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Final Report

Chemical Inventory and Database Development for Recycled Material Substitutes

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16. Abstract (Limit: 200 words)

Mn/DOT engineers are increasingly looking to recycled materials as readily available and cost-effective substitutes for natural aggregate and to fly ash as a material that can be used in the stabilization of sub-base soils. These recycled wastes have the potential to contain unacceptably high levels of some chemicals. This project produced chemical data on wastes, non-surface background soils, and natural aggregates for use in a due diligence screening tool in current service by Mn/DOT and developed by the Office of Environmental Services (OES). These data will be used by OES for their internal Mn/DOT due diligence determinations using their streamlined hazard evaluation process. A future Local Road Research Board project will transform the OES streamlined hazard evaluation process into a CD-based product for use by the larger transportation community. Data developed by this current project will be used to populate the future CD-based product electronic database. This project will maintain consistency with the current in use Office of Environmental Services (OES) streamlined hazard evaluation process for waste recycling in Mn/DOT infrastructure projects.

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Chemical Inventory and Database Development for Recycled Material Substitutes

Final Report

Prepared by:

Kim E. Grosenheider
Paul R. Bloom
Thomas R. Halbach
Department of Soil, Water, and Climate
University of Minnesota

Matt Simcik
Department of Public Health
University of Minnesota

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Research Services Section
395 John Ireland Boulevard, MS 330
St. Paul, Minnesota 55155-1899

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Executive Summary

Coal combustion fly ash can be used as a component of good quality sub-base under roads at lower cost than conventional construction (Federal Highway Administration, 2003). Cementitious fly ash when mixed with soil at 7% to 20% (w:w) produces a strong sub-base with greatly reduced shrinking and swelling (Iowa State Report, 2005; Fly Ash Facts, 2004). This is especially useful for soils with high clay content that almost always have high shrink-swell potential.

Ground asphalt pavement can be a good addition to aggregate mixes or can become a component of sub-base aggregate when incorporated directly during the process of cold in-place recycling of old pavements, with or without the addition of fly ash.

When these two materials are used in this way, questions arise as to possible negative environmental or human health consequences from potentially toxic components of fly ash and asphalt. Fly ash contains twenty-one trace elements that may be potentially above risk assessment limits. These trace elements or “contaminants of concern” (COC) were chosen for evaluation through a risk assessment due to their potential toxicity. Some of these COCs include arsenic, barium, mercury, and vanadium. Asphalt contains polycyclic aromatic hydrocarbons (PAH), some of which are carcinogenic. Seventeen species of PAHs are identified as “contaminants of concern” to be evaluated through a risk assessment due to their potential toxicity. In this report we will focus on the potential human health risks from the use of these two materials in sub-base under roads, addressing the following questions:

> What is the level of concentration of COC in coal combustion fly ash from the major fly ash sources that could be available for soil stabilization in Minnesota?
>
> What is the level of concentration of these COC in Minnesota soils that are candidates for stabilizations?
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> What is the level of concentration of COC in asphalt that has been used on Minnesota streets and roads?
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> If fly ash is used for soil stabilization and asphalt is incorporated as a component of the aggregate, will COC and PAHs leach to groundwater and increase concentrations to greater than allowed by the Minnesota Department of Health Risk Limits?
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> If roads are reconstructed or abandoned, could sub-base with fly ash and/or asphalt be placed in residential settings, and could this result in unacceptable risk to resident children and adults?

We sampled fly ash from 18 coal burning plants in Minnesota and nearby sites in Wisconsin and South Dakota and analyzed for COC. The sampling included major electrical power generators plus sugar processors. Because fly ash used in sub-base stabilization is a low value commodity and large volumes are needed when used in soil stabilization, users will want to obtain ash from nearby sources. Sampling was done over time to assess the variability in ash. All of the ash generators sampled use low sulfur coals from the Powder River Basin in Wyoming and Montana but have different boiler and pollution control devices.

We sampled fourteen high clay sub-soils that are typical of problematic soils that would benefit from stabilization with fly ash, and analyzed for COC. Sampling sites were chosen after creating a map that identified regions with areas of high clay soils. All the sampling sites were in areas of minimal disturbance, commonly, airports and parks.

We addressed the human health questions concerning sub-soil stabilization with fly ash by using Minnesota Pollution Control Agency (MPCA) worksheets, which use risk-based criteria for calculation of maximal allowable concentrations of COC at environmental clean-up sites. We used the MPCA Soil Reference Value (SRV) worksheet for assessment of risk resulting from direct human contract with soil and the Soil Leaching Value (SLV) worksheet to calculate upper limits that will minimize the potential for contamination of groundwater. The worksheet risk limits were compared to the COC concentrations calculated for various mixtures of soil and fly ash. In this evaluation we used a worst-case scenario assuming fly ash treated sub-base is used in the future as surface soil in a residential setting, with shallow groundwater. This is the approach we used in a previous project to develop a risk-based screening tool called Screening Tool for the Utilization of Waste Materials in Paving Projects (STUWMPP). This tool compares COCs in soil/fly ash mixtures to SRV and SLV worksheet limits to provide a yes or no decision on acceptability of a given mixture.

We found that the concentrations of COC vary greatly in fly ash depending on the coal source, addition of auxiliary fuels, type of burner, and type of pollution control devices. Generally ash from eastern bituminous coals is more problematic for soil stabilization because of higher arsenic compared to western coals. However, all the ash generators we sampled are currently burning sub bituminous coal from the Powder River Basin (PRB) in Wyoming and Montana. The cleanest ash sources were from pulverized coal injection burners with Wyoming PRB coal, with or without wood as an added fuel. Among these ash sources, the cleanest was the Xcel Sherco 3 plant, which uses lime scrubbing to remove SO_2 from the stack gases. The lime dilutes the minor elements. However, this ash source is not acceptable for soil stabilization due to the high sulfur content, which causes unwanted expansion in stabilized soils. Cyclone boilers require a higher heat value fuel than PRB sub bituminous coal and another fuel must be added. This can increase concentrations of some elements. Vanadium and nickel are higher in the King and Riverside 8 ash due to the addition of petroleum coke. Cyclone boilers also produce a high carbon ash, which removes mercury from the flue gas increasing the Hg concentration in the ash. The Ottertail Power Big Stone plant adds waste tires and sewage sludge to the fuel mix, which produces an ash that is more than five times higher in zinc than any of the other ash sources. The American Crystal Sugar plants burn Montana PBR coal using traveling grate boilers. This yields an ash that is high in arsenic.

Generally COC have higher concentrations in ash than in soils and the addition of any amount of ash will increase concentrations of COC. We evaluated ash/soil mixes of 10% and 20%, representing a realistic range of fly ash application rates for soil stabilization. In these calculations we added ash to a soil with mean concentrations of COC. The SLV limits were calculated for a silty clay soil with a pH 7 and a distance to water table of 3 ft. The shallow water table assumption was used to illustrate a worst-case situation. The results showed that strontium, silver, tin and antimony and lead, are never problematic for the ash sources we sampled. The most problematic elements were arsenic, barium, vanadium, and copper, but copper is problematic only if the 2006 residential limits are used. We found that SRV, and not SLV limits, set the upper concentration for ash addition. When the 1999 SRV limits were used, our calculations suggest that six of the ash sources could be used at 20% and eight of the sources can be used at greater than 10% but not at 20%. Only the American Crystal Sugar ash sources and the Minnesota Power Hibbard plant ash cannot be used in 10% mixtures. This is due to high arsenic contents.

We did an initial assessment of the potential risk of PAHs in asphalt using literature data. This led us to hypothesize that asphalt made for petroleum does not pose a high risk to human health but that coal tar asphalts are problematic.

We then conducted a small study to assess if our hypothesis was correct for asphalt pavements in Minnesota. The City of Minneapolis was chosen as the sampling area because the City has good records of street construction and their engineering staff was willing to help in coring asphalt pavements. We obtained 23 pavement cores from different streets in Minneapolis that were paved with asphalt on dates ranging from 1918 to 2003. We also analyzed one sample of asphalt from a road in Roseville that was known to contain coal tar. This gave us a wide variety of asphalt samples representing pavements constructed over the last 90 years. We used Soxhlet solvent extraction to dissolve the PAHs from crushed cores and analyzed for 17 different PAH compounds using an adaptation of the USEPA method TO-13A for PAHs in air. This involved the use of gas chromatography (GC) with mass spectrometry (MS) detection. Known quantities of deuterated PAHs were added to the Soxhlet extraction to assess recovery and in addition deuterated internal standards were added just before analysis. Our data, taken together with the literature data, were compared against the SRV and SLV worksheets limits for PAHs using the same assumptions we use to assess the risk for fly ash in sub base.

Asphalt pavement concentrations of PAHs in Minneapolis streets appear not to be problematic for placement of recycled pavement under roads except when coal tar has been used. Coal tar appears to be rare in the streets of Minneapolis even for roads that date back to 1918 and it is rather easy to detect because it is sticky and has a unique odor. The benzo(a)pyrene (BaP) equivalency concentrations can exceed the residential SRV limits for some streets but this should not limit the reuse of these asphalts as aggregate or in the incorporation into the sub base during recycling. The dilution with soil or other aggregate materials will decrease PAH concentrations below the residential SRV limits. The asphalt PAH concentrations do not exceed SLV limits, which suggest leaching should not be a problem. The Minneapolis data suggest that, in general, asphalt incorporation into aggregate or sub base in Minnesota will not cause problems due to PAH contents unless coal tar has been used in the asphalt.

Chapter 1: Introduction

The beneficial use of waste materials is not a new concept. People have tried to find uses for materials that were considered "waste" for a very long time. Our challenge is to develop criteria, methods and tools to capture the most total value for society from the waste materials that we have without negatively impacting human health and the environment.

In construction the re-use of stones, bricks, sand, gravel, timbers, and metals has also been an accepted practice for thousands of years. These materials were used to build roads, buildings and sports stadiums. This is true in every culture throughout the world.

Since 1970 the United States Congress has passed many environmental laws, rules and programs that mandate the use of waste materials in beneficial and environmentally acceptable uses. (Resource Conservation and Recovery Act, etc.) To be a "beneficial use" a material must be more economical to use than other alternative materials. It must be used in such a way that it adequately protects the quality of the environment and it must produce an acceptable value to society.

In addition to simple re-use of materials we have developed the concept of recycling. Metals, Glass, and some plastics are recycled to reduce pollution, and energy use. Recycling also occurs in road construction.

The current US-EPA's Coal Combustion Products Partnership (C^2P^2) program is a cooperative effort between the U.S. Environmental Protection Agency, American Coal Ash Association, Utility Solid Waste Activities Group, US Department of Energy, and US Federal Highway Administration to help promote the beneficial use of Coal Combustion Products (CCPs) and the environmental benefits that result from their use.

Governments are continuously experiencing tightening budgets that require highway engineers to look for lower cost alternatives to conventional raw materials and to find better engineering practices that extend roadway useable life. This study tries to add to our knowledge and our ability to use recycled materials while protecting human health and the environment. This study focused on two specific materials, fly ash and asphalt pavement.

Coal combustion fly ash can be used as a component of good quality sub-base under roads at lower cost than conventional construction (Federal Highway Administration 2003). Cementitious fly ash when mixed with soil at 7% to 20% (w:w) produces a strong sub-base with greatly reduced shrinking and swelling (Iowa State Report, 2005; Fly Ash Facts 2004). This is especially useful for soils with high clay content that almost always have high shrink-swell potential.

Ground asphalt pavement can be a good addition to aggregate mixes or can become a component of sub-base aggregate when incorporated directly during the process of cold in-place recycling of old pavements, with or without the addition of fly ash.

When these two materials are used in this way questions arises as to possible negative environmental or human health consequences from potentially toxic components of fly ash and asphalt. Fly ash contains twenty one trace elements that may be potentially above risk assessment limits. These trace elements or "contaminants of concern" (COC) are chose to be evaluated through a risk assessment due to their potential toxicity. Some of these COCs include arsenic, barium, mercury, and vanadium. Asphalt contains polycyclic aromatic hydrocarbons (PAH), some of which are carcinogenic. Seventeen species of PAHs are identified as "contaminants of concern" to be evaluated through a risk assessment due to their potential toxicity. In this report we will focus on the potential human health risks from the use of these two materials in sub-base under roads, addressing the following questions:

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We sampled fly ash from 18 coal burning plants in Minnesota and nearby sites in Wisconsin and South Dakota and analyzed them for the 21 elements. The sampling included major electrical power generators plus sugar processors. Because fly ash used in sub-base stabilization is a low value commodity and large volumes are needed when used in soil stabilization, users will want to obtain ash from nearby sources. Sampling was done over time to assess the variability in ash. All of the ash generators sampled use low sulfur coals from the Powder River Basin in Wyoming and Montana but have different boiler and pollution control devices.

We sampled fourteen high clay sub-soils that are typical of problematic soils that would benefit from stabilization with fly ash, and analyzed them for the same elements as in the fly ash study. Sampling sites were chosen after creating a map identifying regions with areas of high clay soils. All the sampling sites were in areas of minimal disturbance; commonly, airports and parks.

