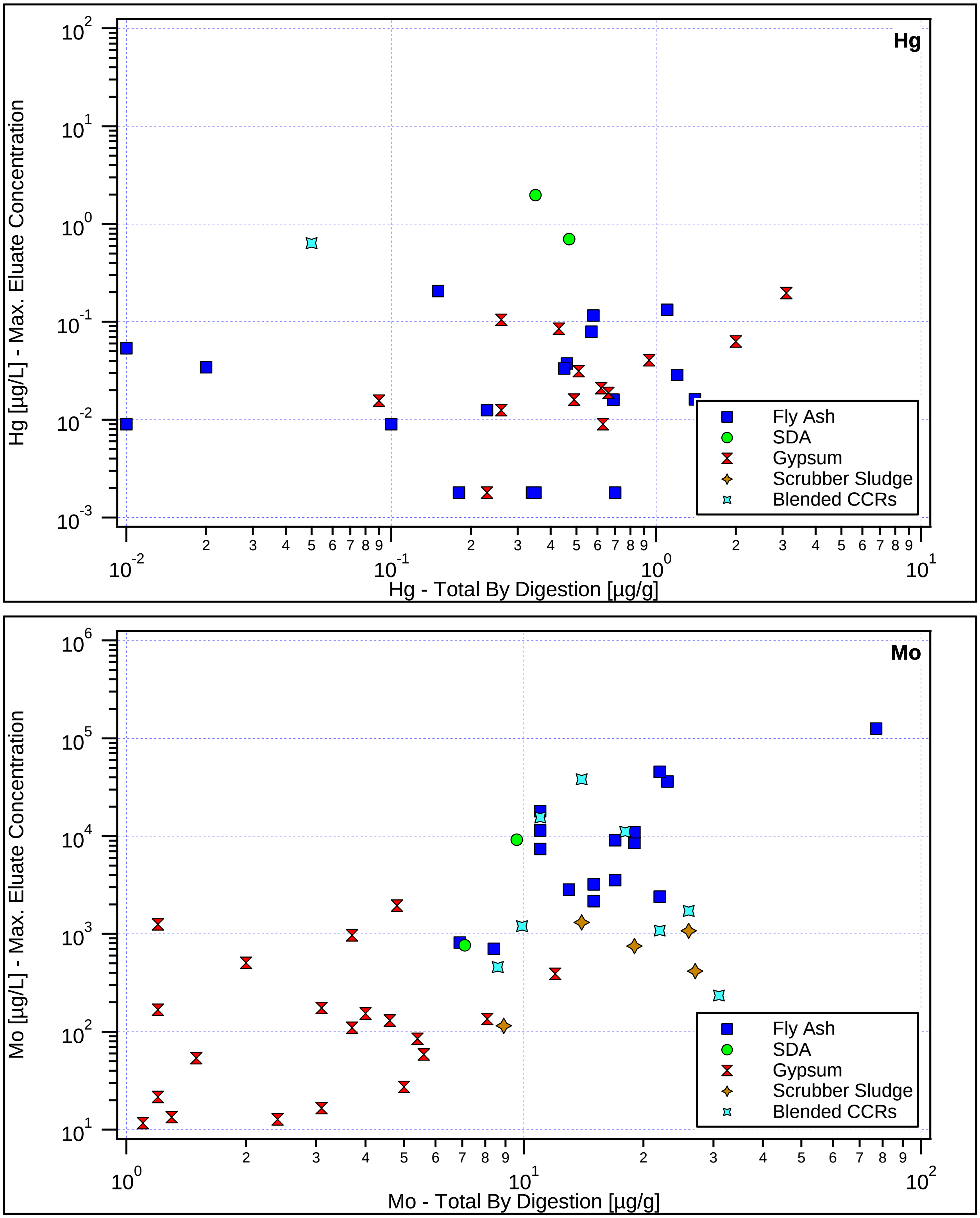


Figure 74 and Figure 75. Mercury and Molybdenum. Maximum eluate concentration (5.4 ≤ pH ≤ 12.4) as a function of total content by digestion.

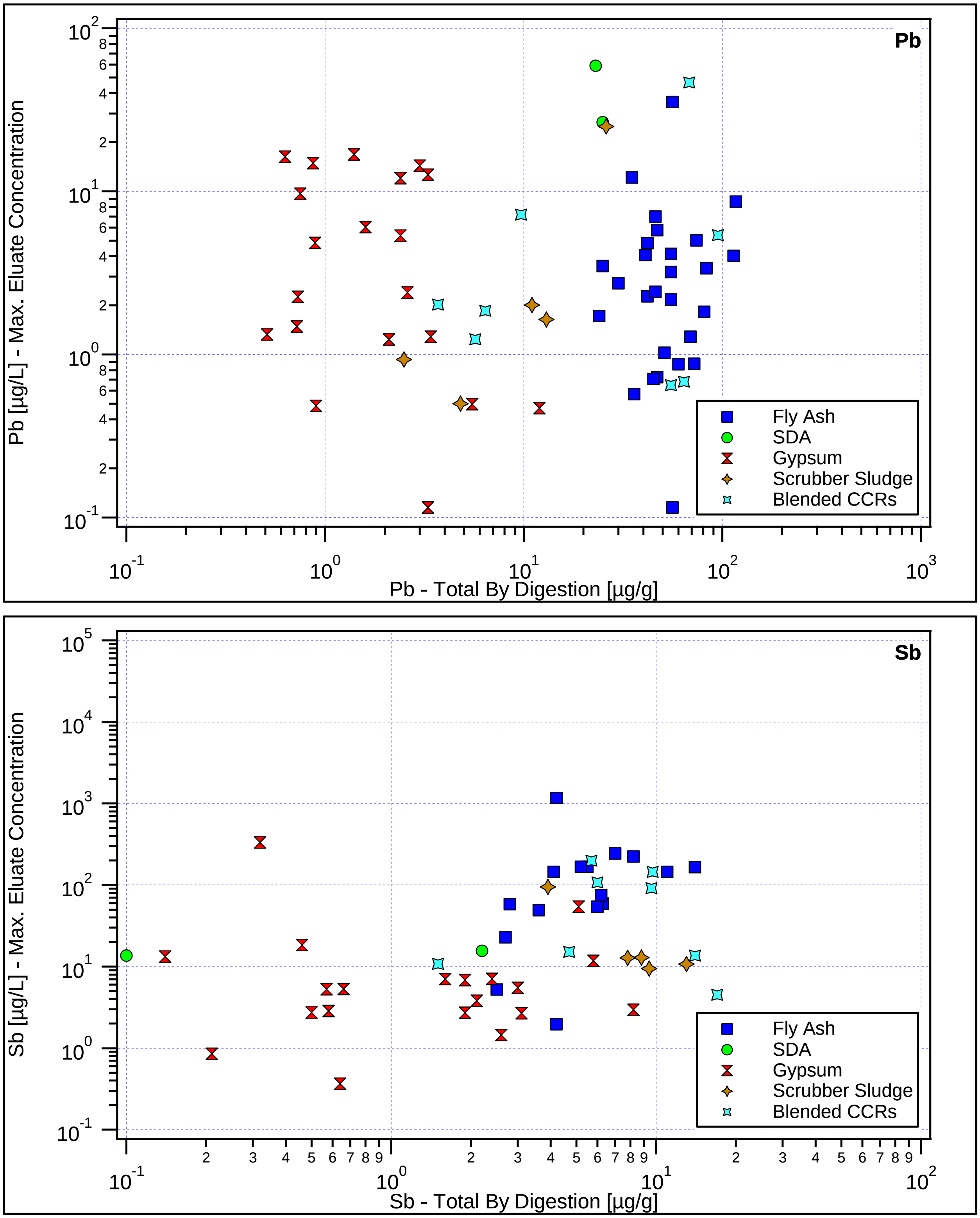


Figure 76 and Figure 77. Lead and Antimony. Maximum eluate concentration (5.4 ≤ pH ≤ 12.4) as a function of total content by digestion.

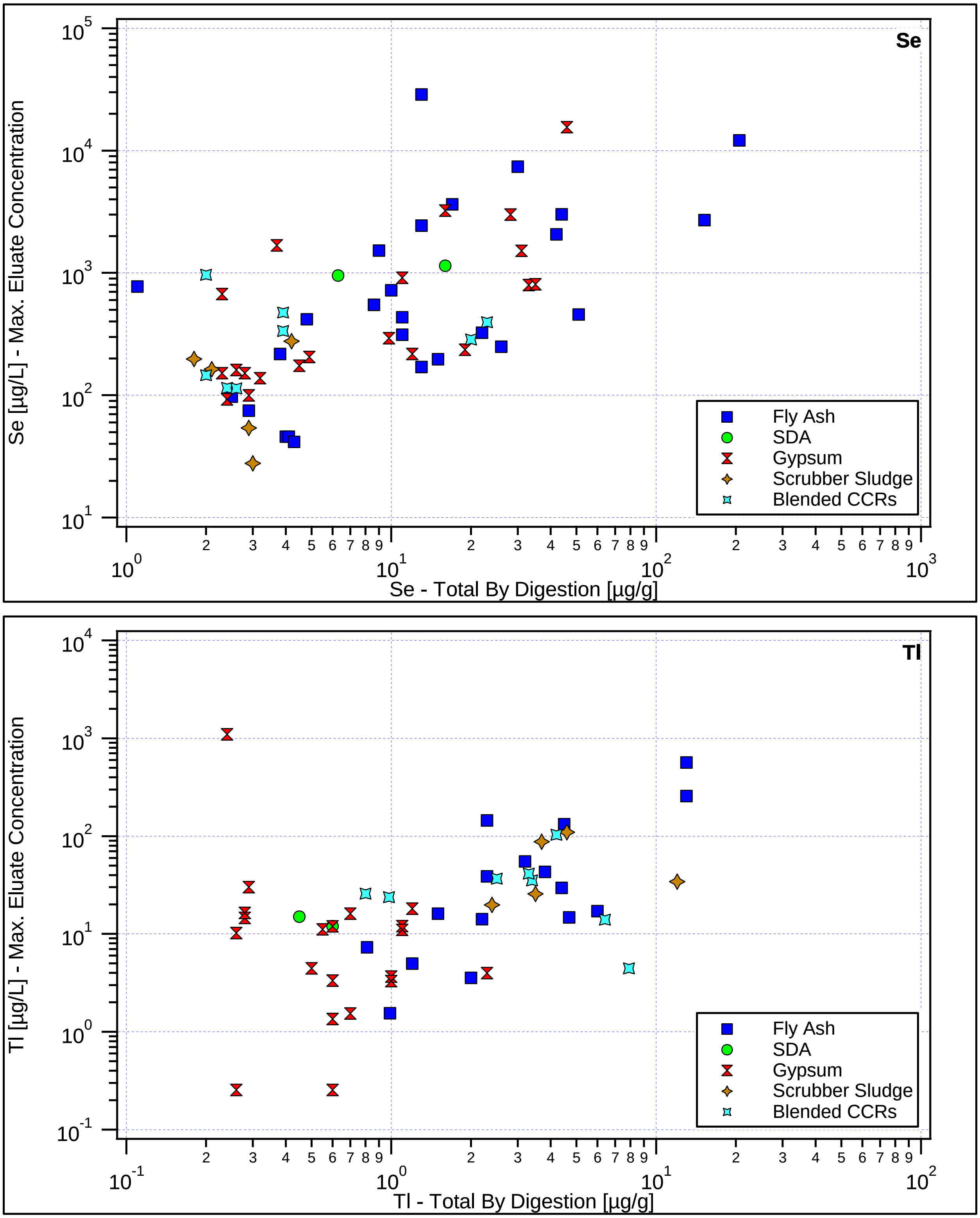


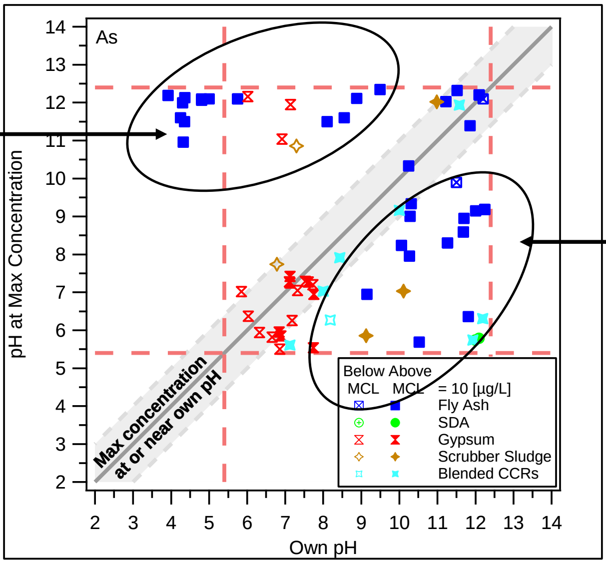
Figure 78 and Figure 79. Selenium and Thallium. Maximum eluate concentration (5.4 ≤ pH ≤ 12.4) as a function of total content by digestion.

3.2.4. pH at the Maximum Concentration Value versus the Materials' Own pH

Figure 81 through Figure 93 plot the pH at which the maximum eluate concentration for a CCR sample occurs over the domain $5.4 \leq pH \leq 12.4$ as a function of the own pH for the same sample. Results for arsenic are annotated as Figure 80. The diagonal gray line indicates a slope equal to one; when a data point falls on or near (within the light gray band) this line, the maximum eluate concentration occurs at or near the own pH for the specific CCR sample. Data points indicated with an open symbol have maximum eluate concentrations that are less than either the MCL or DWEL as indicated for the element of interest. Data points indicated with a filled symbol have maximum eluate concentrations that are greater than either the MCL or DWEL. When a sample falls above the gray diagonal line, processes that result in increased elution pH (e.g., mixing with other materials such as lime, other CCRs or other alkaline materials) are indicated to lead to increased leachate concentration for that element. When a sample falls below the gray diagonal line, processes that result in decreased elution pH (e.g., mixing with other more acidic materials or uptake of atmospheric carbon dioxide) are indicated to lead to increased leachate concentration for that element. For example, uptake of atmospheric carbon dioxide (carbonation) occurs when pore solution pH is greater than 8, with the most pronounced effect when pore solution pH is greater than 10. Carbonation results in decreases in pH typically to between 8 and 9. These potential changes must be qualified with the caveat that changes that result in increased or decreased elution pH may also result in significantly changed chemistry (e.g., redox changes) that may also influence leaching.

Important observations from these figures include:

1. Often the maximum eluate concentration occurs at a pH other than the material's own pH, regardless of the element or material being evaluated.
2. The maximum eluate concentration varies over a wide range in pH and is different for different CCR types and elements. This indicates that there is not a single pH for which testing is likely to provide confidence in release estimates over a wide range of disposal and beneficial use options, emphasizing the benefit of multi-pH testing.
3. Multi-pH testing provides useful insights into the CCR management scenarios that have the potential to increase release of specific constituents beyond that indicated by monofill management scenarios.