We addressed the human health questions concerning sub-soil stabilization with fly ash by using Minnesota Pollution Control Agency (MPCA) worksheets which use risk-based criteria for calculation of maximal allowable concentrations of (COC) at environmental clean up sites. We used the MPCA Soil Reference Value (SRV) worksheet for assessment of risk resulting from direct human contract with soil and the Soil Leaching Value (SLV) worksheet to calculate upper limits that will minimize the potential for contamination of groundwater. The worksheet risk limits were compared to the COC concentrations calculated for various mixtures of soil and fly ash. In this evaluation we used a worst-case scenario assuming fly ash treated sub-base is used in the future as surface soil in a residential setting, with shallow groundwater. This is the approach we used in a previous project to develop a risk-based screening tool called Screening Tool for the Utilization of Waste Materials in Paving Projects (STUWMPP). This tool compares COCs in soil/fly ash mixtures to SRV and SLV worksheet limits to provide a yes or no decision on acceptability of a given mixture.

The first step in assessing the potential risk of asphalt PAHs in aggregate mixes or in the sub-base was to do a review of the scientific literature of PAH contents of asphalts used in pavements. This was needed because little information is readily available about the PAH contents in asphalt in United States. The second step was to conduct a limited study of PAHs in asphalt pavements in Minnesota to determine if there is a potential for PAHs to be a problem. The City of Minneapolis was chosen as the sampling area because the City has good records of street construction and their engineering staff was willing to help in coring asphalt pavements. We obtained 23 pavement cores from different streets in Minneapolis that were paved with asphalt on dates ranging from 1918 to 2003. This gave us a wide variety asphalt samples representing pavements constructed over the last 90 years. We extracted crushed cores with solvent and analyzed for 17 different PAH compounds or COC. Our data, taken together with the literature data, were compared against the SRV and SLV worksheets limits for PAHs using the same assumptions we used to assess the risk for the COCs in soil stabilization.

In Chapter 2 we present the results of our study of the potential toxic trace elements in soil/fly ash mixtures. We discuss the data in relation to the possible utilization of the fly ash for sub-base stabilization in road construction.

In Chapter 3 we review the scientific literature on PAH contents in asphalts around the world and we present the results of our study of PAH contents in the asphalt streets of Minneapolis. We discuss the data in relation to the possible utilization of the asphalt in aggregate mixes or in sub-base.

In Chapter 4 we discuss the conclusions that we draw from our studies especially in relation to the possible human health implication of using fly ash and asphalt under roads in Minnesota.

Chapter 2: Contaminants of Concern in Soil and Fly Ash

To assist in the evaluation, a computer calculation tool to test the environmental acceptability of the fly ash mixtures with soil was created using the SRV and SLV limits. The calculation tool is called the Screening Tool for the Utilization of Waste Materials in Paving Projects (STUWMPP). STUWMPP compares concentrations of COC in a soil and ash mixture to the SRV and SLV worksheets to make evaluations. The soil and fly ash data needed for STUWMPP to test allowable limits of an addition of fly ash to soil are given in Appendix A. We discuss the soil and fly ash data and evaluate them with respect to risk limits. In addition, we examine factors effecting COC concentration's in fly ash.

Use of SRV and SLV Worksheets for Risk Assessment

The SRV worksheet evaluates the human health risk associated with a contaminated soil through dermal contact, inhalation, or ingestion exposure pathway. The SRV worksheet has different options that account for different exposure durations, which will vary depending on use of a site. The most restrictive exposure scenario is residential or Tier 1 SRV, which STUWMPP uses to set end points. The Tier 1 SRV assumes a 24-hour-per-day exposure. Complete description of the SRV worksheet is available at the MPCA website (Minnesota Pollution Control Agency, 1999). The Tier 1 SRV was recently changed based on new toxicology information. STUWMPP currently uses the 1999 SRV limits and a decision to update to the 2006 SRV limits is currently under discussion by Minnesota Department of Transportation (Mn/DOT) staff. Table 2.1 lists the 2006 and 1999 SRV limits. For this report, both the 1999 and 2006 SRV will be discussed.

The SLV worksheet evaluates the human health risk associated with COC from a contaminated soil leaching to shallow aquifers, creating drinking water noncompliance. COC leaching is highly dependent on soil/site conditions. Two Tiers exist for the SLV based on soil and site conditions. The Tier 1 SLV (default) assumes a worst-case scenario for the leaching of most COC. The default values include sandy soil with a pH of 7 and COC mixture depth of 15 feet directly above the water table. The SLV Tier 2 allows for the adjustment of soil/site parameters in its calculations to better represent COC leaching on a specific site. The SLV (Tier 2) concentration limits, presented in Table 2.1, were calculated using typical soil/site conditions for areas in need of soil stabilization before road construction. Input parameters include a soil with silty clay loam texture, 0.2% fraction of organic carbon, pH of 7 and in climate zone D. Aquifer conditions were left at defaults (aquifer hydraulic conductivity of 0.005 cm/sec, hydraulic gradient of 0.005, length of source parallel to groundwater flow of 2.048 m, and aquifer thickness of 914.4 cm). It was assumed that the soil/ash mixture thickness was one foot (typical maximum for soil stabilization applications). It was also assumed that three feet of soil lies between the soil-ash mixture and the water table. Complete description of the SLV worksheet is available at the MPCA website (Minnesota Pollution Control Agency, 1998).

Table 2.1. SRV and SLV COC Concentration Limits

COC (ppm)	2006 SRV Tier 1	1999 SRV Tier 1	SLV Tier 2 (typical soil/site)
Beryllium, Be	55	55	5.44
Boron, B	6000	3000	582
Cobalt, Co	600	2000	120
Nickel, Ni	560	520	353
Copper, Cu	11	100	1610
Zinc, Zn	8700	8700	6020
Arsenic, As	5	10	58.5
Selenium, Se	160	170	5.46
Strontium, Sr	18000	NA	77200
Molybdenum, Mo	NA	NA	24.3
Silver, Ag	160	NA	15.9
Cadmium, Cd	25	35	17.6
Tin, Sn	9000	15000	11900
Antimony, Sb	12	14	10.9
Barium, Ba	1200	1200	3380
Thallium, Tl	3	3	NA
Lead, Pb	300	400	2100
Chromium, Cr	87	71	73
Manganese, Mn	3600	1400	NA
Vanadium, V	30	210	2000
Mercury, Hg	0.50	0.70	6.58

Methods of Analysis for COC Quantification in Soil and Ash

The USEPA specifies three different methods for COC extraction from soil or fly ash; EPA Methods 3050, 3051, or 3052. Significant differences among the methods lie in the variation in time, cost, ease of method, and aggressiveness of extraction.

Method 3050 is commonly used in environmental clean-up assessment and is a leachate method that “simulates the potential of leaching of materials in the environment in order to establish pollution hazard (worst-case *(long-term)* scenarios)" (Kingston and Walter, 1992). Method 3051 was developed as an alternative method to 3050, and is expected to produce similar results. In Methods 3050 and 3051, concentrated nitric acid is added to the sample, heated and then filtered. Method 3051 involves heating concentrated nitric acid to 175 degrees Celsius for 4.5 minutes in a microwave. Method 3050 involves heating in a hot block using incremental doses of concentrated nitric acid until digestion is completed. Comparison of these methods for a soil yields similar results for most elements (Table 2.2). Full descriptions of these methods can be found at http://www.epa.gov/epaoswer/hazwaste/test/3_series.htm.

Method 3052 is a total digestion method that involves breaking down the entire sample matrix to determine the total COC concentrations, including elements bound in crystalline structures. Method 3052 is "appropriate for those applications requiring a total decomposition for research purposes (i.e., geological studies such as mineralogy studies and mass balances) or in response to a regulation that requires total sample decomposition" (Environmental Protection Agency, 1996a). Method 3052 involves sample digestion with concentrated nitric acid, concentrated hydrofluoric acid (significantly more dangerous than nitric acid) with the option of adding hydrochloric acid and hydrogen peroxide. The samples and acid are heated to 180 degrees C in a sealed Teflon container for 9.5 minutes in a microwave. A complete method description can be found at http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3052.pdf. Method 3052 procedure is more time consuming, more dangerous and expensive compared to EPA Method 3050 or Method 3051.

Table 2.2. Data Comparing Recoveries from Method 3050 and Method 3051 for Soils

	Percentage Recovered of Certified Total Values
Element:	NIST-2709[1]
	Method 3050 – 3051
Cadmium, Cd	98(+/- 3) – 97(+/- 1)
Copper, Cu	94(+/- 1.8) – 89(+/- 3.2)
Lead, Pb	96(+/- 6.7) – 95(+/- 3)
Nickel, Ni	101(+/- 13) – 80(+/- 9.4)
Zinc, Zn	97(+/- 3.5) – 93(+/- 3.2)

[1] National Institute of Standards and Testing (Wei, Y.L., H.M. Shyu, K.L. Joehuang, 1997)

Elements bound in silicate structures will not be totally dissolved by Methods 3050 and 3051, resulting in differences in recoveries between Method 3050/3051 and Method 3052. However, the elements bound in silicate structures are not mobile in the environment, or bioavailable to plants and animals. For these reasons, in most environmental clean-up operations Methods 3050/3051 are used for assessment (Environmental Protection Agency, 1996b).

After test runs with Method 3050 and Method 3051, we decided that Method 3051 would be used; since it required less time and was less subjective (Decisions of digestion completeness must be made for 3050). Literature comparisons of fly ash data among the various methods are not available; however comparisons with soil data are available.

Some data are available for the comparison of Method 3050 to total (3052) values (Environmental Protection Agency, 1996a). Table 2.3 shows the ranges obtained from three National Institute of Standards and Testing (NIST), Standard Reference Materials (SRM). Despite the fact that all SRM were soils, elemental ranges were still relatively variable. The third column shows the variation between two laboratories using the same soil NIST SRM. It is apparent from the data given in Table 2.3 that results of Method 3050 will vary depending with differences in sample matrix and with different laboratories. Less than 60% recoveries (of total amounts) for more recalcitrant elements like antimony, chromium, selenium and vanadium were found.

Table 2.3. COC Results as Percentages of Total using Method 3050

	Leachate concentration as percent of certified	
COC	Method 3050 3 NIST SRMs (soils)[1]	Method 3050 NIST SRM-2709 (soil) (2 different labs)[1]
Antimony, Sb	bdl – 21%	
Arsenic, As	bdl – 94%	
Barium, Ba	28 – 51%	41 – 46%
Cadmium, Cd	bdl – 96%	Bdl
Chromium, Cr	43 – 61%	61 – 75%
Cobalt, Co	82 – 90%	90 – 99%
Copper, Cu	88 – 92%	92 – 99%
Lead, Pb	69 – 95%	65 – 69%
Manganese, Mn	76 – 87%	
Molybdenum, Mo	bdl – 100	
Nickel, Ni	71 – 89%	89 – 99%
Silver, Ag	bdl – 86%	
Selenium, Se	<1%	
Strontium, Sr	20 – 40%	44 – 45%
Vanadium, V	51 – 56%	55 – 65%
Zinc, Zn	85 – 94%	94 – 100%

[1] National Institute of Standards and Testing, Standard Reference Materials (Kane, J.S., 1995)
[2] (Environmental Protection Agency, 1996b)
bdl=below detection limit

Quantification of Elements in Leachate

After samples have been digested, the COC concentration in the leachate solution can be quantified using inductively coupled plasma with atomic emission spectrophotometer (ICP-AES), inductively coupled plasma with mass spectrophotometer (ICP-MS) or other analytical detection instruments (flame atomic absorption, graphite furnace atomic absorption, etc.). ICP-AES and ICP-MS were chosen due to their sensitivity, availability on the University of Minnesota campus, and affordability. Advantages and disadvantages exist for both ICP-AES and ICP-MS. In general, ICP-MS has the ability to detect smaller concentrations compared to ICP-AES. However, the process used in ICP-MS may require more computer adjustments due to elemental interferences than for ICP-AES. Depending on specific element, one method may have an advantage over the other. Table 2.4 lists all of the COC, the instrument used, and detection limits. Many elements are successfully quantified using either instrument. Overall, we recommend the use of ICP-AES if possible, due to the more direct quantification involved in the AES.

Table 2.4. Analytical Instrument and Detection Limit for each COC

Element	Analytical Instrument Used	ICP-MS Detection Limit (ppm)	ICP-AES Detection Limit (ppm)
Antimony, Sb	ICP-MS	0.001	
Arsenic, As	ICP-MS	0.002	
Barium, Ba	ICP-AES		0.60
Beryllium, Be	ICP-MS	0.001	
Boron, B	ICP-MS	0.019	
Cadmium, Cd	ICP-MS	0.001	
Chromium, Cr	ICP-AES		1.4
Cobalt, Co	ICP-MS	0.001	
Copper, Cu	ICP-AES		2.6
Lead, Pb	ICP-MS	0.30	
Manganese, Mn	ICP-AES		0.30
Molybdenum, Mo	ICP-MS	0.001	
Nickel, Ni	ICP-AES		2.2
Selenium, Se	ICP-MS	0.021	
Silver, Ag	ICP-MS	0.002	
Strontium, Sr	ICP-AES		0.30
Thallium, Tl	ICP-MS	0.001	
Tin, Sn	ICP-MS	0.002	
Vanadium, V	ICP-AES		1.8
Zinc, Zn	ICP-AES		0.70

Problems with Barium in High Sulfur Ash

Ash from some of the plants: King, Sherco 3, Riverside 8 and American Crystal Sugar's East Grand Forks, Moorhead and Crookston Plants contain high concentrations of sulfur (>25,000 ppm) compared to the other plants (<10,000 ppm). When high sulfur ash is digested using method 3051, involving 0.5 grams of ash in 10 mL of concentrated nitric acid, a barium sulfate precipitation will form. This precipitate will be trapped with solids during the filtration process, and therefore the concentration of barium measured will not be representative of actual barium concentration that can be leached from the ash. To address the problem, a modified 3051 method was used to increase the sample to acid ratio by ten fold when determining barium concentrations (0.05 grams of ash in 10 mL acid) in high sulfur ash. Sample dilution results in significantly higher barium concentrations, with an increase range from 33% to 1480% (see Table 2.5). The increase in barium concentration is greater at higher SO_4 concentrations.