Processes **increasing pH** may lead to increased concentration

(e.g., mixing with other materials such as lime, other CCRs, or alkaline materials)

Processes **decreasing pH** may lead to increased concentration

(e.g., carbonation or mixing with other more acidic materials)

Figure 80. An example of pH identity plot. Dashed red lines are used to indicate the pH domain of 5.4 to 12.4.

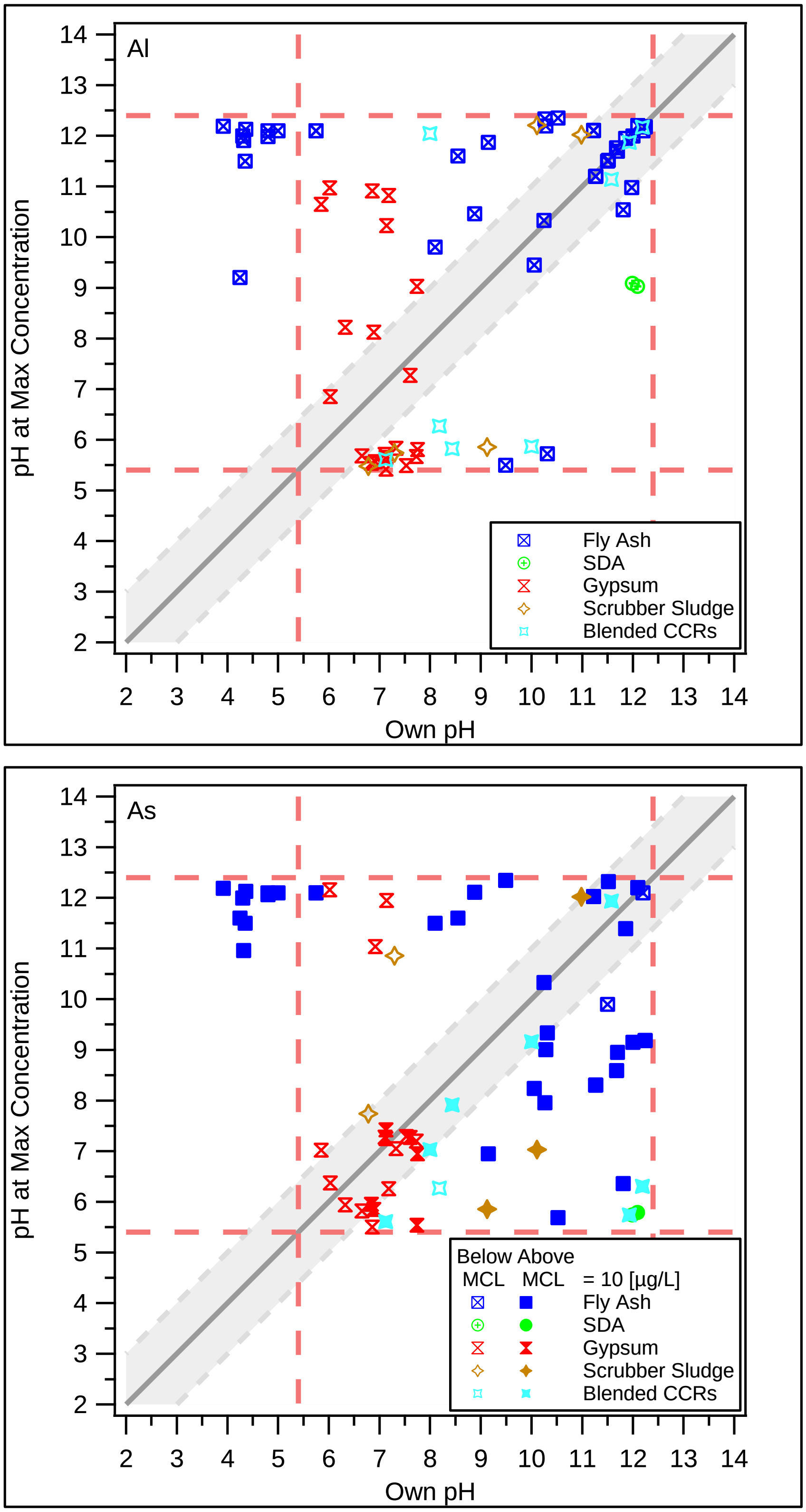


Figure 81 and Figure 82. Aluminum and Arsenic. pH identity plots.

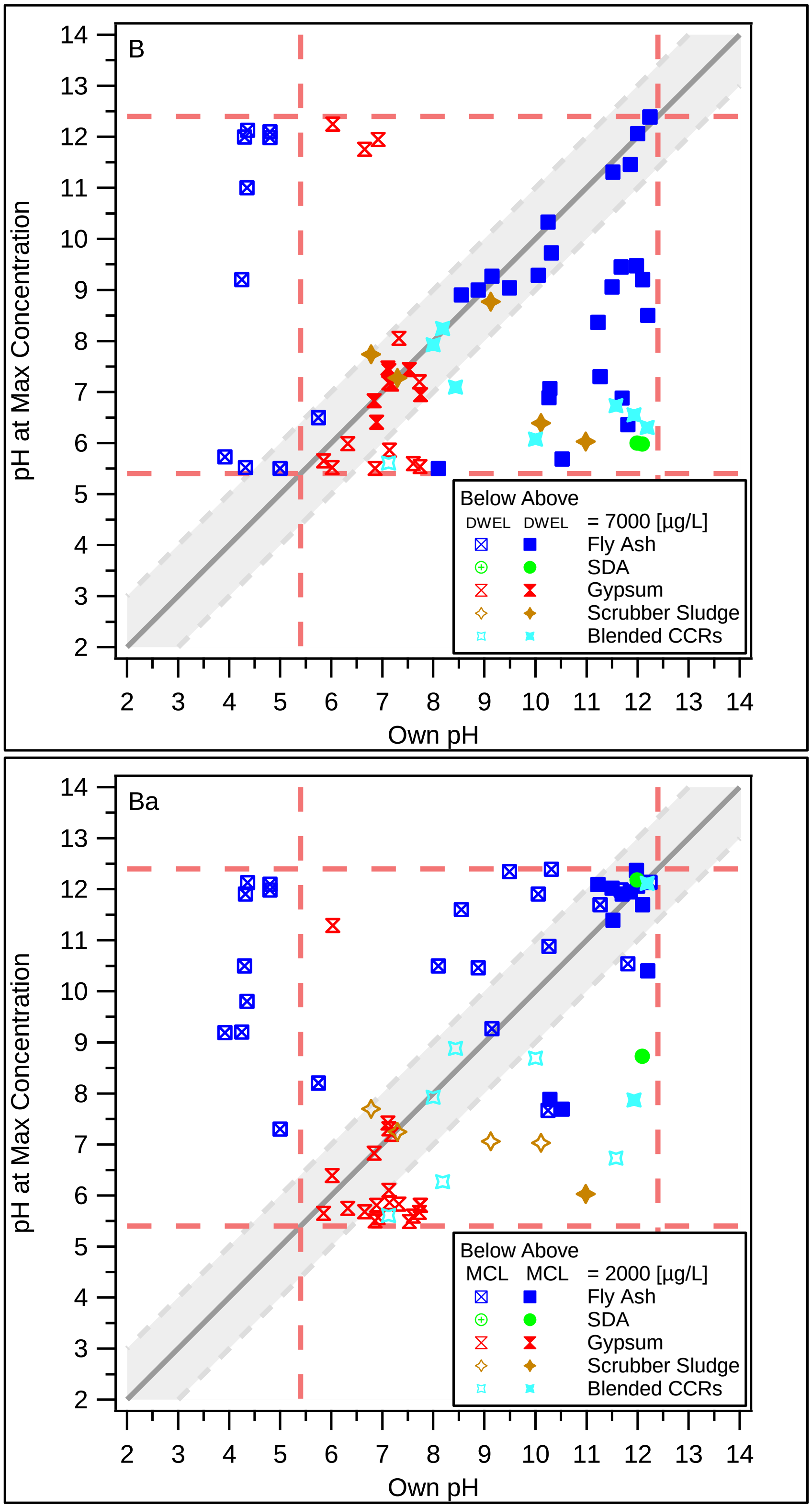


Figure 83 and Figure 84. Boron and Barium. pH identity plots.

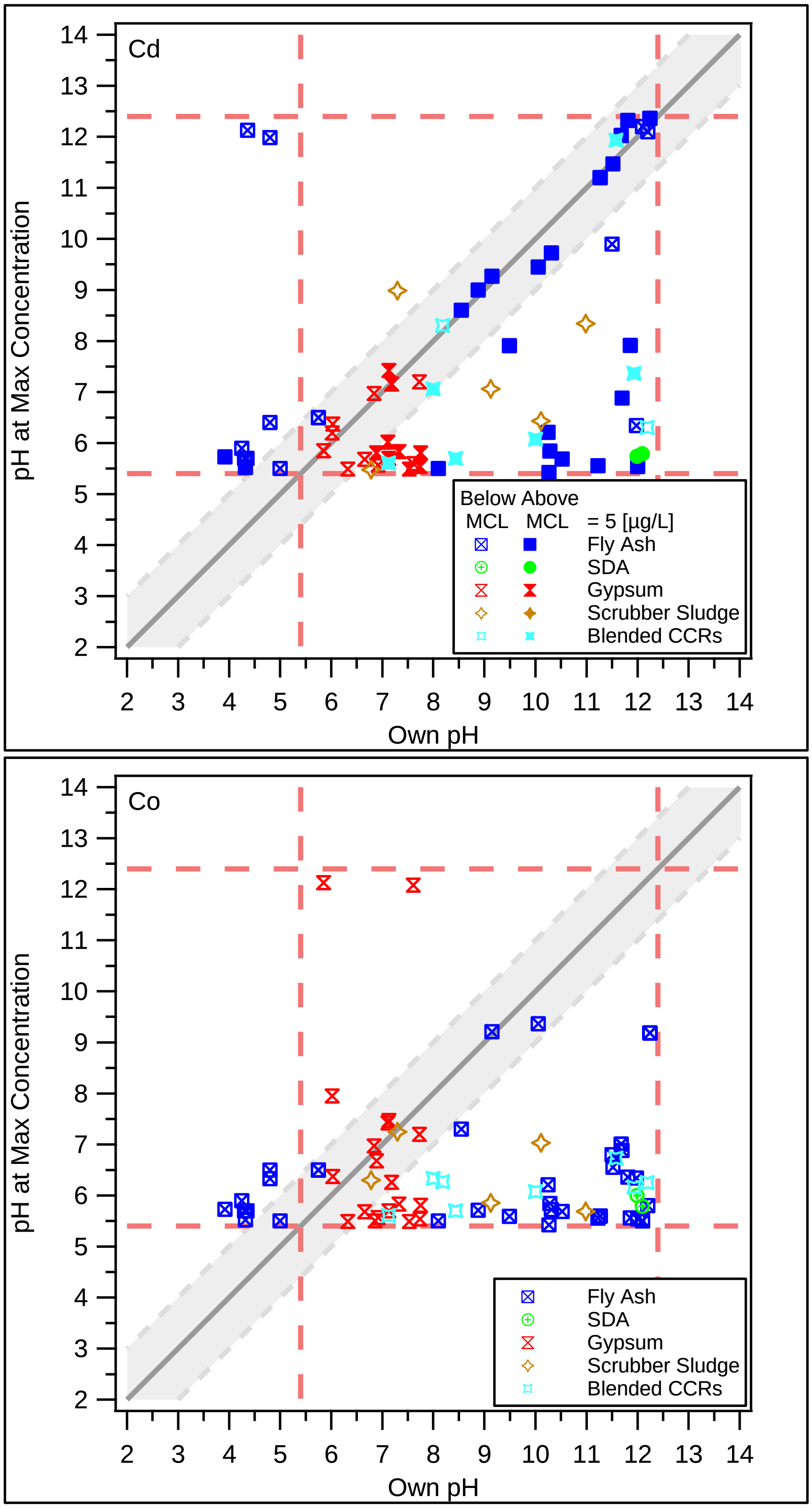
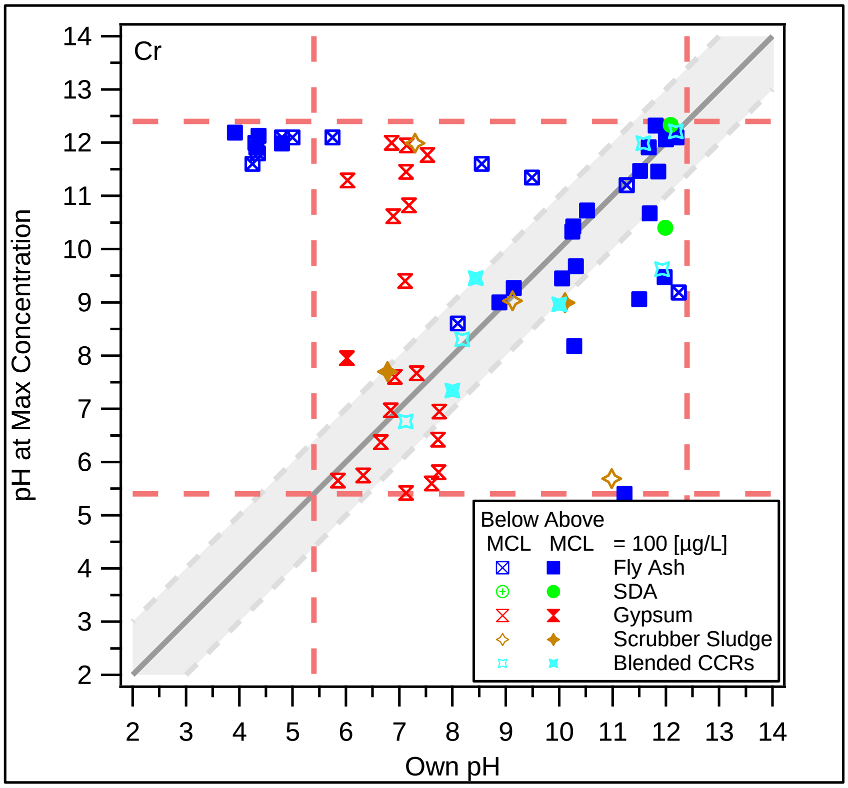


Figure 85 and Figure 86. Cadmium and Cobalt. pH identity plots.