Table 2.5. Effect of Dilution on Barium Leachate from Fly Ash with High Sulfur

	Sulfur (ppm)	Barium (ppm)	Barium (ppm) 10x dilution	% increase
King	27500	3410	4950	45%
King	26900	3770	5020	33%
King	26500	2507	5020	101%
Riverside 8	30100	3600	5830	62%
Riverside 8	28400	3300	4790	45%
ACS EGF	58200	1170	12300	946%
ACS EGF	53200	1340	12100	800%
Sherco	59100	959	2590	170%
Sherco	56400	1300	2530	95%
ACS Moorhead	80100	848	10200	1100%
ACS Moorhead	91200	644	9030	1300%
ACS Crookston	99200	698	11000	1480%
ACS Crookston	85700	771	8740	1030%

Total Chromium in Ash and Soil

Chromium in fly ash and soil is composed of two different forms, or oxidation states, with widely different mobility and toxicity. Hexavalent Cr (VI) (chromate, CrO_4^{2-}) is highly toxic and very mobile, while the toxicity and mobility of trivalent Cr (III) is much lower. The SLV and SRV Cr limits are for hexavalent Cr (VI), the more toxic form. However, the trivalent species is typically the predominant species in soils. Commonly, Cr concentrations are reported as total

Cr, as in our data. Therefore an overestimate of the toxicity is given in our assessments. Analytic procedures that separate the two forms are available but are not routine and can be relatively expensive. However, measuring Cr (VI) separately would result in a better estimate of actual Cr risk.

Mercury Analysis

Mercury can not be easily determined by ICP-AES or ICP-MS. Thus, the soil and ash samples were subjected to EPA Method 1631, "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" (Environmental Protection Agency, 2002) for mercury quantification. Ash samples were digested according to EPA Method 3051. Soil samples were digested in a slightly different manner. Approximately 1 g of soil was weighed and added to a Nalgene® digestion bomb vial. The sample was oxidized using 5mL each of trace metal grade nitric acid (HNO_3) and sulfuric acid (H_2SO_4) then heated gently in tightly closed vial at 65 degrees C overnight. This procedure converted the various mercury forms to Hg^{2+}.

Next, the ash extract solution and the soil extract solution were reduced (converting Hg^{2+} ions to Hg^{o}) using a stannous chloride solution ($SnCl_2{*}2H_2O$). Then the samples were spurged with nitrogen gas and the Hg^0 was trapped on gold coated glass beads. The mercury quantification was done using a Brooks-Rand Model III Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS). Dilutions were in ultra-clean 30 mL vials using water generated from a Barnsted E-Pure 4 cartridge system coupled to a DI/DS source. All analyses were done in a room with a positive pressure high-efficiency particulate air filtering (HEPA) system to ensure an ultra clean environment.

Contaminants of Concern in Typical Minnesota Clayey Sub-Soils

In the evaluation of human health risk, the SRV and SLV worksheets use total COC concentrations in the soil/ash mixture. Therefore soil COC data are needed for risk calculations. Fourteen clayey Minnesota sub-soils, likely to benefit from stabilization before road construction, were sampled and evaluated for COC concentration (Table 2.6). To choose proper sampling locations, a map of clay soils was created (Figure 1.1) All soil sampling was done in summer of 2004. At each site, a ten-meter by ten-meter area grid was marked. Sets of coordinates were generated before visiting the site using a random number table. Using the one-meter segmented boarders as axes, ten flags were placed using the coordinates previously generated. Soil cores were collected at each of the ten coordinates. Cores were collected using a one-inch diameter hammer driven soil probe with a plastic liner. The cores were driven to a depth of sixty centimeters, or as far as the probe would allow. The ends of the plastic tube were caped, labeled and transported back to the University of Minnesota.

In the lab, each core was examined for major color change, which indicates the boarder between topsoil and sub-soil. Cores were cut either at the color change or at a depth of forty centimeters (measured from the top) if no color change was present. The topsoil was discarded and the sub-soil was kept for analysis. Each set of ten sub-soil cores were combined to form one sample for each site. Samples were then dried and ground to pass through a two millimeter plastic sieve and finally homogenized using a Tungsten SPEX 5300 Mixer Mill. Next, the samples were digested according to EPA Method 3051, previously described.

Figure 2.1 Minnesota Map of Clayey Soils Highlighted

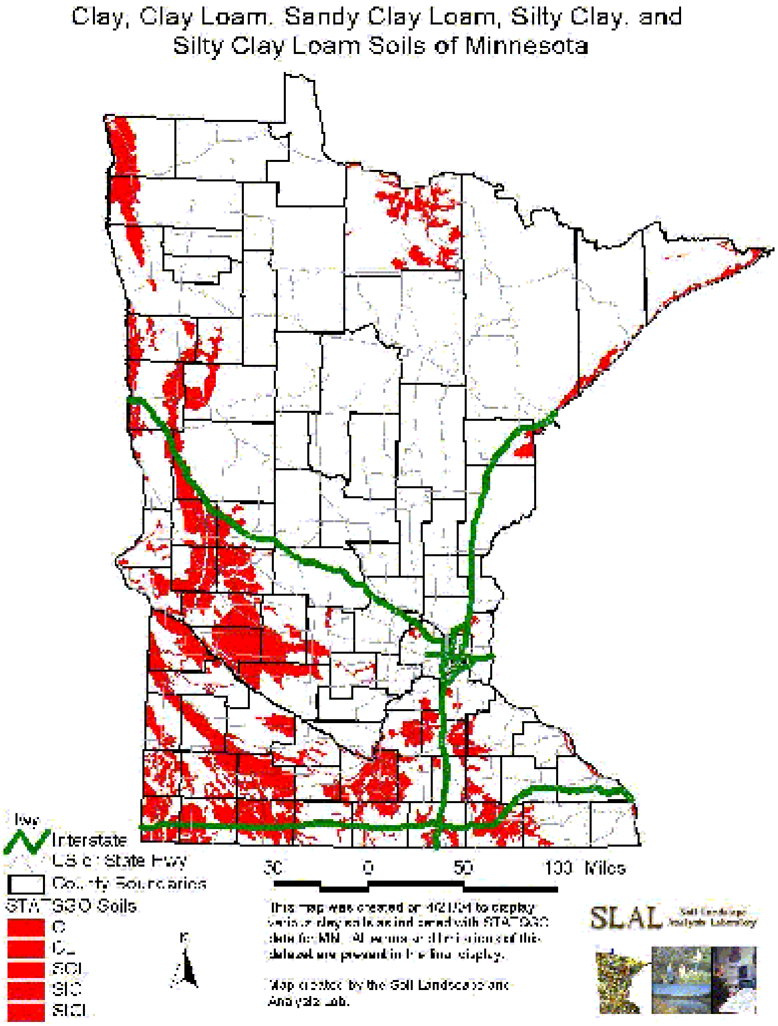

Table 2.6. Soil Sample Details

County	Town	Site	Soil Type	pH
Grant	Herman	Herman Airport	Hamerly-Parnell complex	7.73
Blue Earth	Mankato	Mankato Airport	LeSueur	6.91
Marshall	Warren	City Park	Colvin	8.14
Rock	Kenneth	City Park	Everly	7.80
Swift	Murdock	Murdock Airport	Parnell	7.74
Polk	Crookston	City Park	Bearden-Colvin complex	8.42
Clay	Moorhead	City Park	Fargo complex	7.64
Scott	Jordan	Grass Lot, 6525 218st W	Lester	8.01
Chippewa	Maynard	City Park	Colvin-Spicer	8.23
Waseca	Waseca	Maplewood Park	Webster	7.11
Lac Qui Parle	Marietta	City Park	Parnell	7.14
Faribault	Blue Earth	Rest Stop off I-90, west of Blue Earth	Shorewood	6.38
Nobles	Worthington	Worthington Airport	Waldorf	7.78
Jackson	Jackson	Jackson Airport	Webster	7.80

These data are available in STUWMPP for quick screening proposed ash/soil mixtures. Minnesota soils are variable in COC concentrations due to differences in parent material, location in a landscape, climate, hydrology, degree of weathering, and biological processes. Therefore caution should be practiced when using these data, as site conditions may be different for each particular construction site. It is recommended that COC concentrations be determined for soil samples collected at actual site to determine a more accurate risk assessment.

Summary statistics including COC minimum, maximum, mean, standard deviation and upper 95% confidence interval for the sampled 14 sub-soils are given in Table 2.7. The upper 95% confidence interval is calculated to represent the likely upper limit for COC concentrations in soils in need of stabilization in Minnesota. In addition, the SRV Tier 1 1999 and 2006 values are given for reference. Values are also given for the SLV Tier 2 for typical soil/site conditions.

Table 2.7. Summary Statistics for all Soils

COC (ppm)	SRV Tier 1 (1999)	SRV Tier 1 (2006)	SLV Tier 2 (typical site/soil)	Min:	Max:	Mean:	Std Dev:	Upper 95% C.I.
Be	55	55	5.44	0.34	0.88	0.60	0.14	0.87
B	3000	6000	582	6.57	32.2	17.6	6.86	31.3
Co	2000	600	120	7.53	23.4	13.6	4.62	22.8
Ni	520	560	353	15.6	37.4	25.6	5.79	37.2
Cu	100	11	1610	10.5	22.4*	15.8*	3.36	22.5*
Zn	8700	8700	6020	33.4	69.4	49.2	11.2	71.61
As	10	5	58.5	1.67	9.56*	5.45*	2.28	10.0*[+]
Se	170	160	5.46	0.59	1.24	0.87	0.21	1.29
Sr	NA	18000	77200	24.9	107	48.3	29.0	106
Mo	NA	NA	24.3	0.27	1.70	0.63	0.37	1.37
Ag	NA	160	15.9	0.47	12.5	2.06	3.29	8.63
Cd	35	25	17.6	0.17	0.55	0.38	0.12	0.62
Sn	15000	9000	11900	0.21	1.50	0.71	0.43	1.56
Sb	14	12	10.9	0.02	0.23	0.09	0.07	0.24
Ba	1200	1200	3380	83.4	222	150	44.0	238
Tl	3	3	NA	0.21	0.73	0.40	0.15	0.69
Pb	400	300	2100	5.52	13.2	9.99	2.05	14.1
Cr	71	87	73	12.4	44.0	21.3	8.71	38.7
Mn	1400	3600	NA	219	1350	675	284	1240
V	210	30	2000	12.5	43.9*	25.6	9.15	43.9*
Hg	0.70	0.50	6.58	0.01	0.05	0.03	0.01	0.05

*exceed the 2006 SRV
[+]exceed the 1999 SRV
[#]exceed the SLV

The 2006 SRV endpoints will cause major problems when calculating human health risk for any soil/ash mixture. All soils except one exceed the 2006 copper SRV of 11 ppm (Table 2.7). Half of the soils exceed the 2006 arsenic SRV of 5 ppm and four exceed the 2006 vanadium SRV of 30 ppm. The SLV and SRV were designed to offer endpoints for the clean-up of contaminated sites. The fact that some of the COC in soils naturally exceed the SLV and SRV is a fundamental problem. It is not practical to clean-up a site beyond natural conditions. Does this mean that natural COC concentrations in soils are at levels that supply an unacceptable risk to human health or does this mean that the SLV and SRV concentrations are too restrictive? These questions need to be addressed by policy makers.

Individual Plants Evaluations: Contaminants of Concern in Coal Fly Ash

Coal contains varying amounts of COC. Contaminants of concern in coal can originate from several sources during coal formation: deposited plants, water present during formation or during digenesis, clays and other soil materials. For example eastern bituminous coals were formed in coastal marine swamps where SO_4 in ocean water was reduced to pyrite (FeS_2) under anaerobic conditions. During coal formation, this pyrite was deposited within the coal. Western coals were created in freshwater swamps and therefore have lower concentrations of sulfur (pyrite). Because of COC variations in coal, COC also vary in fly ash. Other factors besides formation of coal can lead to different concentrations of COC in fly ash and will be discussed in section IV, “Factors Effecting COC in Ash”.

Fly ash is formed from inorganic minerals within coal and is collected in pollution control devices (PCD). These inorganic minerals are mostly made of oxides of silicon, aluminum, iron and calcium (United States Department of Transport, 2004). Minor amounts of other trace elements (some being COC) are present in fly ash. COC present in coal before combustion are distributed into three major sinks after combustion.

The first sink is bottom ash, which is collected directly below the boiler. Dense, nonvolatile elements such as iron and aluminum are generally deposited in bottom ash. Remaining elements travel with flue gas to PCD. These devices capture COC through various methods that will be discussed in section IV. The material captured in PCD is termed fly ash, the second sink. The temperature of PCD is greatly lower than boiler conditions; therefore some elements that were volatile will condense on fly ash particles and be collected. The third sink is the atmosphere via the smoke stack. Elements that are extremely volatile (e.g. mercury) will have a significant fraction escape past PCD (except in specially designed PCD) and be released into the atmosphere. In addition, elements that are associated with very fine particles that are not captured by PCD will also leave through the smoke stack. Commonly, elements will be in all three sinks at varying fractions. Our study focused on fly ash exclusively.

Comparison of ash data in Table 2.8 with the soil data in Table 2.7 shows that concentrations of COC in ash exceed soil, except for silver and manganese. In soil stabilization typically 10-20% ash is mixed with soil thus elevating most COC concentrations compared to soil alone. If COC levels in ash are high enough they may cause the mixture to exceed SRV and SLV limits. Table 2.8 shows overall COC statistics for all ashes sampled. The data in Table 2.8 show that Ag, Cd, Sn and Sb are below SRV and SLV limits for all ash. In addition, Zn, Sr, Mo, Tl, Cr and Mn mean concentrations are below SRV and SLV limits.

Table 2.8. Summary Statistics for all Plants (n=132)

COC (ppm)	SRV Tier 1 (1999)	SRV Tier 1 (2006)	SLV Tier 2 (typical site/soil)	Min:	Max:	Mean:	Std Dev:	Upper 95% C.I.
Be	55	55	5.44	0.70	5.45[#]	3.00	0.89	4.77
B	3000	6000	582	221	1250[#]	585[#]	238	1060[#]
Co	2000	600	120	2.14	201[#]	20.4	26.6	73.6
Ni	520	560	353	7.26	958*[+#]	136	260	655*[+#]
Cu	100	11	1610	18.7*	348*[+]	152*[+]	76.3	304*[+]
Zn	8700	8700	6020	33.7	8650[#]	484	1610	3700
As	10	5	58.5	3.55	99.1*[+#]	19.2*	16.4	52.0*
Se	170	160	5.46	0.91	20.4[#]	9.21[#]	3.70	16.6[#]
Sr	NA	18000	77200	701	7030	3000	1520	6030
Mo	NA	NA	24.3	2.06	111[#]	20.01	30.2	80.4[#]
Ag	NA	160	15.9	0.20	8.43	1.63	1.07	3.77
Cd	35	25	17.60	0.53	10.1	1.87	1.51	4.88
Sn	15000	9000	11900	0.18	5.59	0.99	0.79	2.56
Sb	14	12	10.9	0.01	1.07	0.15	0.13	0.42
Ba	1200	1200	3380	917	12300*[+#]	4440*[+#]	2290	9020*[+#]
Tl	3	3	NA	0.10	3.66*[+]	0.74	0.59	1.92
Pb	400	300	2100	8.56	120	37.2	22.5	82.1
Cr	71	87	73.0	12.1	102*[+#]	58.8	21.3	101*
Mn	1400	3600	NA	57.6	1760*[+]	281	332	945
V	210	30	2000	23.0	1810*[+]	384*[+]	485	1350*[+]
Hg	0.70	0.50	6.58	0.03	1.20*[+]	0.41	0.37	1.14*[+]

*exceed the 2006 SRV
[+] exceed the 1999 SRV
[#] exceed the SLV

Contaminants of concern that exist in ash at levels exceeding the SRV or SLV are presented in Table 2.9. This list represents all of the ash data; although individual plant results are varied and will be discussed later. However, SRV and SLV limits are intended for COC concentrations in the total ash/soil mixture. Typically in soil stabilization, 10% to 20% ash is mixed with soil. In most cases since the soil constitutes the bulk of the mixture fewer COC will exceed the

SRV/SLV limits for the mixture compared to pure ash. Copper, arsenic and vanadium will exceed the 2006 SRV for all mixtures when using an mean soil (from 14 sampled sub-soils discussed earlier) since soil values are in excess of limits. To give realistic ideas of mixture COC levels, mixing simulations will be presented for each plant. Note, only the ten COC listed in Table 2.9 are included in these mixing simulations since all other COC are very unlikely to exceed either SRV or SLV.

Table 2.9. COC in Ash that Exceed the SRV or SLV.

Ash Mean Exceeds the:			Ash Upper 95% Exceeds the:		
SRV (2006)	SRV (1999)	SLV (typical site*)	SRV (2006)	SRV (1999)	SLV (typical site*)
Cu, As, Ba, V	Cu, As, Ba	B, As, Se, Ba	Cu, As, Ba, Cr, V, Hg	Cu, As, Ba, Cr, V, Hg	B, Ni, As, Se, Mo, Ba, Cr

As mentioned before, COC concentration in coal fly ash varies. Any COC present in coal will contribute to COC in ash. In addition, fuel inputs, type and functioning of pollution control devices and boilers can affect the COC in fly ash. These factors can contribute to the variation of COC seen in different plants. Plant operators rarely change fuel source and pollution control systems, therefore COC in an individual plant's ash remains relatively constant.

Soil/ash mixture simulations for COC listed in Table 2.9 are given for each plant. Four mixing simulations are given, two with 10% ash and two with 20% ash and all with an mean soil (soil mean values). Each 10% and 20% ash mixing is conducted with an mean COC value for the ash, to give typical conditions, and with an upper 95% confidence interval for the ash to give an upper threshold value.

Xcel Energy

High Bridge

Xcel Energy's High Bridge is a 267 megawatt plant, built in 1964. It is located in St Paul, Minnesota. The facility burns Powder River Basin (PRB) coal and is equipped with a pulverized coal boiler and electrostatic precipitator. Table 2.10 gives summary statistics for COC in High Bridge ash. Some Cu, As, Se, Ba and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of High Bridge ash, mixing simulations with a mean soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.11). The calculated concentrations did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.10. COC Summary Statistical Data for High Bridge Ash (Sampled 11/16/04 – 12/17/04; n=10)

High Bridge (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	3.06	3.51	3.35	0.13	3.61	55.0	55.0	5.44
B	354	420	391	21.3	434	6000	3000	582
Co	16.6	19.6	18.1	0.82	19.7	600	2000	120
Ni	23.4	39.1	33.0	4.15	41.3	560	520	353
Cu	136*+	152*+	143*+	4.94	153*+	11.0	100	1610
Zn	63.9	88.0	80.9	7.22	95.3	8700	8700	6020
As	8.88*	10.6*+	9.92*	0.56	11.0*+	5.00	10.0	58.5
Se	7.66#	8.71#	8.07#	0.36	8.79#	160	170	5.46
Sr	2660	2930	2810	79.3	2970	18000	NA	77200
Mo	5.87	6.49	6.19	0.18	6.54	NA	NA	24.3
Ag	1.20	3.29	1.91	0.82	3.55	160	NA	15.9
Cd	0.79	0.91	0.85	0.04	0.93	25.0	35.0	17.6
Sn	0.35	1.25	0.67	0.32	1.31	9000	15000	11900
Sb	0.04	0.36	0.13	0.10	0.32	12.0	14.0	10.9
Ba	4310*+#	5310*+#	4880*+#	268	5410*+#	1200	1200	3380
Tl	0.28	0.65	0.40	0.13	0.67	3.00	3.00	NA
Pb	25.9	30.0	27.8	1.44	30.7	300	400	2100
Cr	56.8	66.8	61.7	3.16	68.0	87.0	71.0	73.0
Mn	124	136	130	4.08	138	3600	1400	NA
V	200*	215*+	205*	5.15	215*+	30.0	210	2000
Hg	-	-	0.05	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

Table 2.11. Mixing Simulation for Mean Soil with High Bridge Ash

High Bridge (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	55.0	59.3	92.4	101	6000	3000	582
Ni	25.6	26.4	27.2	27.1	28.8	560	520	353
Cu	15.8*	28.5*	29.5*	41.3*	43.2*	11.0	100	1610
As	5.45*	5.90*	6.01*	6.34*	6.57*	5.0	10.0	58.5
Se	0.87	1.59	1.66	2.31	2.45	160	170	5.46
Mo	0.63	1.19	1.22	1.74	1.81	NA	NA	24.3
Ba	150	623	676	1100	1200	1200	1200	3380
Cr	21.3	25.4	26.0	29.4	30.7	87.0	71.0	73.0
V	25.6	43.5*	44.5*	61.4*	63.5*	30.0	210	2000
Hg	0.03	0.03	-	0.03	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Black Dog

Xcel Energy's Black Dog is a 538 megawatt plant, built in 1955. It is located in Burnsville, Minnesota. This facility like High Bridge, burns PRB coal and is equipped with a pulverized coal boiler and electrostatic precipitator. Table 2.12 gives summary statistics for COC in Black Dog ash. Some B, Co, Cu, As, Se, Ba, Cr and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Black Dog ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.13). Like the ash from High Bridge, all mixtures did not exceed the 1999 SRV limits and all mixtures exceed the 2006 SRV for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.12. COC Summary Statistical Data for Black Dog Ash (Sampled 3/24/05 – 4/27/04; n=10)

Black Dog (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	2.84	3.98	3.46	0.42	4.31	55.0	55.0	5.44
B	392	661$^{\#}$	503	72.4	648$^{\#}$	6000	3000	582
Co	17.9	201$^{\#}$	56.2	72.9	202$^{\#}$	600	2000	120
Ni	36.1	43.5	39.8	2.23	44.3	560	520	353
Cu	130*$^{+}$	157*$^{+}$	142*$^{+}$	7.97	158*$^{+}$	11.0	100	1610
Zn	94.3	115	103	6.53	116	8700	8700	6020
As	10.7*$^{+}$	13.0*$^{+}$	11.9*$^{+}$	0.70	13.3*$^{+}$	5.00	10.0	58.5
Se	8.18$^{\#}$	11.2$^{\#}$	9.61$^{\#}$	0.91	11.4$^{\#}$	160	170	5.46
Sr	2670	2900	2780	82.9	2950	18000	NA	77200
Mo	5.93	7.37	6.61	0.41	7.44	NA	NA	24.3
Ag	1.02	6.23	2.30	1.83	5.97	160	NA	15.9
Cd	0.87	0.99	0.93	0.03	1.00	25.0	35.0	17.6
Sn	0.28	1.34	0.67	0.35	1.36	9000	15000	11900
Sb	0.04	0.25	0.13	0.07	0.27	12.0	14.0	10.9
Ba	4680*$^{+\#}$	5130*$^{+\#}$	4930*$^{+\#}$	145	5220*$^{+\#}$	1200	1200	3380
Tl	0.48	0.79	0.60	0.11	0.81	3.00	3.00	NA
Pb	22.3	32.7	29.5	3.40	36.3	300	400	2100
Cr	60.2	72.4$^{+\#}$	68.0	3.75	75.5$^{+\#}$	87.0	71.0	73.0
Mn	107	147	125	10.4	146	3600	1400	NA
V	188*	203*	198*	4.50	207*	30.0	210	2000
Hg	-	-	0.06	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.13. Mixing Simulation for Mean Soil with Black Dog Ash

Black Dog (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	66.2	80.6	115	144	6000	3000	582
Ni	25.6	27.1	27.5	28.5	29.4	560	520	353
Cu	15.8*	28.4*	30.0*	41.0*	44.2*	11.0	100	1610
As	5.45*	6.09*	6.23*	6.73*	7.02*	5.0	10.0	58.5
Se	0.87	1.74	1.93	2.62	2.98	160	170	5.46
Mo	0.63	1.23	1.31	1.83	1.99	NA	NA	24.3
Ba	150	628	657	1110	1160	1200	1200	3380
Cr	21.3	26.0	26.7	30.7	32.2	87.0	71.0	73
V	25.6	42.8*	43.7*	60.0*	61.8*	30.0	210	2000
Hg	0.03	0.03	-	0.03	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Riverside 6&7

Xcel Energy's Riverside 6&7 is a 142 megawatt plant, built in 1987. It is located in Minneapolis, Minnesota. The facility burns PRB coal and is equipped with a pulverized coal boiler and baghouse. Table 2.14 gives summary statistics for COC in Riverside 6&7 ash. Some Cu, As, Se, Ba, Cr, V and Hg concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Riverside 6&7 ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.15). Calculated barium concentrations exceed the 1999 and 2006 SRV limits for mixtures of 20%. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.14. COC Summary Statistical Data for Riverside 6&7 Ash (Sampled 3/14/05 – 4/19/05; n=10)