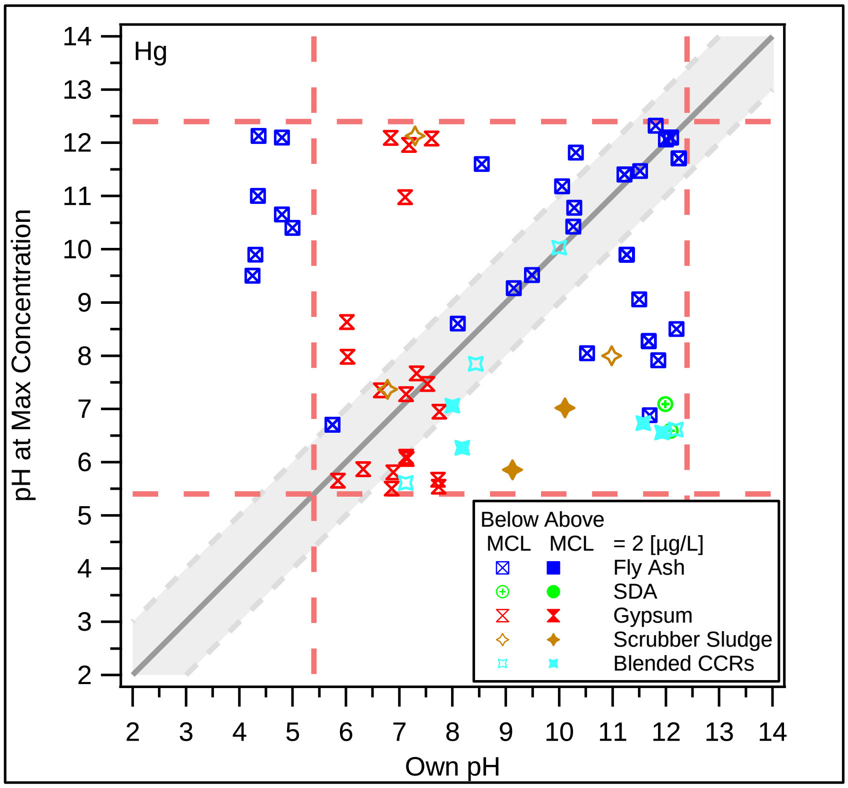
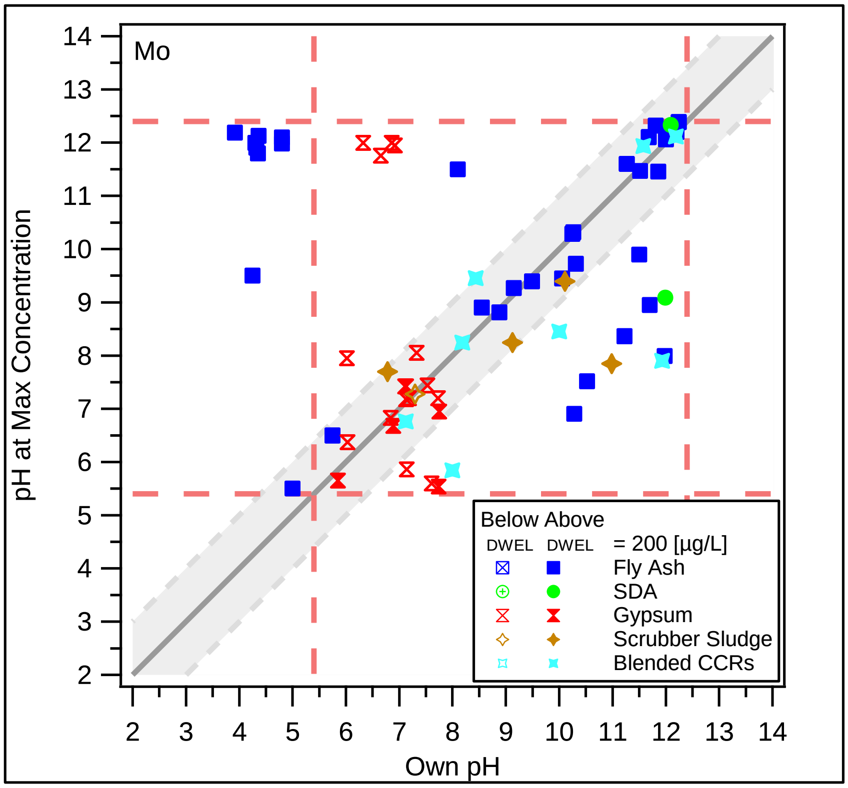


Figure 87 and Figure 88. Chromium and Mercury. pH identity plots.



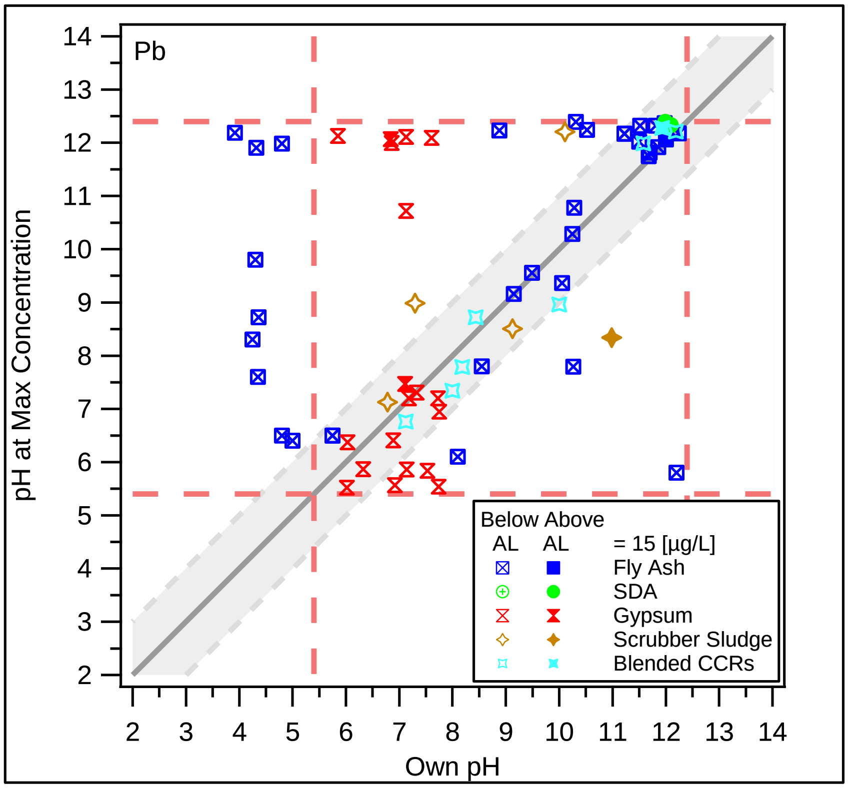


Figure 89 and Figure 90. Molybdenum and Lead. pH identity plots.

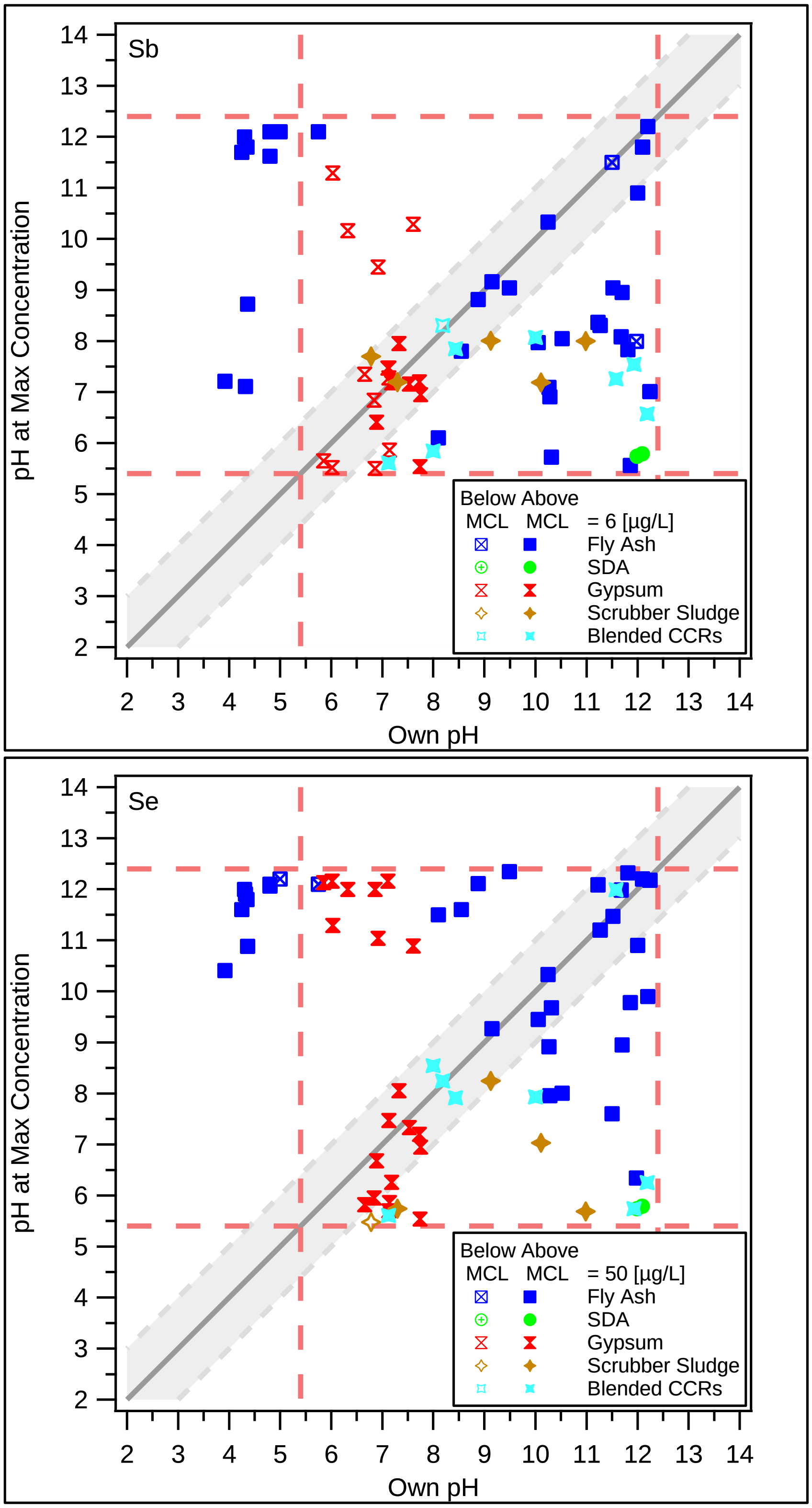


Figure 91 and Figure 92. Antimony and Selenium. pH identity plots.

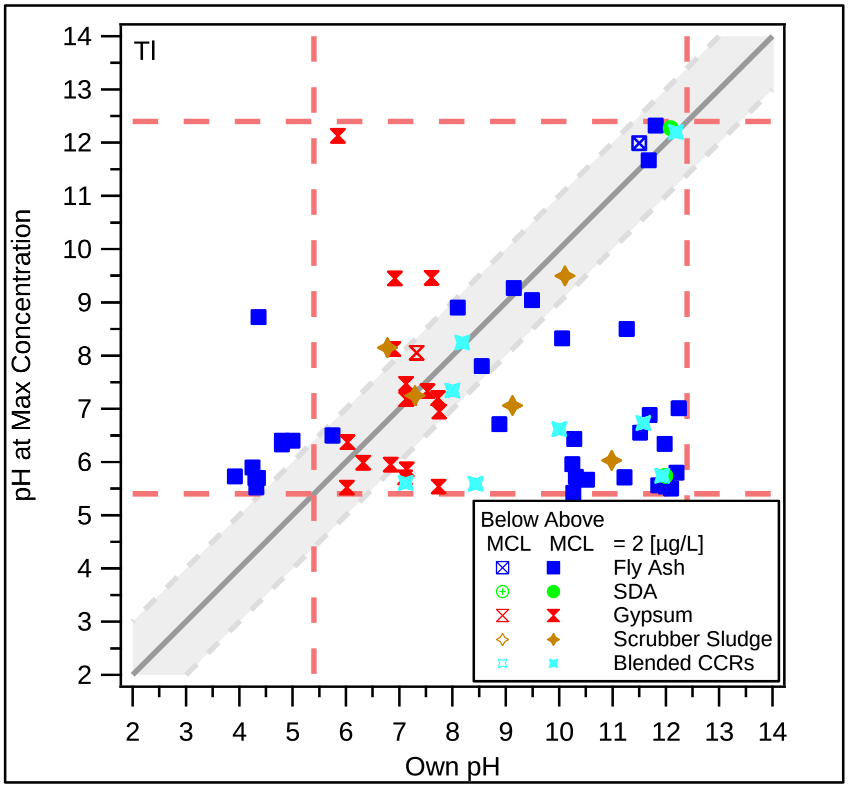


Figure 93. Thallium. pH identity plots.

3.2.5. Comparison of Constituent Maximum Concentrations and Concentrations at the Materials' Own pH from Laboratory Testing Grouped by Material Type with Measurements of Field Samples and the EPA Risk Report Database

Figure 94 through Figure 106 provide summary comparisons for each element by material type of (i) the maximum eluate concentration observed during leaching testing as a function of pH (SR002.1) and as a function of LS (SR003.1)[42] over the domain $5.4 \leq \text{pH} \leq 12.4$, and (ii) the eluate concentration observed at "own pH" by leaching with deionized water at LS=10 mL/g (SR002.1), and (iii) reference data ranges derived from the EPRI database of field leachate and pore water concentrations (surface impoundments - "EPRI SI"; landfills – "EPRI LF") and derived from the EPA Risk Report (EPA, 2007b). These are the same reference data ranges used previously as part of this study (Sanchez et al., 2008). Tabular results are provided in Appendix J.

The category "Fly Ash" includes data from all fly ash samples tested (n=34), including those from all coal types and all air pollution control configurations. The category "SDA" represents the results of the two samples of spray dryer residue tested. The category "Gypsum" represents the results from all FGD gypsum samples tested (n=20), including unwashed and washed gypsum samples from all coal types and air pollution control configurations. The category "FGD Residues" represents the results from all FGD scrubber residue samples (n=5) except gypsum. The category "Blended CCRs" represents mixed residues as managed (n=8), including mixtures of fly ash with scrubber residues and with or without added lime, and one as managed sample that was comprised of mixed fly ash with gypsum. The distinction between Blended CCRs and SDA categories was made because Blended CCRs are formed by blending materials captured as separate streams in the air pollution control system, while for SDA fly ash and scrubber residue are captured together.