Riverside 6&7 (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	2.79	3.47	3.18	0.22	3.62	55.0	55.0	5.44
B	343	404	368	22.2	412	6000	3000	582
Co	19.2	22.9	21.1	1.45	24.0	600	2000	120
Ni	41.5	51.1	46.7	3.64	54.0	560	520	353
Cu	155*$^{+}$	178*$^{+}$	169*$^{+}$	6.56	182*$^{+}$	11.0	100	1610
Zn	96.8	142	124	13.4	151	8700	8700	6020
As	10.2*$^{+}$	13.4*$^{+}$	11.8*$^{+}$	0.88	13.6*$^{+}$	5.00	10.0	58.5
Se	9.15$^{\#}$	11.0$^{\#}$	10.0$^{\#}$	0.53	11.1$^{\#}$	160	170	5.46
Sr	2800	2960	2890	60.1	3010	18000	NA	77200
Mo	5.79	7.31	6.51	0.48	7.48	NA	NA	24.3
Ag	1.08	1.99	1.57	0.30	2.17	160	NA	15.9
Cd	0.96	1.25	1.07	0.11	1.29	25.0	35.0	17.6
Sn	0.24	1.08	0.52	0.24	1.00	9000	15000	11900
Sb	0.04	0.08	0.06	0.02	0.10	12.0	14.0	10.9
Ba	4940*$^{+\#}$	5870*$^{+\#}$	5450*$^{+\#}$	311	6070*$^{+\#}$	1200	1200	3380
Tl	0.37	0.71	0.47	0.10	0.67	3.00	3.00	NA
Pb	23.3	37.9	31.8	4.50	40.8	300	400	2100
Cr	82.3$^{+\#}$	102*$^{+\#}$	91.9*$^{+\#}$	5.97	104*$^{+\#}$	87.0	71.0	73.0
Mn	122	151	137	9.35	156	3600	1400	NA
V	214*$^{+}$	243*$^{+}$	228*$^{+}$	11.2	251*$^{+}$	30.0	210	2000
Hg	-	-	0.65*$^{+}$	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.15. Mixing Simulation for Mean Soil with Riverside 6&7 Ash

Riverside 6&7 (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	52.7	57.1	87.7	96.6	6000	3000	582
Ni	25.6	27.8	28.5	29.9	31.3	560	520	353
Cu	15.8*	31.1*	32.4*	46.5*	49.1*	11.0	100	1610
As	5.45*	6.09*	6.26*	6.72*	7.07*	5.00	10.0	58.5
Se	0.87	1.78	1.89	2.70	2.91	160	170	5.46
Mo	0.63	1.22	1.31	1.81	2.00	NA	NA	24.3
Ba	150	680	742	1210*+	1330*+	1200	1200	3380
Cr	21.3	28.4	29.6	35.4	37.8	87.0	71.0	73.0
V	25.6	45.8*	48.1*	66.1*	70.6*	30.0	210	2000
Hg	0.03	0.09	-	0.15	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

Sherco 3

The Sherburne County plant (Sherco) in Becker, Minnesota is Xcel Energy's largest power generator producing a total of 859 megawatt. Three boilers are in operation; however only boiler number 3 (Sherco 3, built in 1987) was sampled. The facility burns PRB coal and is equipped with a pulverized coal boiler, spray dry-scrubber (using slaked lime ($Ca(OH)_2$) and re-circulated ash) and baghouse. The lime scrubber is designed to capture sulfur (source of acid rain). High amounts of sulfur in ash can create expansion problems when fly ash hydrates. Therefore Sherco ash may not be suitable for soil stabilization. Table 2.16 gives summary statistics for COC in Sherco ash. Because of the high Ca and S, the COC values are lower than for the plants discussed previously. Some B, Cu, As, Ba and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Sherco ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.17). The calculated concentrations did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu and As. Vanadium exceeds the 2006 SRV for mixtures of 20%. None of the mixtures exceeded the SLV limits.

Table 2.16. COC Summary Statistical Data for Sherco Ash (Sampled 11/1/04 – 11/15/04; n=2)

Sherco (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	2.06	2.30	2.18	0.17	2.52	55.0	55.0	5.44
B	808$^{\#}$	854$^{\#}$	831$^{\#}$	32.3	895$^{\#}$	6000	3000	582
Co	5.87	6.76	6.31	0.63	7.57	600	2000	120
Ni	15.9	17.6	16.7	1.17	19.1	560	520	353
Cu	43.8*	46.2*	45.0*	1.70	48.4*	11.0	100	1610
Zn	33.9	36.0	34.9	1.48	37.9	8700	8700	6020
As	6.58*	10.8*$^{+}$	8.68*	2.96	14.6*$^{+}$	5.00	10.0	58.5
Se	4.28	4.72	4.50	0.31	5.11	160	170	5.46
Sr	3160	3520	3340	255	3850	18000	NA	77200
Mo	6.97	7.25	7.11	0.20	7.51	NA	NA	24.3
Ag	0.55	0.69	0.62	0.10	0.83	160	NA	15.9
Cd	0.53	0.58	0.56	0.03	0.62	25.0	35.0	17.6
Sn	1.88	1.88	1.88	0.00	1.89	9000	15000	11900
Sb	0.09	0.10	0.10	0.01	0.11	12.0	14.0	10.9
Ba	2530*$^{+}$	2590*$^{+}$	2560*$^{+}$	46.7	2650*$^{+}$	1200	1200	3380
Tl	0.27	0.32	0.29	0.04	0.37	3.00	3.00	NA
Pb	28.1	28.7	28.4	0.40	29.2	300	400	2100
Cr	28.9	29.8	29.4	0.62	30.6	87.0	71.0	73.0
Mn	430	465	447	25.4	498	3600	1400	NA
V	60.8*	61.1*	60.9*	0.24	61.4*	30.0	210	2000
Hg	-	-	0.03	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.17. Mixing Simulation for Mean Soil with Sherco Ash

Sherco (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	98.9	105	180	193	6000	3000	582
Ni	25.6	24.8	25.0	23.9	24.3	560	520	353
Cu	15.8*	18.7*	19.0*	21.6*	22.3*	11.0	100	1610
As	5.45*	5.77*	6.37*	6.10*	7.28*	5.0	10.0	58.5
Se	0.87	1.23	1.30	1.60	1.72	160	170	5.46
Mo	0.63	1.28	1.32	1.93	2.01	NA	NA	24.30
Ba	150	391	400	632	651	1200	1200	3380
Cr	21.3	22.1	22.3	22.9	23.2	87.0	71.0	73.0
V	25.6	29.1	29.1	32.6*	32.7*	30.0	210	2000
Hg	0.03	0.03	-	0.03	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^+$exceed the 1999 SRV
$^\#$exceed the SLV

King

Xcel Energy's Allen S. King is a 529 megawatt capacity plant built in 1968. It is located in Oak Park Heights, Minnesota. The facility burns PRB coal with 8% petroleum coke and is equipped with a cyclone boiler and electric static precipitator. Table 2.18 gives summary statistics for COC in King ash. Because of the addition of petroleum coke many of the COC values are greater than for the previously discussed Xcel plants and some B, Ni, Cu, As, Se, Mo, Ba, V and Hg concentrations exceed the SRV or SLV limits.

For a realistic evaluation of King ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.19). Vanadium concentrations exceeded the 1999 SRV values for 20% mixtures. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.18. COC Summary Statistical Data for King Ash (Sampled 11/19/04 – 3/18/05; n=8)

King (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	3.10	3.63	3.33	0.15	3.63	55.0	55.0	5.44
B	880[#]	1020[#]	967[#]	56.2	1080[#]	6000	3000	582
Co	20.5	24.6	23.3	1.50	26.3	600	2000	120
Ni	737*[+#]	958*[+#]	821*[+#]	72.9	967*[+#]	560	520	353
Cu	209*[+]	235*[+]	224*[+]	9.51	243*[+]	11.0	100	1610
Zn	140	198	172	22.3	216	8700	8700	6020
As	17.4*[+]	21.3*[+]	19.0*[+]	1.35	21.8*[+]	5.00	10.0	58.5
Se	12.8*[+#]	16.0*	14.0*[+#]	1.03	16.1*[+#]	160	170	5.46
Sr	3150	3730	3450	193	3840	18000	NA	77200
Mo	84.8*[+#]	111*[+#]	96.3*[+#]	9.05	114*[+#]	NA	NA	24.3
Ag	0.74	1.57	1.12	0.34	1.80	160	NA	15.9
Cd	1.71	2.05	1.85	0.12	2.09	25.0	35.0	17.6
Sn	0.35	1.33	0.70	0.36	1.42	9000	15000	11900
Sb	0.07	0.20	0.12	0.04	0.21	12.0	14.0	10.9
Ba	4950*[+#]	5020*[+#]	4990*[+#]	42.7	5080*[+#]	1200	1200	3380
Tl	0.73	1.02	0.81	0.10	1.00	3.00	3.00	NA
Pb	66.5	120	88.8	24.1	137	300	400	2100
Cr	50.4	60.5	55.5	3.67	62.9	87.0	71.0	73.0
Mn	228	302	262	31.3	325	3600	1400	NA
V	1340*[+#]	1750*[+#]	1490*[+#]	139	1770*[+#]	30.0	210	2000
Hg	-	-	0.68*[+#]	-	-	0.50	0.70	6.58

*exceed the 2006 SRV

[+] exceed the 1999 SRV

[#] exceed the SLV

Table 2.19. Mixing Simulation for Mean Soil with King Ash

King (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	113	124	207	230	6000	3000	582
Ni	25.6	105	120	185	214	560	520	353
Cu	15.8*	36.5*	38.4*	57.3*	61.1*	11.0	100	1610
As	5.45*	6.81*	7.08*	8.17*	8.71*	5.0	10.0	58.5
Se	0.87	2.19	2.39	3.50	3.91	160	170	5.46
Mo	0.63	10.2	12.0	19.8	23.4	NA	NA	24.3
Ba	150	634	643	1120	1140	1200	1200	3380
Cr	21.3	24.7	25.5	28.2	29.6	87.0	71.0	73.0
V	25.6	172*	200*	318*$^{+}$	374*$^{+}$	30.0	210	2000
Hg	0.03	0.09	-	0.16	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Riverside 8

Xcel Energy's Riverside 8 is a 231 megawatt plant, built in 1964. This plant shares the same site as Riverside 6&7 in Minneapolis, Minnesota. However, Riverside 8 is a completely separate boiler and has separate ash collection. Like the King plant, Riverside 8 burns PRB coal with 8% petroleum coke and is equipped with a cyclone boiler, and electrostatic precipitator. Table 2.20 gives summary statistics for COC in Riverside 8 ash. Because the fuel and pollution control are similar the COC concentrations are similar to those in the ash from the King plant. Some B, Ni, Cu, As, Se, Mo, Ba, V and Hg concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Riverside 8 ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.21). Vanadium concentrations exceeded the 1999 SRV values for 20% mixtures. Barium exceeds the SRV for 20% mixtures using upper 95% confidence interval data. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.20. COC Summary Statistical Data for Riverside 8 Ash (Sampled 10/28/04 – 11/22/04; n=10)

Riverside 8 (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	2.83	3.81	3.14	0.35	3.84	55.0	55.0	5.44
B	553$^{\#}$	717	649$^{\#}$	64.3	778$^{\#}$	6000	3000	582
Co	21.5	29.0	24.2	2.21	28.6	600	2000	120
Ni	680*$^{+\#}$	850*$^{+\#}$	756*$^{+\#}$	58.2	873*$^{+\#}$	560	520	353
Cu	210*$^{+}$	250*$^{+}$	234*$^{+}$	13.7	261*$^{+}$	11.0	100	1610
Zn	113	203	146	30.1	206	8700	8700	6020
As	15.3*$^{+}$	19.8*$^{+}$	17.9*$^{+}$	1.66	21.3*$^{+}$	5.00	10.0	58.5
Se	11.4$^{\#}$	15.5$^{\#}$	13.5$^{\#}$	1.35	16.2$^{\#}$	160	170	5.46
Sr	2310	2640	2470	108	2690	18000	NA	77200
Mo	79.7$^{\#}$	104$^{\#}$	93.1$^{\#}$	7.50	108$^{\#}$	NA	NA	24.3
Ag	0.77	2.67	1.28	0.57	2.41	160	NA	15.9
Cd	1.67	2.26	1.94	0.24	2.42	25.0	35.0	17.6
Sn	0.24	1.17	0.54	0.29	1.11	9000	15000	11900
Sb	0.05	0.16	0.10	0.04	0.17	12.0	14.0	10.9
Ba	4790*$^{+\#}$	5820*$^{+\#}$	5310*$^{+\#}$	731	6770*$^{+\#}$	1200	1200	3380
Tl	0.51	0.86	0.64	0.11	0.86	3.00	3.00	NA
Pb	45.4	66.0	54.6	6.80	68.2	300	400	2100
Cr	53.9	75.5$^{+\#}$	64.5	7.15	78.9$^{+\#}$	87.0	71.0	73.0
Mn	125	144	134	6.18	146	3600	1400	NA
V	1420*$^{+}$	1810*$^{+}$	1610*$^{+}$	125	1860*$^{+}$	30.0	210	2000
Hg	-	-	0.68*	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.21. Mixing Simulation for Mean Soil with Riverside 8 Ash

Riverside 8 (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	80.8	93.6	150	170	6000	3000	582
Ni	25.6	98.7	110	172	195	560	520	353
Cu	15.8*	37.6*	40.3*	59.4*	64.9*	11.0	100	1610
As	5.45*	6.70*	7.03*	7.95*	8.61*	5.0	10.0	58.5
Se	0.87	2.13	2.40	3.39	3.93	160	170	5.46
Mo	0.63	9.88	11.4	19.1	22.1	NA	NA	24.3
Ba	150	666	812	1180	1470*$^{+}$	1200	1200	3380
Cr	21.3	25.6	27.1	30.0	32.8	87.0	71.0	73.0
V	25.6	184*	209*	342*$^{+}$	392*$^{+}$	30.0	210	2000
Hg	0.03	0.09	-	0.16	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Otter Tail Power

Hoot Lake (unit 2 & 3)

Otter Tail Power's Hoot Lake has two boilers, unit 2 (1959) and unit 3 (1964) which generate 53.5 megawatt and 66 megawatt respectively. The plant is located in Fergus Falls, Minnesota. Each unit burns PRB coal and is equipped with a pulverized coal boiler, and electrostatic precipitator. Table 2.22 and 1.23 gives summary statistics for COC in Hoot Lake unit 2 and unit 3. Because the fuel and environmental controls are similar to Xcel Energy High Bridge and Black Dog plants, the Hoot Lake fly ash has similar concentrations of COC. However, some elements e.g. As and Mo are higher compared to High Bridge and Black Dog. Some B, Cu, As, Se, Ba, Cr and V concentrations exceed the SRV or SLV limits in Unit 2 and Unit 3. Some Mo at Unit 2 is at concentrations that exceed the SLV.