When five or more data points were available in a given category of test data ("Maximum Values" and "Values at Own pH"), a "box plot" was used to represent the data set, with the following information indicated (from bottom to top of the box and whisker symbol): (i) minimum value (the lowermost whisker), (ii) 5th percentile (mark on lower whisker), (iii) 10th percentile (mark on lower whisker), (iv) 25th percentile (bottom of box), (v) 50th percentile or median value (middle line in box), (vi) 75th percentile (top of box), (vii) 90th percentile (mark on upper whisker), (viii) 95th percentile (mark on upper whisker), (ix) maximum value (the uppermost whisker). To the left of each box plot figure, open circles represent each individual value within the data set. This representation of individual values is used to provide an indication of the distribution of values within the data set because they typically are not normally distributed and in some cases the maximum or minimum values may be very different from the next value or majority of the data. For the SDA category, only each value is displayed because only two data values are contained in the set.

Representation of "Reference Data Ranges" indicates the 5th, median, and 95th percentile of field data for surface impoundments ["EPRI SI"] and landfills ["EPRI LF"]. Ranges of field observations are included for comparison as derived from the EPRI database, considering only observations from disposal sites associated with facilities that have wet FGD scrubbers. Surface

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[42] Including results from testing as a function of LS allows consideration of potentially higher concentrations observed for initial releases that may occur at low LS ratios in the field.

impoundment data are comparable with scrubber sludge results because scrubber sludges are most likely to be disposed in this manner. Landfill data are comparable to blended CCR data because these blended materials are likely to be disposed in landfills. Also included for comparison is the 5th percentile, median, and 95th percentile of the database used to carry out human and ecological health risk evaluations in the EPA Risk Report (EPA, 2007) (“CCW Ash,” “CCW FGD,” and “CCW Ash and Coal Waste” referring to monofilled fly ash, disposed FGD scrubber sludge, and combined CCR disposal, respectively).

The MCL or DWEL or AL (for lead) if available is included in each figure as a green dashed horizontal line to provide a reference value. The TC, if available, is included in each figure as a maroon dashed line as a second reference value. However, the concentration ranges indicated in the figures as results of this study are direct measurements of laboratory eluates and do not consider attenuation that may occur in the field.

For almost all constituents, a greater range of observed values was evident from laboratory testing compared to the reference data sets. The upper bound concentrations observed for laboratory testing over the domain of $5.4 \leq \text{pH} \leq 12.4$ exceeded the upper bound of reference data sets by one or more orders-of-magnitude for Ba, Cr, Hg, Mo, Sb, Se, and Tl. The upper bound concentrations observed for laboratory testing over the domain of $5.4 \leq \text{pH} \leq 12.4$ were less than the upper bound of reference data sets by one or more orders-of-magnitude for Co and Pb. The MCL or DWEL values were exceeded by the maximum laboratory eluate concentration by one or more samples for fly ash (As, B, Ba, Cd, Cr, Mo, Sb, Se, Tl), SDA residues (As, B, Ba, Cd, Cr, Mo, Sb, Se, Tl), gypsum (As, B, Cd, Cr, Mo, Sb, Se, Tl), FGD residues (As, B, Ba, Cr, Hg, Mo, Sb, Se, Tl), and blended CCRs (As, B, Ba, Cd, Cr, Hg, Mo, Sb, Se).

The observation that most constituent concentrations, both maximum values and own pH values in laboratory eluates, as well as field observations spanned several orders-of-magnitude indicates the very substantial roles that coal type, facility design and operating conditions, and field conditions have on expected concentrations of constituents of concern in leachates from beneficial use or disposal. For example, the observed laboratory eluate concentrations from fly ash samples spanned more than four orders of magnitude, both for maximum values and own pH values.