For a realistic evaluation of Hoot Lake ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.24 and Table 2.25). Arsenic concentrations exceeded the 1999 SRV values for 20% mixtures using 95% confidence interval data in both Unit 2 and Unit 3. Barium exceeds the SRV for 20% mixtures in both Units (at Unit 3, 20% mean ash mixture is lower than SRV limit). The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the

2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.22. COC Summary Statistical Data for Hoot Lake unit 2 Ash (Sampled 2/01/05 – 3/04/05; n=10)

Hoot Lake Unit 2 (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	2.34	5.00	3.32	0.81	4.94	55.0	55.0	5.44
B	281	596$^{\#}$	458	99.3	656$^{\#}$	6000	3000	582
Co	11.3	17.8	14.4	1.93	18.3	600	2000	120
Ni	26.8	37.3	31.2	3.12	37.4	560	520	353
Cu	113*$^{+}$	154*$^{+}$	133*$^{+}$	13.0	159*$^{+}$	11.0	100	1610
Zn	54.8	91.0	73.2	11.1	95.3	8700	8700	6020
As	18.6*$^{+}$	35.0*$^{+}$	25.4*$^{+}$	6.25	37.9*$^{+}$	5.00	10.0	58.5
Se	6.31$^{\#}$	13.2$^{\#}$	10.2$^{\#}$	1.96	14.1$^{\#}$	160	170	5.46
Sr	4370	7030	5760	847	7450	18000	NA	77200
Mo	4.49	25.9$^{\#}$	11.4	8.28	27.9$^{\#}$	NA	NA	24.3
Ag	1.31	2.38	1.76	0.40	2.56	160	NA	15.9
Cd	0.78	0.97	0.89	0.07	1.03	25.0	35.0	17.6
Sn	1.01	1.78	1.31	0.24	1.80	9000	15000	11900
Sb	0.05	0.22	0.13	0.06	0.25	12.0	14.0	10.9
Ba	3810*$^{+\#}$	8790*$^{+\#}$	6290*$^{+\#}$	1390	9070*$^{+\#}$	1200	1200	3380
Tl	0.62	1.20	0.84	0.18	1.20	3.00	3.00	NA
Pb	16.1	22.1	18.8	1.69	22.2	300	400	2100
Cr	47.6	58.3	54.7	3.44	61.6	87.0	71.0	73.0
Mn	214	296	263	23.0	309	3600	1400	NA
V	183*	276*$^{+}$	211*$^{+}$	27.7	266*$^{+}$	30.0	210	2000
Hg	-	-	0.05	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.23. COC Summary Statistical Data for Hoot Lake unit 3 Ash

Hoot Lake Unit 3 (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	2.52	4.73	3.29	0.75	4.79	55.0	55.0	5.44
B	326.1	551	459	66.5	592$^{\#}$	6000	3000	582
Co	12.2	18.1	14.4	1.97	18.3	600	2000	120
Ni	26.6	37.6	32.0	3.21	38.5	560	520	353
Cu	87.9*$^{+}$	170*$^{+}$	126*$^{+}$	21.3	169*$^{+}$	11.0	100	1610
Zn	50.5	92.0	64.7	12.4	89.5	8700	8700	6020
As	15.7*$^{+}$	31.1*$^{+}$	21.7*$^{+}$	5.01	31.7*$^{+}$	5.00	10.0	58.5
Se	7.20$^{\#}$	12.3$^{\#}$	9.18$^{\#}$	1.75	12.7$^{\#}$	160	170	5.46
Sr	3630	7030	5630	1230	8100	18000	NA	77200
Mo	2.18	17.5	8.33	4.56	17.5	NA	NA	24.3
Ag	1.30	2.62	1.83	0.51	2.86	160	NA	15.9
Cd	0.65	1.02	0.80	0.10	1.01	25.0	35.0	17.6
Sn	0.77	1.60	1.13	0.29	1.71	9000	15000	11900
Sb	0.05	0.20	0.12	0.06	0.23	12.0	14.0	10.9
Ba	3620*$^{+\#}$	7560*$^{+\#}$	4890*$^{+\#}$	1350	7590*$^{+\#}$	1200	1200	3380
Tl	0.51	1.17	0.71	0.22	1.14	3.00	3.00	NA
Pb	11.5	22.0	16.6	2.99	22.6	300	400	2100
Cr	43.7	58.5	52.9	5.52	63.9	87.0	71.0	73.0
Mn	194	273	239	23.9	287	3600	1400	NA
V	160*	215*$^{+}$	186*	14.9	216*$^{+}$	30.0	210	2000
Hg	-	-	0.21	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.24. Mixing Simulation for Mean Soil with Hoot Lake unit 2 Ash (Sampled 2/01/05 – 3/04/05; n=10)

Hoot Lake Unit 2 (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	61.6	81.5	106	145	6000	3000	582
Ni	25.6	26.2	26.8	26.7	28.0	560	520	353
Cu	15.8*	27.4*	30.0*	39.1*	44.3*	11.0	100	1610
As	5.45*	7.45*	8.70*	9.45*	12.0*$^{+}$	5.0	10.0	58.5
Se	0.87	1.80	2.19	2.73	3.51	160	170	5.46
Mo	0.63	1.70	3.36	2.78	6.09	NA	NA	24.3
Ba	150	764	1040	1380*$^{+}$	1930*$^{+}$	1200	1200	3380
Cr	21.3	24.7	25.3	28.0	29.4	87.0	71.0	73.0
V	25.6	44.1*	49.6*	62.6*	73.6*	30.0	210	2000
Hg	0.03	0.03	-	0.03	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.25. Mixing Simulation for Mean Soil with Hoot Lake unit 3 Ash

Hoot Lake Unit 3 (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	61.8	75.1	106	133	6000	3000	582
Ni	25.6	26.3	26.9	26.9	28.2	560	520	353
Cu	15.8*	26.8*	31.1*	37.9*	46.4*	11.0	100	1610
As	5.45*	7.07*	8.07*	8.69*	10.7*[+]	5.0	10.0	58.5
Se	0.87	1.70	2.05	2.53	3.23	160	170	5.46
Mo	0.63	1.40	2.31	2.17	4.00	NA	NA	24.3
Ba	150	623	894	1100	1640*[+]	1200	1200	3380
Cr	21.3	24.5	25.6	27.6	29.8	87.0	71.0	73.0
V	25.6	41.6*	44.6*	57.6*	63.6*	30.0	210	2000
Hg	0.03	0.04	-	0.06	-	0.50	0.70	6.58

*exceed the 2006 SRV
[+]exceed the 1999 SRV
[#]exceed the SLV

Big Stone

Otter Tail Power's Big Stone is a 414 megawatt plant, built in 1975. It is located in Big Stone City, South Dakota. The facility burns PRB coal mixed with tires and sewage sludge and is equipped with a cyclone coal boiler, with electrostatic precipitator and baghouse. Table 2.26 gives summary statistics for COC in Big Stone ash. Because of the inclusion of tires and sewage sludge in the fuel, some of the COC concentrations, e.g. B, Cu, Zn, Pb, Cr and Hg are higher than other plants. The Zn is especially high because it is used as a coating on the steel belts in tires. Some B, Cu, Zn, As, Se, Ba, Cr, V and Hg concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Big Stone ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.27). Barium exceeds the SRV for 20% mixtures. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.26. COC Summary Statistical Data for Big Stone Ash (Sampled 2/03/05 – 3/04/05; n=6)

Big Stone (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	2.96	4.06	3.52	0.47	4.46	55.0	55.0	5.44
B	897#	1250#	1080#	146	1370#	6000	3000	582
Co	54.6	72.4	63.4	7.31	78.0	600	2000	120
Ni	67.0	73.2	71.1	2.16	75.4	560	520	353
Cu	318*+	348*+	333*+	11.7	357*+	11.0	100	1610
Zn	8270#	8650#	8420#	143	8700*+#	8700	8700	6020
As	17.2*+	24.8*+	20.6*+	3.21	27.1*+	5.00	10.0	58.5
Se	14.0#	20.4#	17.2#	2.60	22.4#	160	170	5.46
Sr	3710	3960	3830	91.5	4020	18000	NA	77200
Mo	8.36	14.6	11.5	2.57	16.6	NA	NA	24.3
Ag	1.83	4.87	2.80	1.15	5.10	160	NA	15.9
Cd	2.32	2.51	2.45	0.07	2.60	25.0	35.0	17.6
Sn	0.36	0.55	0.44	0.08	0.59	9000	15000	11900
Sb	0.11	0.32	0.18	0.08	0.33	12.0	14.0	10.9
Ba	5470*+#	6380*+#	5870*+#	385	6640*+#	1200	1200	3380
Tl	0.86	1.24	1.00	0.14	1.27	3.00	3.00	NA
Pb	62.2	82.3	74.0	7.56	89.1	300	400	2100
Cr	85.9+#	91.8*+#	88.8*+#	2.44	93.7*+#	87.0	71.0	73.0
Mn	174	225	197	23.0	243	3600	1400	NA
V	257*+	281*+	271*+	10.3	291*+	30.0	210	2000
Hg	-	-	1.20*+	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

Table 2.27. Mixing Simulation for Mean Soil with Big Stone Ash

Big Stone (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	123	153	229	288	6000	3000	582
Ni	25.6	30.2	30.6	34.7	35.6	560	520	353
Cu	15.8*	47.5*	49.9*	79.3*	84.0*	11.0	100	1610
As	5.45*	6.97*	7.61*	8.49*	9.77*	5.0	10.0	58.5
Se	0.87	2.51	3.03	4.14	5.18	160	170	5.46
Mo	0.63	1.71	2.23	2.80	3.83	NA	NA	24.3
Ba	150	721	798	1290*+	1450*+	1200	1200	3380
Cr	21.3	28.1	28.6	34.8	35.8	87.0	71.0	73.0
V	25.6	50.1*	52.1*	74.6*	78.7*	30.0	210	2000
Hg	0.03	0.14	-	0.26	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

Dairyland Power

JPM

Dairyland Power’s John P. Madgett (JPM) plant generates 377 megawatt. The plant is located in Alma, Wisconsin and built in 1979. JPM burns PRB coal and is equipped with a pulverized coal boiler and electrostatic precipitator. Table 2.28 gives summary statistics for COC in JPM ash. This plant is similar to the Xcel Energy High Bridge and Black Dog plants and the COC values are similar, except B is higher. Some B, Cu, As, Se, Ba, Cr and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of JPM ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.27). Barium exceeds the SRV for 20% mixtures of the 95% confidence interval ash. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.28. COC Summary Statistical Data for JPM Ash (Sampled 2/16/05 – 3/22/05; n=14)

JPM (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	2.44	3.15	2.85	0.21	3.27	55.0	55.0	5.44
B	508	741[#]	621[#]	64.4	749[#]	6000	3000	582
Co	16.8	20.4	19.2	0.97	21.1	600	2000	120
Ni	39.9	50.1	43.4	3.50	50.4	560	520	353
Cu	152*[+]	196*[+]	174*[+]	14.3	203*[+]	11.0	100	1610
Zn	46.3	84.6	66.0	12.0	90.1	8700	8700	6020
As	8.98*	12.1*[+]	10.7*[+]	0.83	12.4*[+]	5.00	10.0	58.5
Se	8.01[#]	12.2[#]	10.2[#]	1.17	12.6[#]	160	170	5.46
Sr	2600	3650	3230	285	3790	18000	NA	77200
Mo	2.06	7.34	5.98	1.42	8.81	NA	NA	24.3
Ag	0.61	1.83	1.00	0.38	1.76	160	NA	15.9
Cd	0.89	1.16	1.02	0.06	1.15	25.0	35.0	17.6
Sn	0.18	0.70	0.39	0.18	0.74	9000	15000	11900
Sb	0.01	0.09	0.04	0.02	0.08	12.0	14.0	10.9
Ba	3990*[+#]	5280*[+#]	4940*[+#]	340	5620*[+#]	1200	1200	3380
Tl	0.10	0.26	0.16	0.05	0.25	3.00	3.00	NA
Pb	21.3	27.1	25.1	1.41	27.9	300	400	2100
Cr	70.5	89.2	81.8[+#]	4.89	91.6*[+#]	87.0	71.0	73.0
Mn	179	299	232	34.4	301	3600	1400	NA
V	197*	235*[+]	217*[+]	11.2	239*[+]	30.0	210	2000
Hg	-	-	0.04	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
[+] exceed the 1999 SRV
[#] exceed the SLV

Table 2.29. Mixing Simulation for Mean Soil with JPM Ash

JPM (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	77.9	90.8	138	164	6000	3000	582
Ni	25.6	27.4	28.1	29.2	30.6	560	520	353
Cu	15.8*	31.6*	34.4*	47.4*	53.1*	11.0	100	1610
As	5.45*	5.97*	6.14*	6.50*	6.83*	5.0	10.0	58.5
Se	0.87	1.80	2.04	2.74	3.21	160	170	5.46
Mo	0.63	1.17	1.45	1.70	2.27	NA	NA	24.3
Ba	150	629	697	1110	1240*+	1200	1200	3380
Cr	21.3	27.4	28.4	33.4	35.4	87.0	71.0	73.0
V	25.6	44.7*	46.9*	63.8*	68.3*	30.0	210	2000
Hg	0.03	0.03	-	0.03	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

Alma

Dairyland Power's Alma plant generates 210 megawatt. The plant is located in Alma, Wisconsin and built in 1947. Alma burns PRB coal and is equipped with a pulverized coal boiler and electrostatic precipitator. Table 2.30 gives summary statistics for COC in Alma ash. Because the coal source and pollution control devices are similar to that of the JPM plant we expected very similar COC concentrations. However, Cu, Sr, and Ba are much lower and Hg is higher. Some B, Cu, As, Se, Ba and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Alma ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.31). The calculated concentrations did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and Ba. None of the mixtures exceeded the SLV limits.