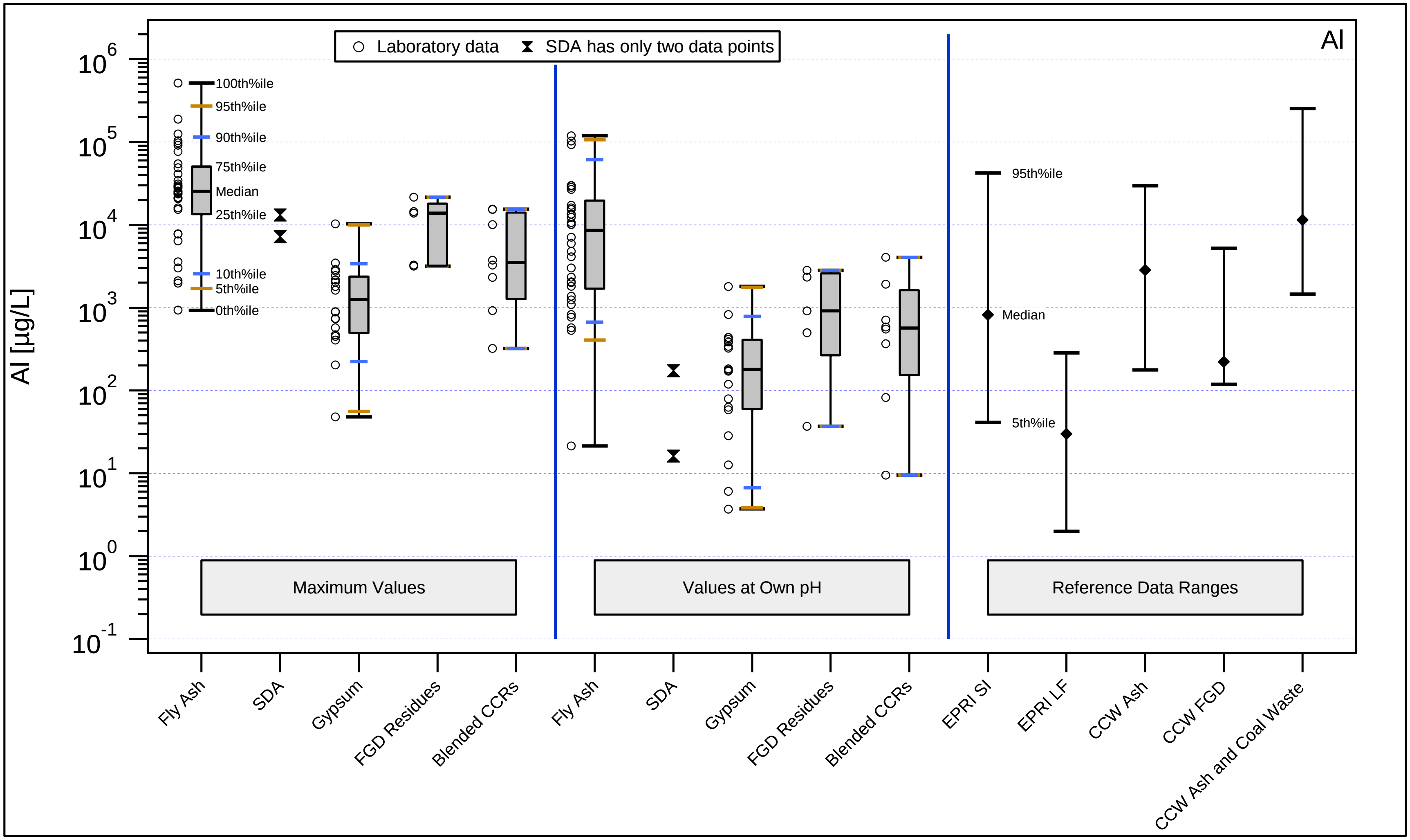

Figure 94. Aluminum. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

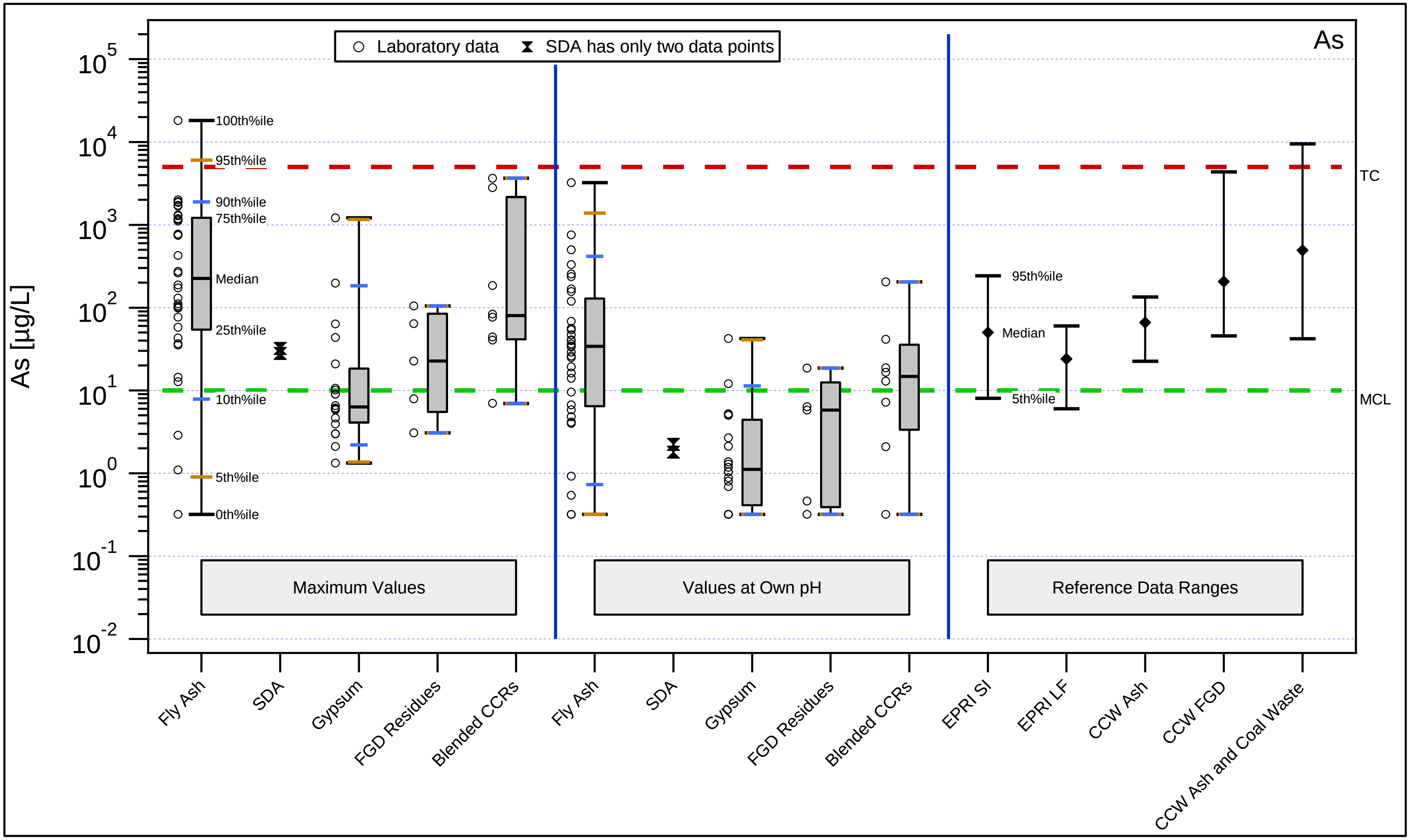

Figure 95. Arsenic. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

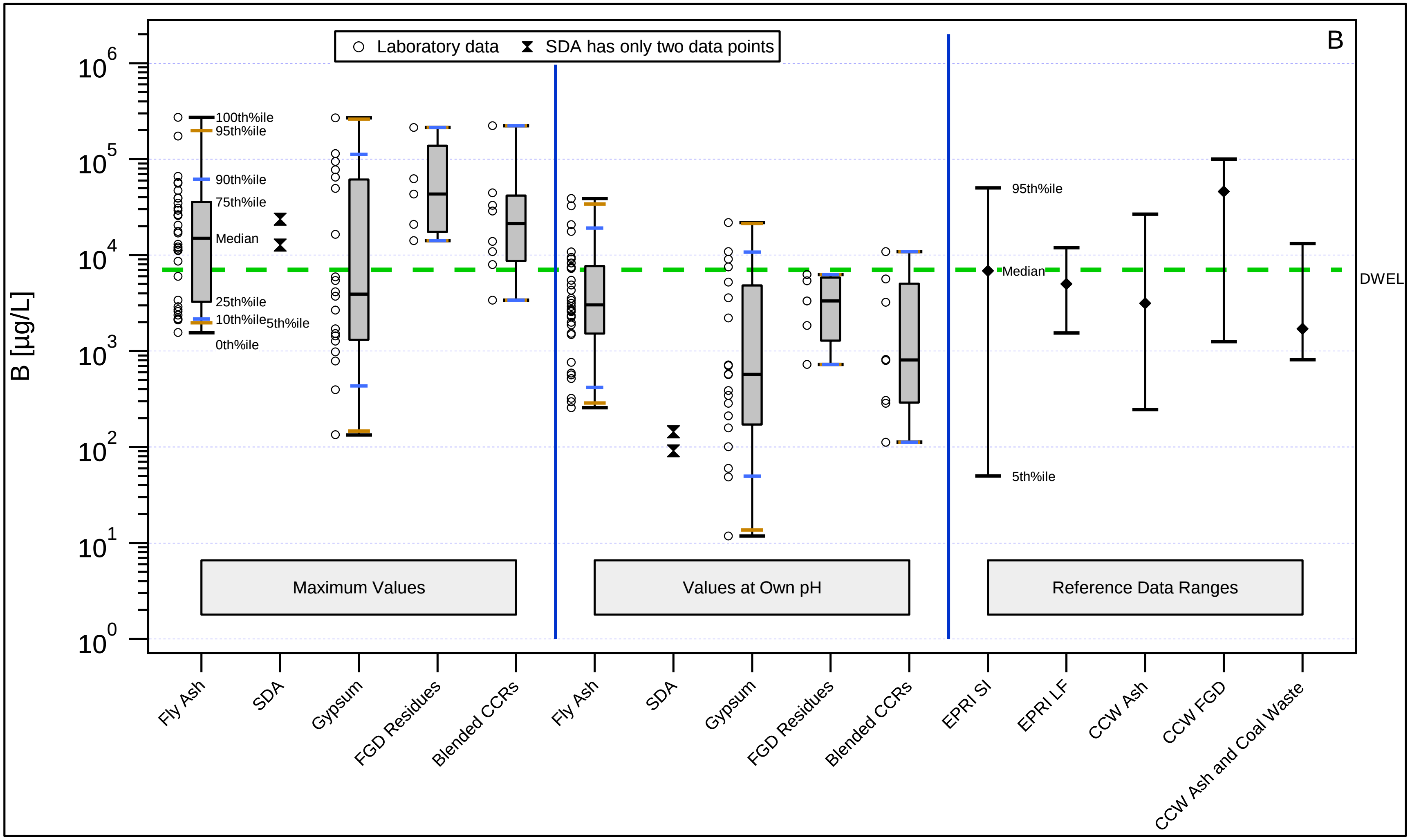

Figure 96. Boron. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

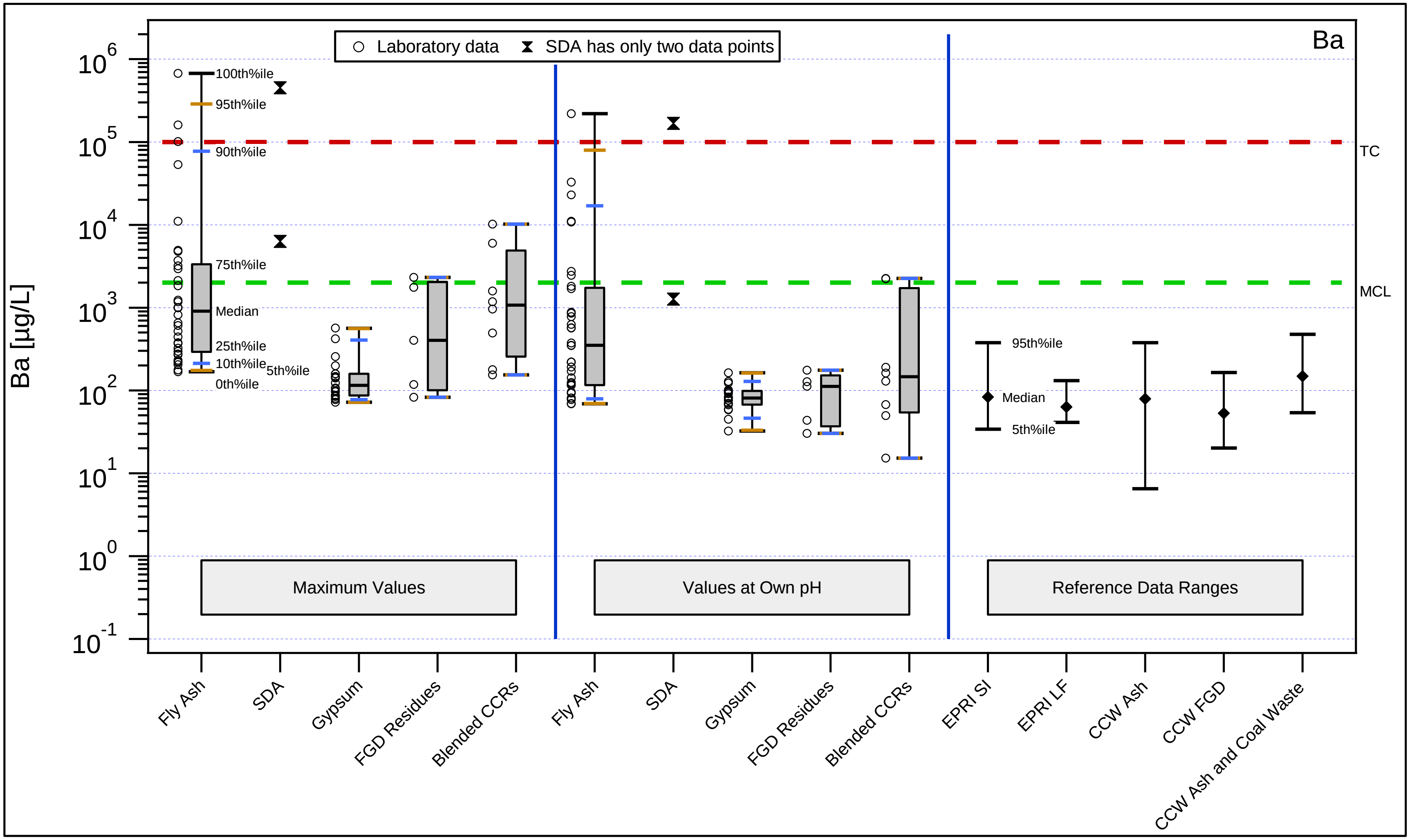

Figure 97. Barium. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

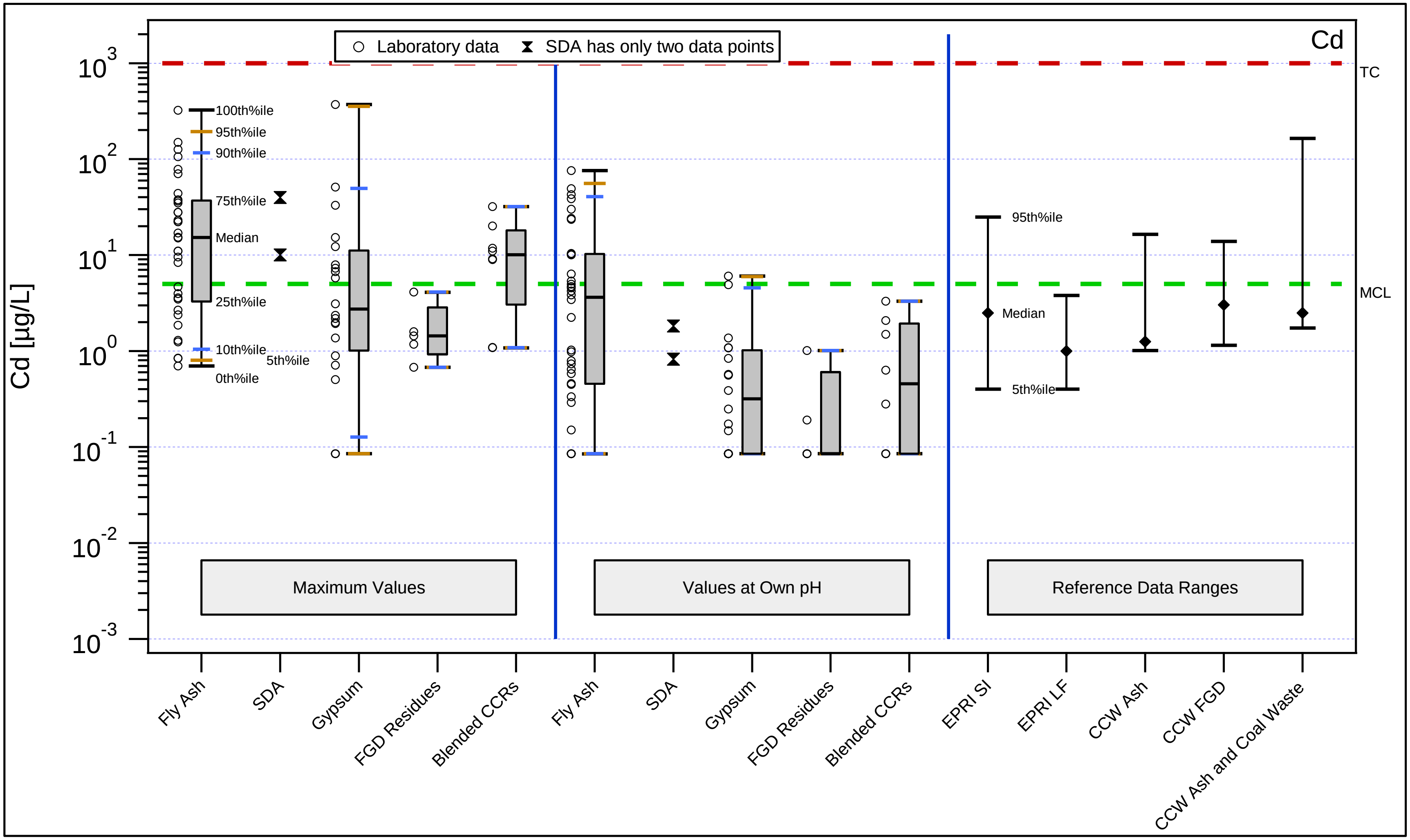

Figure 98. Cadmium. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

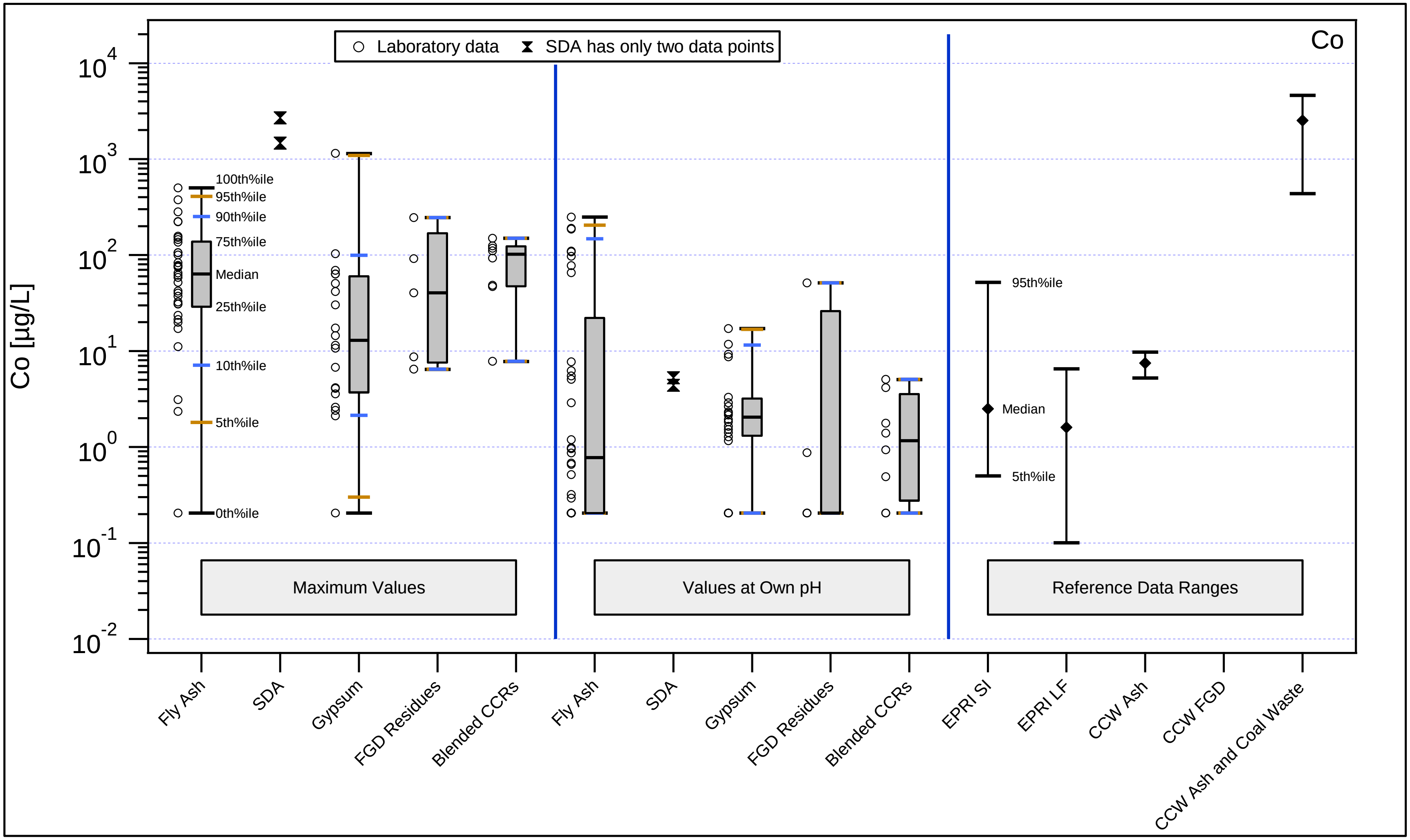

Figure 99. Cobalt. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

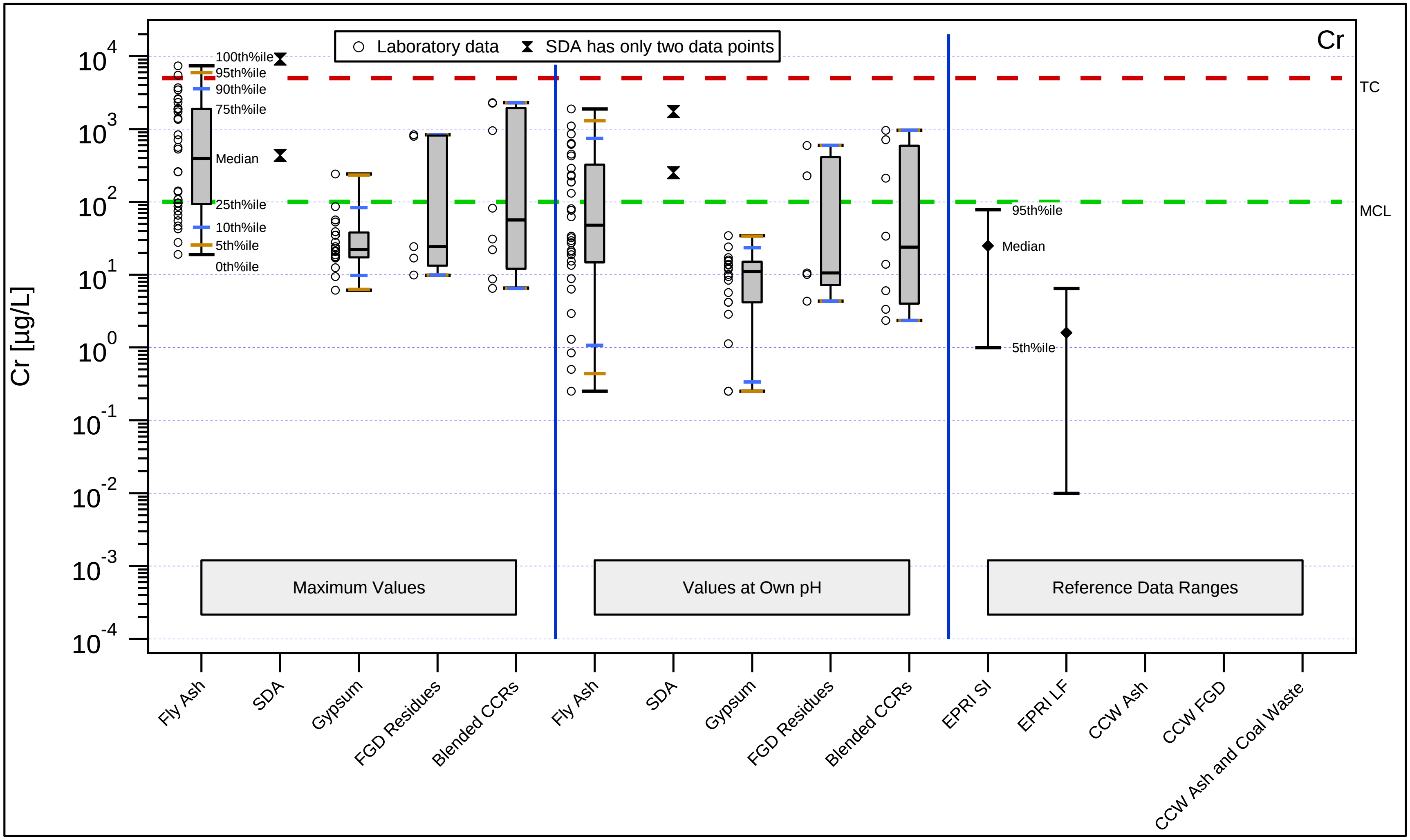

Figure 100. Chromium. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

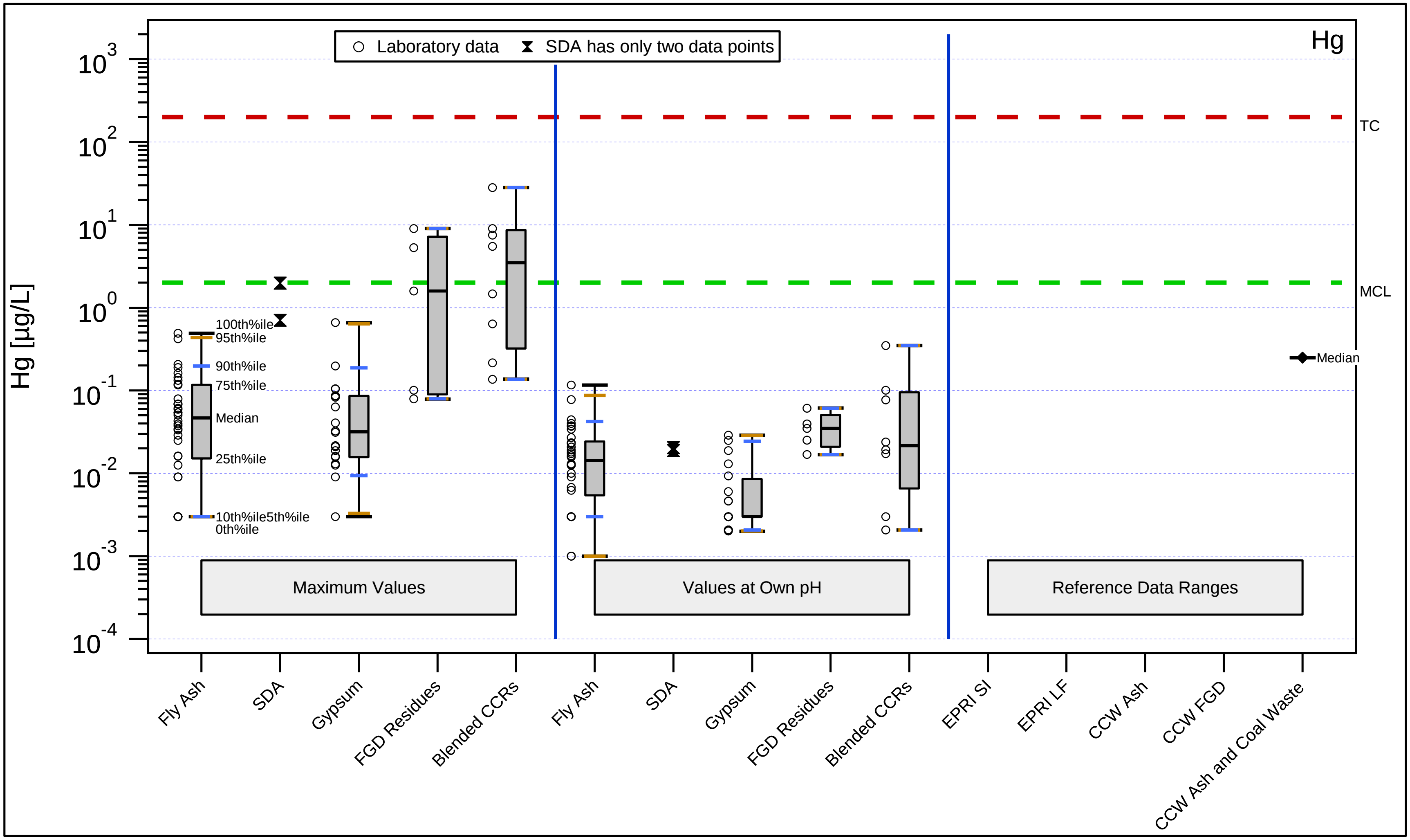

Figure 101. Mercury. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

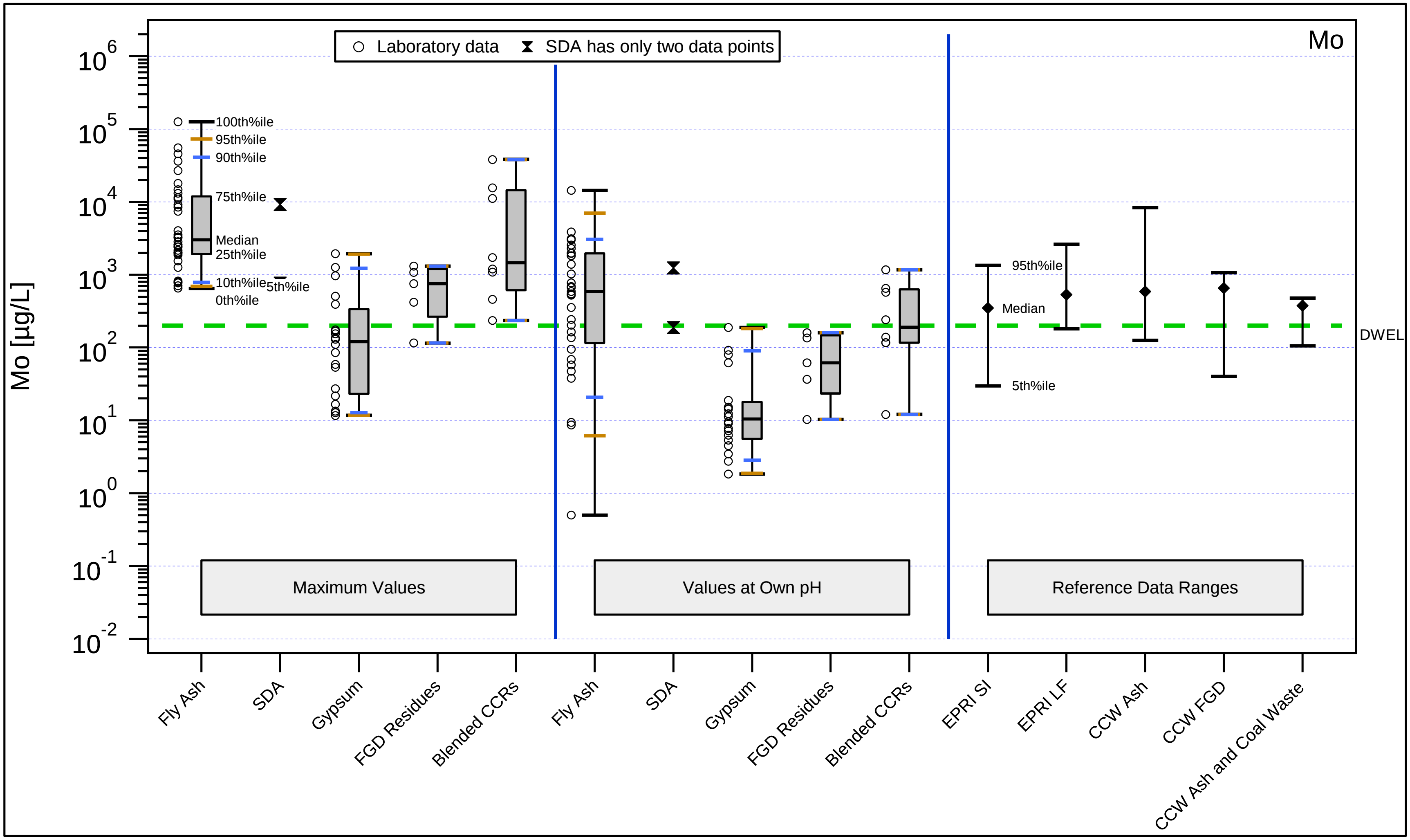

Figure 102. Molybdenum. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

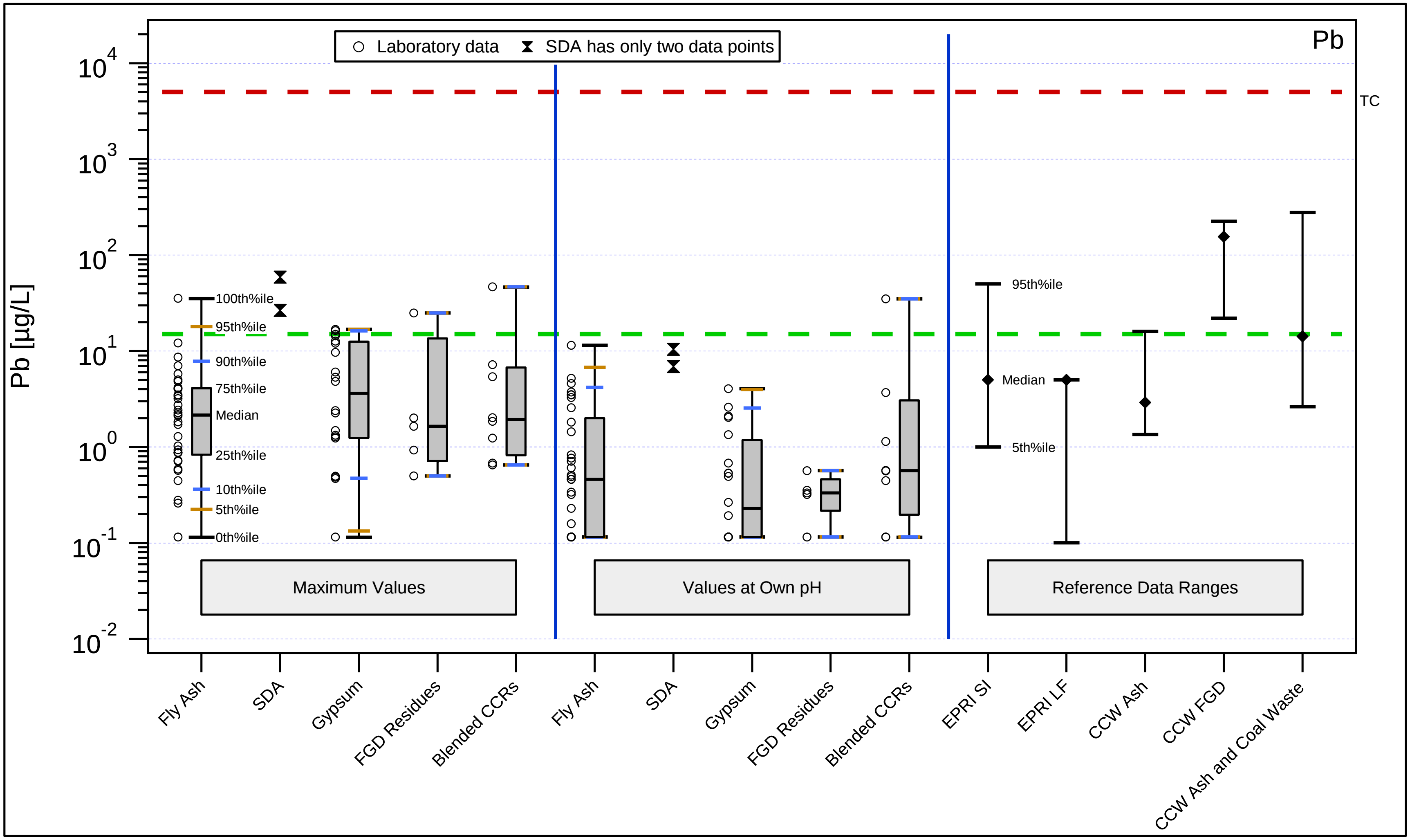

Figure 103. Lead. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

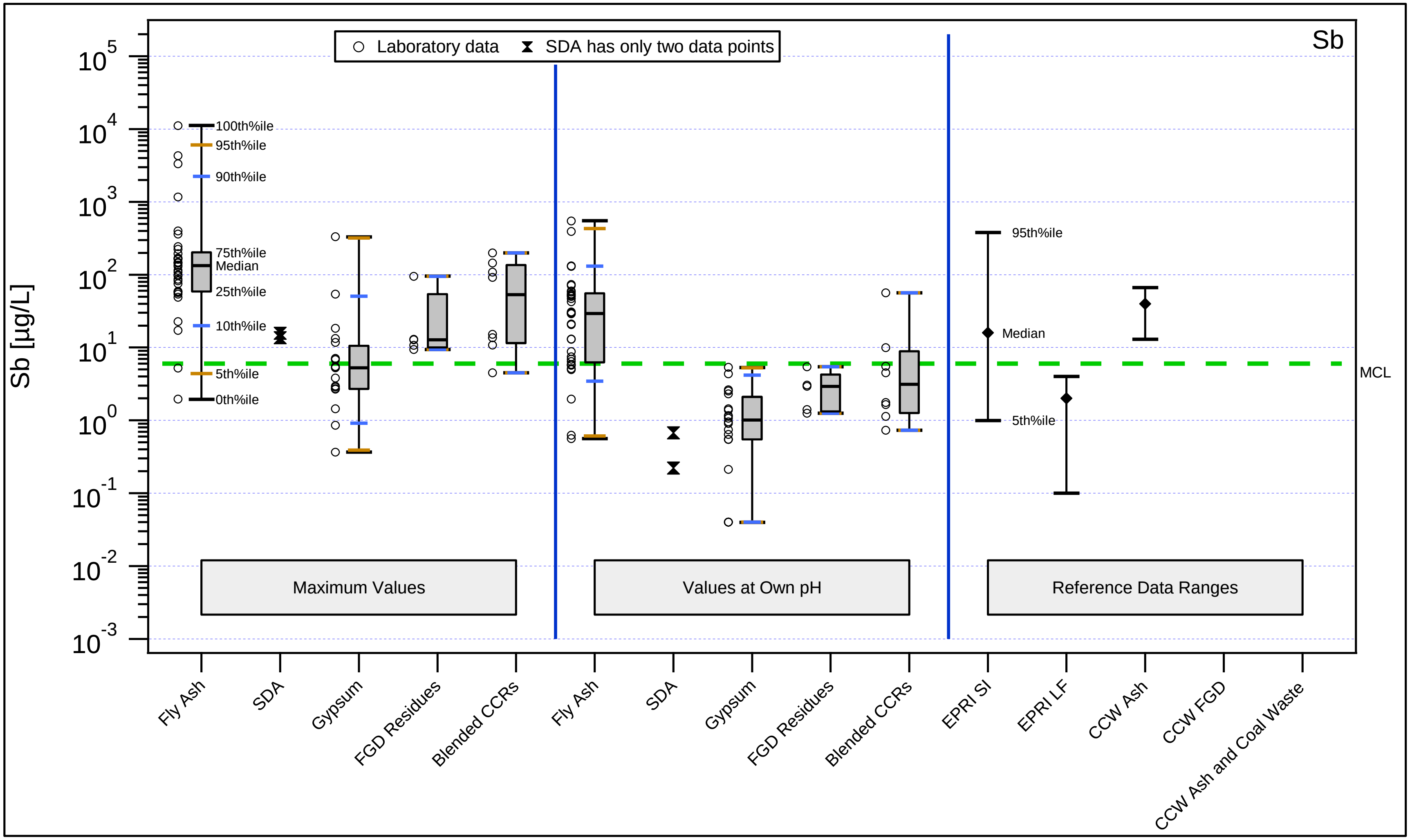

Figure 104. Antimony. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

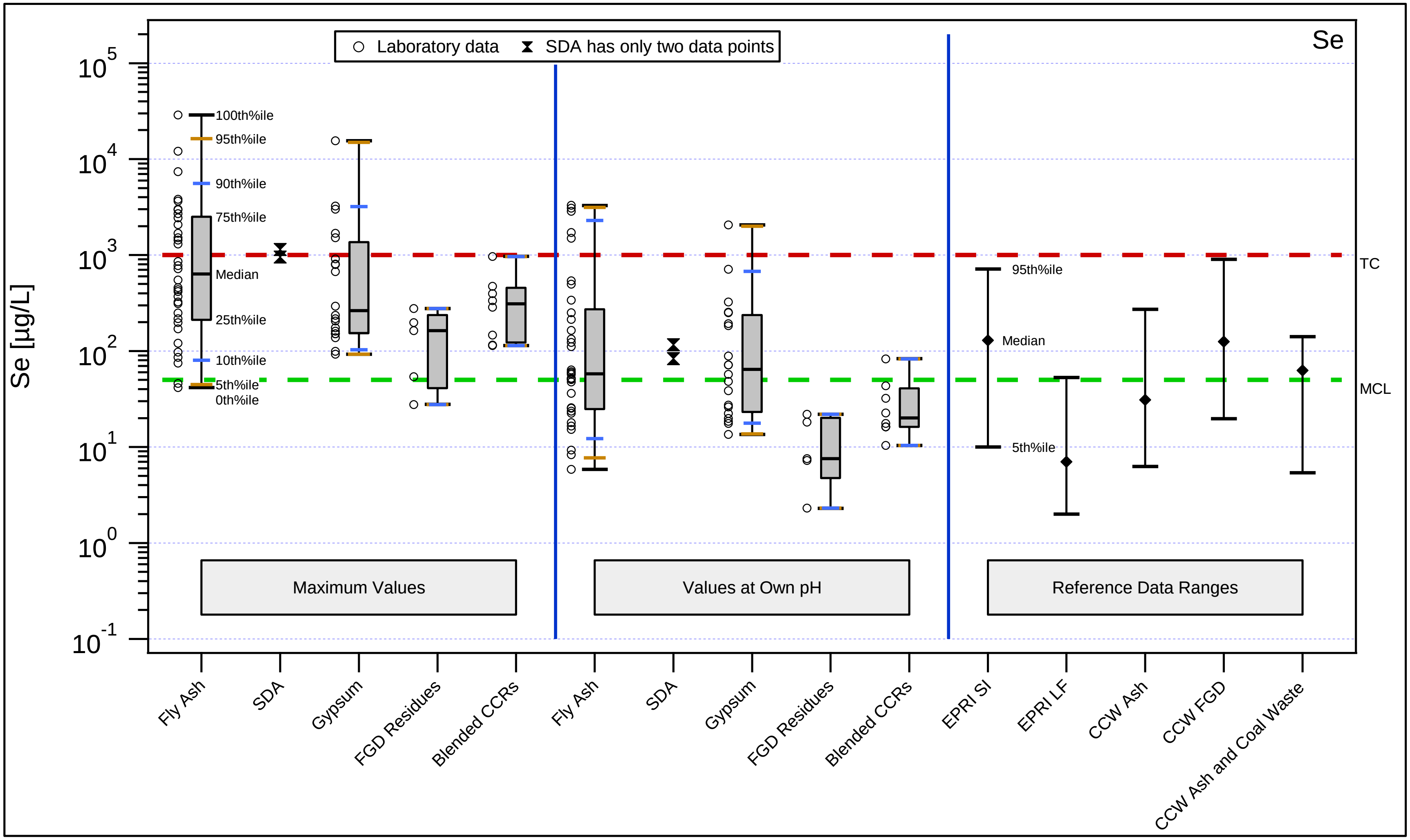

Figure 105. Selenium. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

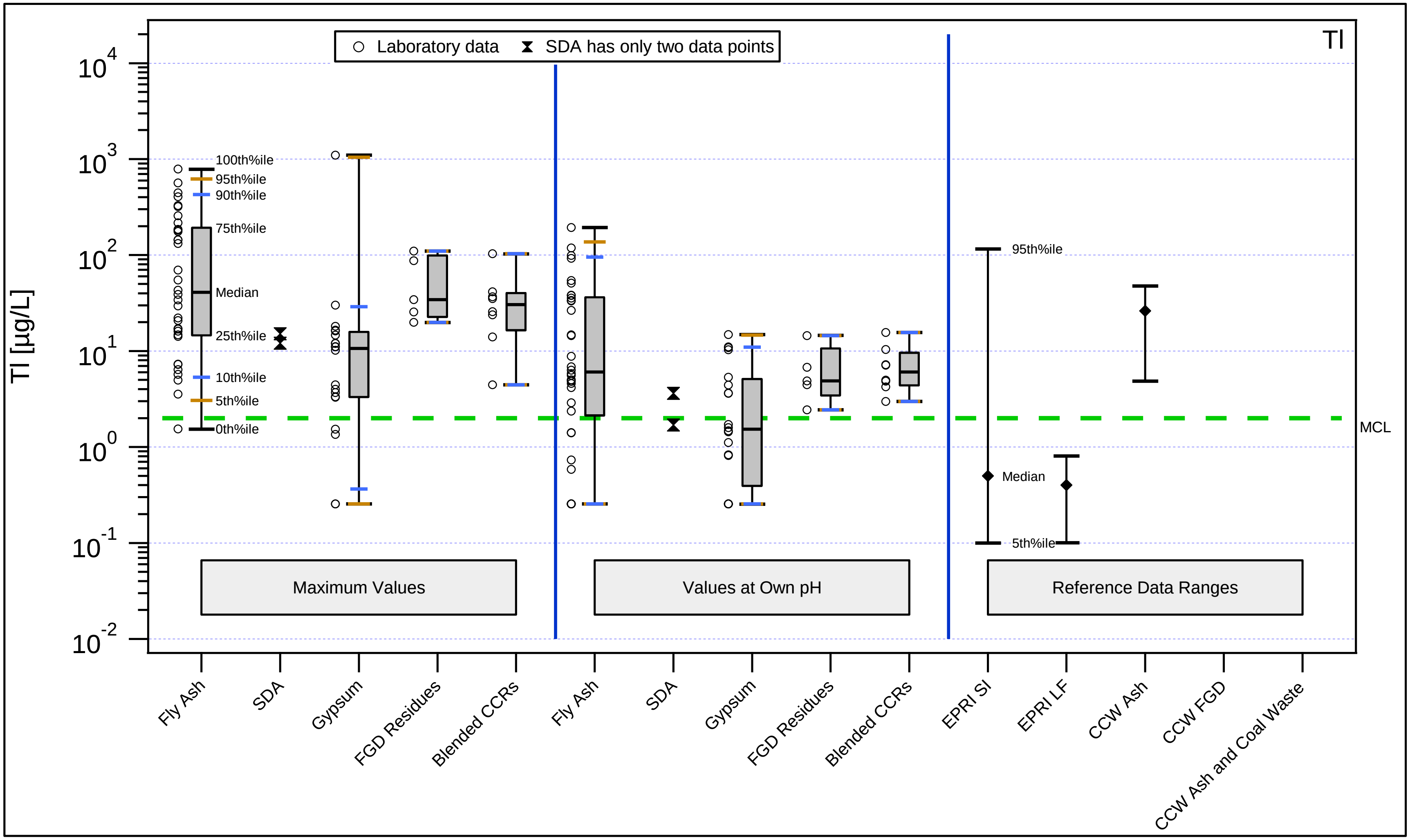

Figure 106. Thallium. Comparison of maximum concentrations observed in SR002.1 and SR003.1 eluates over the pH domain 5.4 ≤ pH ≤ 12.4, own pH concentrations from SR002.1 at LS = 10mL/g, and reference data ranges derived from the EPRI database of field leachate and pore water concentrations (EPRI SI – surface impoundments; EPRI LF – landfills) and the EPA Risk Report (EPA, 2007b).