Table 2.30. COC Summary Statistical Data for Alma Ash (Sampled 2/16/05 – 3/21/05; n=11)

Alma (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	1.67	3.39	2.31	0.49	3.30	55.0	55.0	5.44
B	481	605$^{\#}$	530	41.5	613$^{\#}$	6000	3000	582
Co	2.14	5.78	3.38	1.09	5.56	600	2000	120
Ni	7.26	23.9	13.3	5.67	24.6	560	520	353
Cu	18.7*	41.8*	25.0*	6.76	38.5*	11.0	100	1610
Zn	33.7	92.5	65.1	21.7	108	8700	8700	6020
As	8.84*	10.9*$^{+}$	9.91*	0.58	11.1*$^{+}$	5.00	10.0	58.5
Se	4.91	7.08$^{\#}$	6.00$^{\#}$	0.71	7.43$^{\#}$	160	170	5.46
Sr	701	1050	878	116	1110	18000	NA	77200
Mo	3.69	5.60	4.42	0.54	5.51	NA	NA	24.3
Ag	0.48	2.81	1.23	0.78	2.78	160	NA	15.9
Cd	0.72	3.49	2.22	1.06	4.34	25.0	35.0	17.6
Sn	0.51	1.45	0.89	0.33	1.55	9000	15000	11900
Sb	0.06	0.31	0.16	0.07	0.32	12.0	14.0	10.9
Ba	917	1390*$^{+}$	1050	133	1320*$^{+}$	1200	1200	3380
Tl	0.35	0.76	0.53	0.14	0.81	3.00	3.00	NA
Pb	11.5	25.6	19.1	5.08	29.3	300	400	2100
Cr	17.3	52.7	28.8	11.4	51.5	87.0	71.0	73.0
Mn	57.6	88.3	68.5	8.58	85.6	3600	1400	NA
V	39.1*	79.2*	52.1*	11.9	75.9*	30.0	210	2000
Hg	-	-	0.22	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.31. Mixing Simulation for Mean Soil with Alma Ash

Alma (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	68.8	77.1	120	137	6000	3000	582
Ni	25.6	24.4	25.5	23.2	25.4	560	520	353
Cu	15.8*	16.7*	18.0*	17.6*	20.3*	11.0	100	1610
As	5.45*	5.90*	6.01*	6.34*	6.57*	5.0	10.0	58.5
Se	0.87	1.38	1.53	1.90	2.18	160	170	5.46
Mo	0.63	1.01	1.12	1.39	1.61	NA	NA	24.3
Ba	150	240	266	330	383	1200	1200	3380
Cr	21.3	22.1	24.3	22.8	27.4	87.0	71.0	73.0
V	25.6	28.2	30.6*	30.9*	35.6*	30.0	210	2000
Hg	0.03	0.05	-	0.07	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Genoa

Dairyland Power's Genoa (G-3) plant generates 370 megawatt. The plant is located in Genoa, Wisconsin and built in 1964. Genoa burns PRB coal and is equipped with a pulverized coal boiler and electrostatic precipitator. Table 2.32 gives summary statistics for COC in Genoa ash. This ash is quite similar to the Alma ash but As is higher. Some Be, B, Cu, As, Se, Ba and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Genoa ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.27). The calculated concentrations did not exceed the 1999 SRV limits for any of the mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.32. COC Summary Statistical Data for Genoa Ash (Sampled 2/16/05 – 3/14/05; n=11)

Genoa (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	3.55	5.45[#]	4.34	0.68	5.70[#]	55.0	55.0	5.44
B	784[#]	1190[#]	958[#]	146	1250[#]	6000	3000	582
Co	10.7	13.8	12.5	1.01	14.6	600	2000	120
Ni	27.1	39.9	32.7	3.45	39.7	560	520	353
Cu	70.8*	87.2*	78.9*	4.82	88.5*	11.0	100	1610
Zn	116	252	178	39.2	257	8700	8700	6020
As	16.4*[+]	24.2*[+]	20.4*[+]	2.73	25.9*[+]	5.00	10.0	58.5
Se	4.26	5.50[#]	4.89	0.38	5.66[#]	160	170	5.46
Sr	1310	1440	1360	46.0	1450	18000	NA	77200
Mo	6.76	8.55	7.46	0.56	8.58	NA	NA	24.3
Ag	0.86	8.43	2.59	2.18	6.95	160	NA	15.9
Cd	1.85	5.10	3.42	1.12	5.66	25.0	35.0	17.6
Sn	0.66	1.52	0.98	0.35	1.68	9000	15000	11900
Sb	0.08	0.24	0.15	0.07	0.29	12.0	14.0	10.9
Ba	2410*[+]	2780*[+]	2580*[+]	112	2810*[+]	1200	1200	3380
Tl	1.00	1.60	1.25	0.17	1.59	3.00	3.00	NA
Pb	36.2	80.5	60.6	15.0	90.7	300	400	2100
Cr	54.1	66	58.6	3.73	66.1	87.0	71.0	73.0
Mn	100	114	108	4.71	117	3600	1400	NA
V	138*	157*	145*	5.30	156*	30.0	210	2000
Hg	-	-	0.22	-	-	0.50	0.70	6.58

*exceed the 2006 SRV

[+] exceed the 1999 SRV

[#] exceed the SLV

Table 2.33. Mixing Simulation for Mean Soil with Genoa Ash

Genoa (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	112	141	206	264	6000	3000	582
Ni	25.6	26.4	27.0	27.1	28.4	560	520	353
Cu	15.8*	22.1*	23.0*	28.4*	30.3*	11.0	100	1610
As	5.45*	6.95*	7.50*	8.45*	9.54*	5.0	10.0	58.5
Se	0.87	1.27	1.35	1.68	1.83	160	170	5.46
Mo	0.63	1.31	1.43	2.00	2.22	NA	NA	24.3
Ba	150	393	416	637	682	1200	1200	3380
Cr	21.3	25.1	25.8	28.8	30.3	87.0	71.0	73.0
V	25.6	37.5*	38.6*	49.5*	51.6*	30.0	210	2000
Hg	0.03	0.05	-	0.07	-	0.50	0.70	6.58

*exceed the 2006 SRV

$^{+}$exceed the 1999 SRV

$^{\#}$exceed the SLV

Minnesota Power

M.L. Hibbard Energy Center

Minnesota Power’s M.L. Hibbard generates 70 megawatt and is located in Duluth, Minnesota. M.L. Hibbard burns 2% to 25% PRB coal (mean of 15% in 2004) with the remainder of the fuel coming from wood. M.L. Hibbard is equipped with a traveling grate (stoker fired) boiler, and electrostatic precipitator. Table 2.34 gives summary statistics for COC in its ash. M.L. Hibbard COC concentrations are more variable compared to the other plants e.g. As and Cr. Because M.L. Hibbard burns wood it was expected that COCs would be lower in concentration. Many COC are lower e.g. Be, B and V, however As is much higher. Some Cu, As, Se, Ba, Cr, Mn, and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of M.L. Hibbard ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.35). Arsenic exceeds the SRV except for 10% mixture of mean ash. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.34. COC Summary Statistical Data for M.L. Hibbard Ash (Sampled 11/01/04 – 12/27/04; n=7)

M.L. Hibbard (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	1.16	2.14	1.59	0.42	2.43	55.0	55.0	5.44
B	22	385	312	64.3	441	6000	3000	582
Co	7.96	11.9	10.0	1.56	13.1	600	2000	120
Ni	19.5	46.9	32.4	10.4	53.2	560	520	353
Cu	52.1*	149*[+]	109*[+]	37.4	183*[+]	11.0	100	1610
Zn	141	793	530	241	1010	8700	8700	6020
As	4.36	73.5*[+]	31.0*[+]	24.1	79.2*[+#]	5.00	10.0	58.5
Se	0.91	6.74[#]	3.96	1.81	7.58[#]	160	170	5.46
Sr	1370	2330	1960	338	2630	18000	NA	77200
Mo	5.49	19.0	10.4	4.76	20.0	NA	NA	24.3
Ag	0.57	2.68	1.69	0.70	3.10	160	NA	15.9
Cd	0.66	3.73	2.63	1.02	4.68	25.0	35.0	17.6
Sn	1.33	3.02	2.28	0.67	3.61	9000	15000	11900
Sb	0.10	0.24	0.17	0.06	0.28	12.0	14.0	10.9
Ba	988	3420*[+#]	2000*[+]	750	3490*[+#]	1200	1200	3380
Tl	0.39	0.90	0.57	0.18	0.93	3.00	3.00	NA
Pb	14.5	63.3	40.3	16.0	72.2	300	400	2100
Cr	23.8	75.7[+#]	50.4	20.6	91.6*[+#]	87.0	71.0	73.0
Mn	607	1760[+]	1010	394	1800[+]	3600	1400	NA
V	49.4*	107*	83.0*	19.4	122*	30.0	210	2000
Hg	-	-	0.10	-	-	0.50	0.70	6.58

*exceed the 2006 SRV

[+] exceed the 1999 SRV

[#] exceed the SLV

Table 2.35. Mixing Simulation for Mean Soil with M.L. Hibbard Ash

M.L. Hibbard (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	47.1	60.0	76.6	102	6000	3000	582
Ni	25.6	26.3	28.4	27.0	31.1	560	520	353
Cu	15.8*	25.1*	32.5*	34.4*	49.3*	11.0	100	1610
As	5.45*	8.01*	12.8*[+]	10.6*[+]	20.2*[+]	5.0	10.0	58.5
Se	0.87	1.18	1.54	1.49	2.21	160	170	5.46
Mo	0.63	1.61	2.56	2.59	4.49	NA	NA	24.3
Ba	150	334	484	519	819	1200	1200	3380
Cr	21.3	24.2	28.4	27.1	35.4	87.0	71.0	73.0
V	25.6	31.3*	35.2*	37.0*	44.8*	30.0	210	2000
Hg	0.03	0.03	-	0.04	-	0.50	0.70	6.58

*exceed the 2006 SRV
[+] exceed the 1999 SRV
[#] exceed the SLV

Boswell Energy Center

Minnesota Power's Boswell Energy Center (BEC) generates 914 megawatt. The plant is located in Cohasset, Minnesota. BEC burns PRB coal and is equipped with a pulverized coal boiler, wet scrubber and baghouse. Table 2.36 gives summary statistics for COC in BEC ash. Only two sample were analyzed for BEC so the confidence interval could not be calculated. Some Cu, As, Se, Ba, Cr, Mn, and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of BEC ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.37). Barium exceeds the SRV for the 20% mixture. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures. When the 2006 SRV limits are used, both of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.36. COC Summary Statistical Data for BEC Ash (Sampled 1/12/05 – 1/15/05; n=2)

BEC (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	3.21	3.54	3.37	-	-	55.0	55.0	5.44
B	795[#]	872[#]	834[#]	-	-	6000	3000	582
Co	12.1	13.4	12.7	-	-	600	2000	120
Ni	33.5	35.8	34.6	-	-	560	520	353
Cu	107*[+]	141*[+]	124*[+]	-	-	11.0	100	1610
Zn	56.0	69.8	62.9	-	-	8700	8700	6020
As	24.2*[+]	28.9*[+]	26.6*[+]	-	-	5.00	10.0	58.5
Se	11.9[#]	12.9[#]	12.4[#]	-	-	160	170	5.46
Sr	5130	5460	5300	-	-	18000	NA	77200
Mo	14.9	25.1[#]	20.0	-	-	NA	NA	24.3
Ag	0.97	1.06	1.01	-	-	160	NA	15.9
Cd	1.03	1.04	1.04	-	-	25.0	35.0	17.6
Sn	0.99	1.70	1.34	-	-	9000	15000	11900
Sb	0.06	0.09	0.08	-	-	12.0	14.0	10.9
Ba	5620	5800	5710	-	-	1200	1200	3380
Tl	0.86	0.90	0.88	-	-	3.00	3.00	NA
Pb	27.0	27.8	27.4	-	-	300	400	2100
Cr	51.1	52.9	52.0	-	-	87.0	71.0	73.0
Mn	497	516	506	-	-	3600	1400	NA
V	165*	168*	167*	-	-	30.0	210	2000
Hg	-	-	0.73*[+]	-	-	0.50	0.70	6.58