3.2.6. Attenuation Factors Needed to Reduce Estimated Leachate Concentrations to Less Than Reference Indicators

Comparison of leaching test results to reference indicators does not consider dilution and attenuation factors (collectively referred to here as attenuation factors) that arise as a consequence of disposal or beneficial use designs that limit release and attenuation that occurs during transport from the point of release to the potential receptor. Minimum attenuation factors needed to reduce maximum leach concentrations (based on laboratory test results for $5.4 \leq pH \leq 12.4$) to less than MCL or DWEL values were calculated for each COPC to illustrate the importance of consideration of attenuation factors during evaluation of management options Minimum attenuation factors needed to reduce own pH leach concentrations (based on laboratory test results using DI water as the eluant) to less than MCL or DWEL values also were calculated. The resulting attenuation values were calculated by dividing the appropriate measured laboratory leaching test concentration by the respective MCL or DWEL for each COPC. Thus, values greater than one reflect concentrations greater than the MCL or DWEL. Appendix L provides figures comparing attenuation factors calculated for CCR for individual elements and also provides a summary table of all calculated values.

Based on evaluation of the results for each COPC, one consideration was to evaluate across the entire set of COPCs the minimum attenuation factor needed for each CCR sample to result in all COPCs being less than the MCL or DWEL. Furthermore, this evaluation was used to identify the specific COPC (e.g., As, Cd, etc.) that required the greatest attenuation factor for each CCR sample (i.e., the controlling COPC). Results of this analysis are provided in Figure 107 and Figure 108. For each CCR sample, the minimum attenuation factor needed for all COPCs to be less than the MCL or DWEL is graphed, along with identification of the specific COPC driving the result. Two important observations result from this data analysis:

1. Maximum leaching concentrations between pH 5.4 and 12.4 from all CCRs tested in this study require some attenuation to reduce concentrations to less than the MCL or DWEL across all COPCs evaluated; and,
2. For fly ash, the controlling constituent (i.e., the constituent within each sample that required the largest attenuation factor) and the number of samples (..) in which that constituent is controlling are As (11), Ba (3), Cr (4), Sb (5), Se (3), Tl (8); for gypsum the controlling constituents are As (2), Se (13), Tl (5); for scrubber sludge the controlling constituents are Sb (1), Tl (5); for blended, as managed CCRs the controlling constituents are As (3), Cr (1), Hg (1), Sb (2), Tl (1). Thus, it is important to consider these constituents when evaluating the potential impacts from CCR management on human health and the environment.

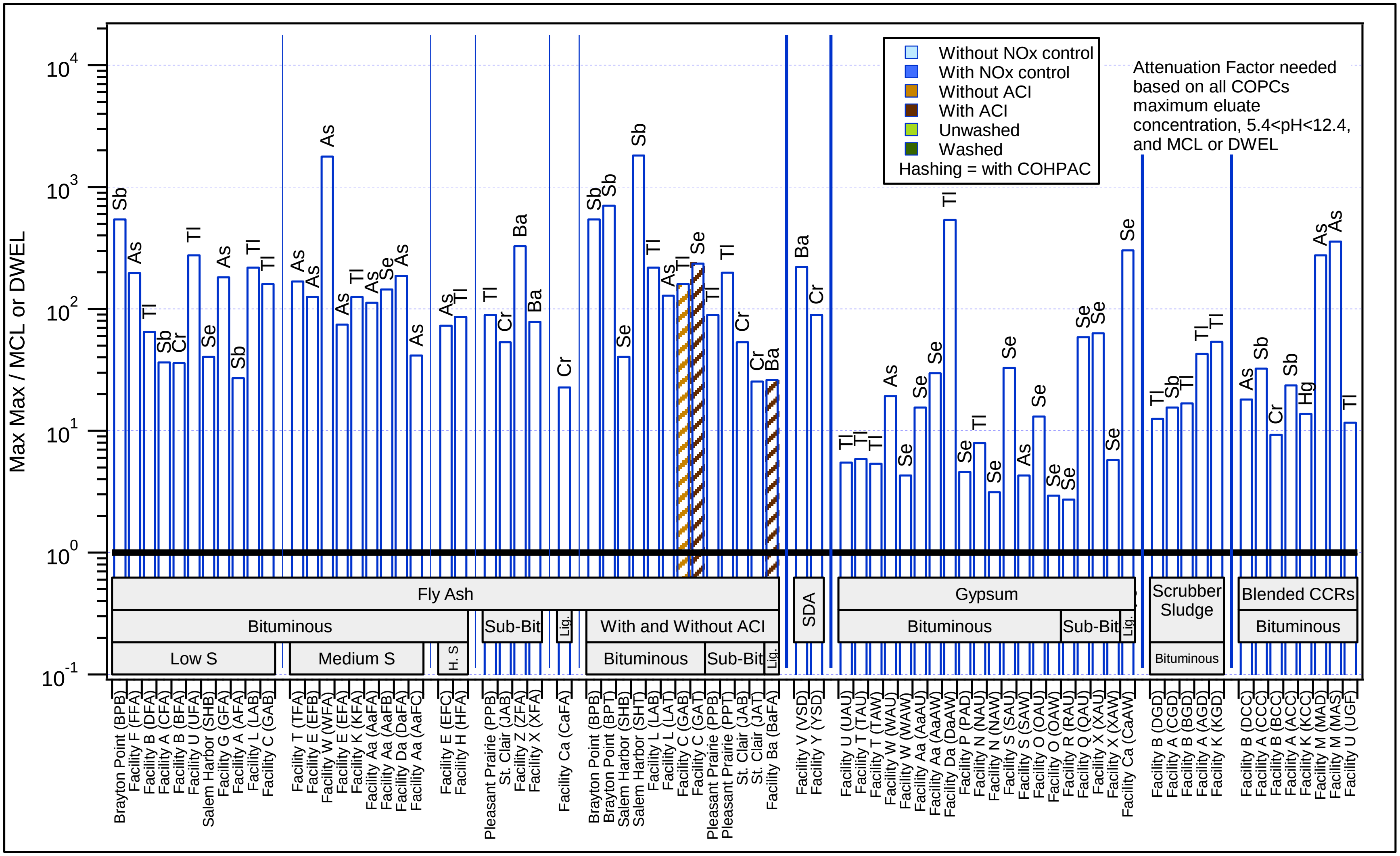

Figure 107. **Minimum attenuation factor** needed for the **maximum eluate concentration** (5.4 ≤ pH ≤ 12.4) to be reduced below the MCL or DWEL for all COPCs considered in this study. COPC requiring the greatest attenuation factor is indicated for each CCR.

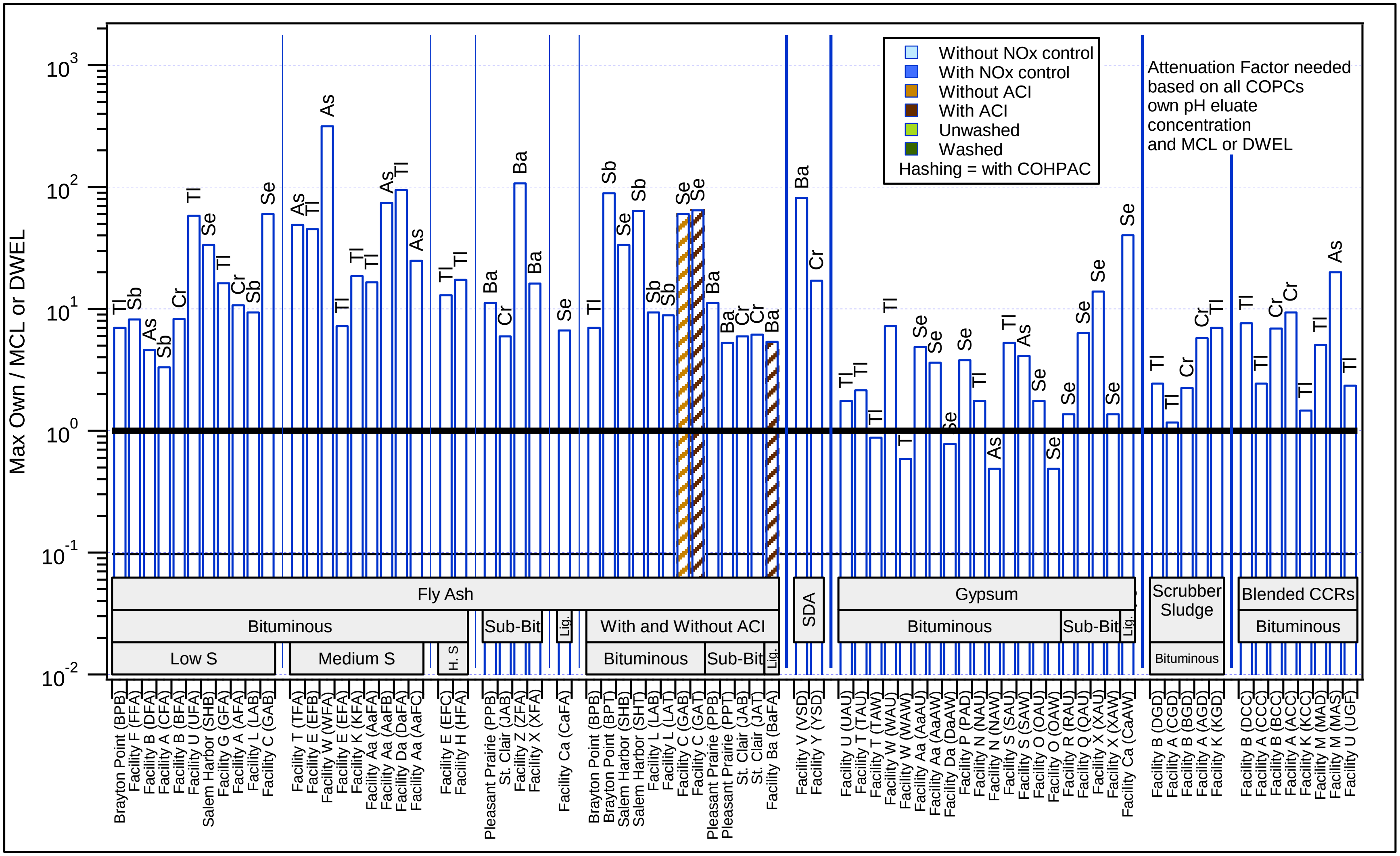

Figure 108. **Minimum attenuation factor** needed for **the own pH eluate concentration** to be reduced below the MCL or DWEL for all COPCs considered in this study. COPC requiring the greatest attenuation factor is indicated for each CCR.

4. SUMMARY OF RESULTS, CONCLUSIONS AND RECOMMENDATIONS

The following sections present conclusions from the results presented in this report.

Changes to fly ash and other coal combustion residues (CCRs) are expected to occur as a result of increased use and application of advanced air pollution control technologies in coal-fired power plants. These technologies include flue gas desulfurization (FGD) systems for SO_2 control, selective catalytic reduction (SCR) systems for NO_x control, and activated carbon injection systems for mercury control. These technologies are being or are expected to be installed in response to federal regulations [e.g., Clean Air Interstate Rule (CAIR), Utility MACT Rule], state regulations, legal consent decrees, and voluntary actions taken by industry to adopt more stringent air pollution control.

The Air Pollution Prevention and Control Division (APPCD) of EPA's Office of Research and Development (ORD) has been working since 2000, to evaluate the potential for leaching and cross media transfer of mercury and other constituents of potential concern (COPCs) from management of these modified CCRs (primarily disposal, but also reuse). This research was cited as a priority in EPA's Mercury Roadmap (http://www.epa.gov/mercury/roadmap.htm) to ensure that the solution to one environmental problem is not causing another.

CCR samples of each material type were collected in an attempt to span the range of likely coal types [i.e., low, medium and high sulfur bituminous, sub-bituminous and lignite] and air pollution control configurations reflecting use of more stringent air pollution control. This report presents results from the evaluation of 73 CCRs from 31 coal-fired power plants with various combinations of particulate matter, NO_x, Hg, and SO_2 control. For several of the 31 plants, samples were obtained before and after changes were made in air pollution control.

CCRs have been grouped into the five categories as shown in Table 12. Each of the CCR samples was analyzed for a range of physical properties, total metals content, and leaching characteristics. The testing methods used in this research assess CCR leaching potential over a range of values for two parameters that both vary in the environment and can affect the rate of constituent leaching from a material. These are: (1) the pH and (2) the amount of water contact [in the test, the ratio of liquid-to-solids (LS) being tested]. These are considered improved leaching test methods that address key concerns with single point testing that were raised by EPA's Science Advisory Board and the National Academy of Sciences. An advantage of using this testing approach is that analysis of the data can be tailored or targeted to particular waste management or use conditions. When key material management conditions are known, the data can be used to estimate leaching over the range of plausible management conditions for that particular material. This can be done for either a broad range of conditions (e.g., in assessing release potential on a national basis) or more narrowly (as in estimating release potential at a particular site or limited set of sites).

Table 12. Identification of CCRs evaluated and included in this Report.

Samples Evaluated by CCR Category	Report 1*	Report 2**	Additional Samples Collected for this report	Total Samples Evaluated in this Report
1. Fly Ash	12	5	17	34
2. FGD Gypsum	-	6	14	20
3. “Other” FGD Residues (primarily calcium sulfite from scrubbers that do not use oxidation to generate gypsum)	-	5	2	7
4. Blended CCRs (typically a mixture of fly ash, calcium sulfite, and lime)	-	7	1	8
5. Wastewater Treatment Filter Cake	-		4	4

* (Sanchez et al., 2006).

** (Sanchez et al., 2008).

Provided below in a summary table for each CCR category are the range of leach results over the pH range of 5.4 and 12.4[43], along with comparison to available regulatory or reference indicators including TC, MCL, and DWEL. In making such comparisons, it is critical to bear in mind that these test results represent an estimate of constituent release from the material as disposed or used on the land. They do not include any attempt to estimate the amount of constituent that may reach an aquifer or drinking water well. Leachate leaving a landfill is invariably diluted in ground water or constituent concentration attenuated by sorption and other chemical reactions in groundwater and sediment. Also, groundwater pH may be different from the pH at the site of contaminant release, and so the solubility and mobility of leached contaminants may change when they reach groundwater. None of these dilution or attenuation processes is incorporated into the leaching values presented, and so comparison with regulatory reference values, particularly drinking water values, must be done with caution.

The principle conclusions are:

1. Review of the data presented in Table 13 and Table 14, for fly ash and FGD gypsum, show a range of total concentration of constituents, but a much broader range (by orders of magnitude) of leaching values, in nearly all cases. This much greater range of leaching values only partially illustrates what more detailed review of the data shows: that for CCRs, the rate of constituent release to the environment is affected by leaching conditions (in some cases dramatically so), and that leaching evaluation under a single set of conditions will, in many cases, lead to inaccurate conclusions about expected leaching in the field.

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[43] This pH range could understate potential concerns when these materials are used in agricultural, commercial, and engineering applications if the field conditions are more variable than during disposal. For example, 9 of the 34 fly ash samples evaluated indicated the eluate pH in deionized water (i.e., the pH generated by the tested material itself) to be more acidic than pH 5.4.

2. Comparison of the ranges of totals values and leachate data also supports earlier conclusions that the rate of constituent leaching cannot be reliably estimated based on total constituent concentration alone or with use of linear K_d partitioning values.
3. The maximum eluate concentration from leaching test results varies over a wide range in pH and is different for different CCR types and elements. This indicates that there is not a single pH for which testing is likely to provide confidence in release estimates over a wide range of disposal and beneficial use options, emphasizing the benefit of multi-pH testing.
4. Distinctive patterns are observed in leaching behavior over the range of pH values that would plausibly be encountered on CCR disposal, depending upon the type of material and element.
5. Summary data in Table 14 on the leach results from evaluation of 34 fly ash samples across the plausible management pH range of 5.4 to 12.4, indicates leaching concentration ranges over several orders of magnitude as a function of pH and ash source:
    a. the leach results at the upper end of the concentration ranges exceeded the TC values for As, Ba, Cr, and Se.
    b. the leach results at the upper end of the concentration ranges exceeded the MCL or DWEL for Sb, As, Ba, B, Cd, Cr, Pb, Mo, Se, and Tl.
6. Summary data in Table 15 on the leach results from evaluation of 20 FGD gypsum samples across the plausible management pH domain of 5.4 to 12.4, indicates leaching concentration ranges over several orders of magnitude as a function of pH and FGD gypsum source:
    a. the leach results at the upper end of the concentration ranges exceeded the TC values for Se.
    b. the leach results at the upper end of the concentration ranges exceeded the MCL or DWEL for Sb, As, B, Cd, Cr, Mo, Se, and Tl.
7. There is considerable variability in total content and the leaching of constituents of potential within a material type (e.g., fly ash, gypsum) such that while leaching of many samples, without adjustment for dilution and attenuation, exceeds one or more of the available reference indicators, many of the other samples within the material type may be less than the available regulatory or reference indicators. This suggests that materials from certain facilities may be acceptable for particular disposal and beneficial use scenarios while the same material type from a different facility or the same facility produced under different operating conditions (i.e., different air pollution controls) may not be acceptable for the same management scenario.

In interpreting these results, please note that the CCRs analyzed in this report are not considered to be a representative sample of all CCRs produced in the U.S. For many of the observations, only a few data points were available. It is hoped that through broader use of the improved leach test methods (as used in this report), that additional data from CCR characterization will become available. That will help better define trends associated with changes in air pollution control at coal-fired power plants.

Table 13. **Fly Ash -** Laboratory leach test eluate concentrations for 5.4 ≤ pH ≤ 12.4 and at "own pH" from evaluation of thirty-four fly ash samples.

	Hg	**Sb**	**As**	**Ba**	**B**	**Cd**	**Cr**	**Co**	**Pb**	**Mo**	**Se**	**TI**
Total in Material (mg/kg)	0.01 – 1.5	3 – 14	17 – 510	590 – 7,000	NA	0.3 – 1.8	66 – 210	16 – 66	24 – 120	6.9 – 77	1.1 – 210	0.72 – 13
Leach results (µg/L)	<0.01 – 0.50	<0.3 – 11,000	0.32 – 18,000	50 – 670,000	210 – 270,000	<0.1 – 320	<0.3 – 7,300	<0.3 – 500	<0.2 – 35	<0.5 – 130,000	5.7 – 29,000	<0.3 – 790
TC (µg/L)	200	-	5,000	100,000	-	1,000	5,000	-	5,000	-	1,000	-
MCL (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2

Note: The shade is used to indicate where there could be a potential concern for a metal when comparing the leach results to the MCL, DWEL, or TC. Note that MCL and DWEL values represent well concentrations; leachate dilution and attenuation processes that would occur in groundwater before leachate reaches a well are not accounted for, and so MCL and DWEL values are compared to leaching concentrations here to provide context for the test results and initial screening.

Table 14. **FGD Gypsum -** Laboratory leach test eluate concentrations for 5.4 ≤ pH ≤ 12.4 and at "own pH" from evaluation of twenty FGD gypsum samples.

	Hg	**Sb**	**As**	**Ba**	**B**	**Cd**	**Cr**	**Co**	**Pb**	**Mo**	**Se**	**TI**
Total in Material (mg/kg)	0.01 – 3.1	0.14 – 8.2	0.95 – 10	2.4 – 67	NA	0.11 – 0.61	1.2 – 20	0.77 – 4.4	0.51 – 12	1.1 – 12	2.3 – 46	0.24 – 2.3
Leach results (µg/L)	<0.01– 0.66	<0.3 – 330	0.32 – 1,200	30 – 560	12 – 270,000	<0.2 – 370	<0.3 – 240	<0.2 – 1,100	<0.2 – 12	0.36 – 1,900	3.6 – 16,000	<0.3 – 1,100
TC (µg/L)	200	-	5,000	100,000	-	1,000	5,000	-	5,000	-	1,000	-
MCL (µg/L)	2	6	10	2,000	7,000 DWEL	5	100	-	15	200 DWEL	50	2

Note: The shade is used to indicate where there could be a potential concern for a metal when comparing the leach results to the MCL, DWEL, or TC. Note that MCL and DWEL values represent well concentrations; leachate dilution and attenuation processes that would occur in groundwater before leachate reaches a well are not accounted for, and so MCL and DWEL values are compared to leaching concentrations here to provide context for the test results and initial screening.

5. REFERENCES

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APPENDICES