*exceed the 2006 SRV

[+] exceed the 1999 SRV

[#] exceed the SLV

Table 2.37. Mixing Simulation for Mean Soil with BEC Ash

BEC (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	99.2	-	181	-	6000	3000	582
Ni	25.6	26.5	-	27.4	-	560	520	353
Cu	15.8*	26.6*	-	37.4*	-	11.0	100	1610
As	5.45*	7.56*	-	9.67*	-	5.0	10.0	58.5
Se	0.87	2.02	-	3.17	-	160	170	5.46
Mo	0.63	2.57	-	4.51	-	NA	NA	24.3
Ba	150	706	-	1260*+	-	1200	1200	3380
Cr	21.3	24.4	-	27.5	-	87.0	71.0	73.0
V	25.6	39.7*	-	53.8*	-	30.0	210	2000
Hg	0.03	0.10	-	0.17	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

Rapid Energy Center

Minnesota Power’s Rapid Energy Center (REC) generates 30 megawatt. The plant is located in Grand Rapids, Minnesota. REC burns 20% to 40% PRB coal with the remainder of the fuel coming from wood. HEC is equipped with a traveling grate (stoker fired) boiler and electrostatic precipitator. Table 2.38 gives summary statistics for COC in REC ash. Because the plant has wood in the fuel mix, many COC concentrations are lower for the coal only plants, e.g. As, Ba and V. Some Cu, As, Ba, Mn, and V concentrations exceed the SRV or SLV limits.

For a realistic evaluation of REC ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.27). The calculated concentrations did not exceed the 1999 SRV limits for either of the two mixtures even when the upper limit of the 95% confidence interval was used for the COC concentrations. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu and As. Vanadium exceeds the 2006 SRV for 20% mixtures of 95% confidence interval ash only. None of the mixtures exceeded the SLV limits.

Table 2.38. COC Summary Statistical Data for REC Ash (Sampled 10/18/04 – 11/01/04; n=6)

REC (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	0.70	1.71	1.06	0.37	1.79	55.0	55.0	5.44
B	272	419	338	53.6	445	6000	3000	582
Co	5.26	5.86	5.56	0.28	6.13	600	2000	120
Ni	8.56	10.8	9.31	0.83	11.0	560	520	353
Cu	111*$^{+}$	183*$^{+}$	142*$^{+}$	27.00	196*$^{+}$	11.0	100	1610
Zn	286	1600	874	517	1910	8700	8700	6020
As	3.55	5.89*	4.50	1.04	6.59*	5.00	10.0	58.5
Se	1.88	3.44	2.67	0.64	3.94	160	170	5.46
Sr	884	2050	1180	478	2140	18000	NA	77200
Mo	4.67	5.39	5.06	0.30	5.67	NA	NA	24.3
Ag	0.20	1.28	0.54	0.42	1.38	160	NA	15.9
Cd	2.01	10.13	5.97	3.40	12.8	25.0	35.0	17.6
Sn	0.60	1.47	0.90	0.31	1.52	9000	15000	11900
Sb	0.09	0.27	0.17	0.07	0.30	12.0	14.0	10.9
Ba	1020	1710*$^{+}$	1290*$^{+}$	268	1830*$^{+}$	1200	1200	3380
Tl	0.21	0.73	0.43	0.21	0.85	3.00	3.00	NA
Pb	8.56	28.1	18.0	7.57	33.1	300	400	2100
Cr	12.1	19.5	14.7	2.62	20.0	87.0	71.0	73.0
Mn	1140	1590^{+}	1390	193	1780^{+}	3600	1400	NA
V	23.0	48.2*	31.9*	9.99	51.8*	30.0	210	2000
Hg	-	-	0.06	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.39. Mixing Simulation for Mean Soil with REC Ash

REC (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	49.6	60.4	81.6	103	6000	3000	582
Ni	25.6	24.0	24.2	22.4	22.7	560	520	353
Cu	15.8*	28.4*	33.8*	41.0*	51.8*	11.0	100	1610
As	5.45*	5.36*	5.56*	5.26*	5.68*	5.0	10.0	58.5
Se	0.87	1.05	1.18	1.23	1.48	160	170	5.46
Mo	0.63	1.07	1.13	1.52	1.64	NA	NA	24.3
Ba	150	264	318	378	485	1200	1200	3380
Cr	21.3	20.7	21.2	20.0	21.1	87.0	71.0	73.0
V	25.6	26.2	28.2	26.8	30.8*	30.0	210	2000
Hg	0.03	0.03	-	0.03	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

American Crystal Sugar

American Crystal Sugar- Moorhead

American Crystal Sugar's Moorhead plant generates steam used to process sugar beets into refined sugar. The plant is located in Moorhead, Minnesota and was built sometime in the 1940's. ACS Moorhead burns PRB coal and is equipped with a traveling grate (stoker fired) boiler and electrostatic precipitator. Table 2.39 gives summary statistics for COC in Moorhead ash. Only two samples were analyzed for the Moorhead plant so confidence intervals could not be calculated. Although the coal is from the PRB as the other plants in this report, it has very high As, Ba and S. These elements suggest the coal was deposited in an environment more like a coastal swamp than a fresh water swamp. Some Cu, As, Se, Mo, Ba, V and Hg concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Moorhead ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.40). Arsenic exceeds the 1999 SRV for both mixtures. Barium exceeds the 1999 and 2006 SRV for 20% mixtures. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.40. COC Summary Statistical Data for ACS Moorhead Ash (Sampled 1/10/05; n=2)

ACS Moorhead (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	1.47	1.93	1.70	-	-	55.0	55.0	5.44
B	340	430	385	-	-	6000	3000	582
Co	10.5	13.0	11.8	-	-	600	2000	120
Ni	29.3	32.3	30.8	-	-	560	520	353
Cu	243*[+]	255*[+]	249*[+]	-	-	11.0	100	1610
Zn	196	220	208	-	-	8700	8700	6020
As	87.7*[+#]	99.1*[+#]	93.4*[+#]	-	-	5.00	10.0	58.5
Se	9.22[#]	11.4[#]	10.3[#]	-	-	160	170	5.46
Sr	1830	2530	2180	-	-	18000	NA	77200
Mo	15.0	24.9[#]	20.0	-	-	NA	NA	24.3
Ag	1.43	1.52	1.48	-	-	160	NA	15.9
Cd	3.58	3.60	3.59	-	-	25.0	35.0	17.6
Sn	1.61	5.59	3.60	-	-	9000	15000	11900
Sb	0.30	1.07	0.68	-	-	12.0	14.0	10.9
Ba	9020*[+#]	10200*[+#]	9590*[+#]	-	-	1200	1200	3380
Tl	2.88	3.06*	2.97	-	-	3.00	3.00	NA
Pb	44.8	54.3	49.6	-	-	300	400	2100
Cr	32.3	38.0	35.2	-	-	87.0	71.0	73.0
Mn	165	206	186	-	-	3600	1400	NA
V	126*	150*	138*	-	-	30.0	210	2000
Hg	-	-	0.79*[+]	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
[+] exceed the 1999 SRV
[#] exceed the SLV

Table 2.41. Mixing Simulation for Mean Soil with ACS Moorhead Ash

ACS Moorhead (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	54.3	-	91.0	-	6000	3000	582
Ni	25.6	26.2	-	26.7	-	560	520	353
Cu	15.8*	39.1*	-	62.4*	-	11.0	100	1610
As	5.45*	14.2*+	-	23.0*+	-	5.0	10.0	58.5
Se	0.87	1.81	-	2.75	-	160	170	5.46
Mo	0.63	2.56	-	4.49	-	NA	NA	24.3
Ba	150	1090	-	2040*+	-	1200	1200	3380
Cr	21.3	22.7	-	24.1	-	87.0	71.0	73.0
V	25.6	36.8*	-	48.0*	-	30.0	210	2000
Hg	0.03	0.10	-	0.18	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

American Crystal Sugar- East Grand Forks

American Crystal Sugar’s East Grand Forks (EGF) plant generates steam used to process sugar beets into refined sugar. The plant is located in East Grand Forks, Minnesota and was built sometime in the 1920’s. ACS EGF burns PRB coal and is equipped with a traveling grate (stoker fired) boiler and electrostatic precipitator. Table 2.42 gives summary statistics for COC in EGF ash. Only two samples were analyzed for EGF so confidence intervals could not be calculated. The ash is very similar to the American Crystal Sugar Moorhead ash. Some Cu, As, Se, Ba, V and Hg concentrations exceed the SRV or SLV limits.

For a realistic evaluation of EGF ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.43). Arsenic and Ba exceed the 1999 SRV for both mixtures. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, Ba and V. None of the mixtures exceeded the SLV limits.

Table 2.42. COC Summary Statistical Data for ACS East Grand Forks Ash (Sampled 1/11/05; n=2)

ACS East Grand Forks (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	1.87	2.40	2.14	-	-	55.0	55.0	5.44
B	398	423	410	-	-	6000	3000	582
Co	11.2	12.0	11.6	-	-	600	2000	120
Ni	29.1	31.3	30.2	-	-	560	520	353
Cu	190*$^{+}$	199*$^{+}$	195*$^{+}$	-	-	11.0	100	1610
Zn	119	132	126	-	-	8700	8700	6020
As	68.4*$^{+\#}$	75.9*$^{+\#}$	72.1*$^{+\#}$	-	-	5.00	10.0	58.5
Se	12.5$^{\#}$	13.3$^{\#}$	12.9$^{\#}$	-	-	160	170	5.46
Sr	3000	3750	3370	-	-	18000	NA	77200
Mo	20.2	21.3	20.7	-	-	NA	NA	24.3
Ag	1.34	2.18	1.76	-	-	160	NA	15.9
Cd	2.24	3.03	2.63	-	-	25.0	35.0	17.6
Sn	3.45	3.79	3.62	-	-	9000	15000	11900
Sb	0.61	0.80	0.70	-	-	12.0	14.0	10.9
Ba	12100*$^{+\#}$	12300*$^{+\#}$	12200*$^{+\#}$	-	-	1200	1200	3380
Tl	2.44	2.90	2.67	-	-	3.00	3.00	NA
Pb	30.4	45.7	38.0	-	-	300	400	2100
Cr	31.3	34.1	32.7	-	-	87.0	71.0	73.0
Mn	189	206	197	-	-	3600	1400	NA
V	162*	172*	167*	-	-	30.0	210	2000
Hg	-	-	0.76*$^{+}$	-	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Table 2.43. Mixing Simulation for Mean Soil with ACS East Grand Forks Ash

ACS East Grand Forks (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	56.9	-	96.2	-	6000	3000	582
Ni	25.6	26.1	-	26.6	-	560	520	353
Cu	15.8*	33.6*	-	51.5*	-	11.0	100	1610
As	5.45*	12.1*+	-	18.8*+	-	5.0	10.0	58.5
Se	0.87	2.08	-	3.28	-	160	170	5.46
Mo	0.63	2.64	-	4.65	-	NA	NA	24.3
Ba	150	1350*+	-	2550*+	-	1200	1200	3380
Cr	21.3	22.5	-	23.6	-	87.0	71.0	73.0
V	25.6	39.7*	-	53.8*	-	30.0	210	2000
Hg	0.03	0.10	-	0.17	-	0.50	0.70	6.58

*exceed the 2006 SRV
+exceed the 1999 SRV
#exceed the SLV

American Crystal Sugar- Crookston

American Crystal Sugar’s Crookston plant generates steam used to process sugar beets into refined sugar. The plant is located in Crookston, Minnesota and was built sometime in the 1940’s. ACS Crookston burns PRB coal and is equipped with a traveling grate (stoker fired) boiler and electrostatic precipitator. Table 2.44 gives summary statistics for COC in Crookston ash. Only two samples were analyzed for Crookston so confidence intervals could not be calculated. Ash from the American Crystal Sugar Moorhead and East Grand Forks plants are very similar to the Crookston ash. Some Cu, As, Se, Ba, Tl, V and Hg concentrations exceed the SRV or SLV limits.

For a realistic evaluation of Crookston ash, mixing simulations with a soil were done and compared to the SRV and SLV using 10% and 20% mixtures (Table 2.45). Arsenic exceeds the 1999 SRV for both mixtures. Barium exceeds the SRV for the 20% mixture. The calculated concentrations for all other COC did not exceed the 1999 SRV limits for either of the two mixtures. When the 2006 SRV limits are used, all of the calculated mixtures exceeded the SRV limits for Cu, As, and V. None of the mixtures exceeded the SLV limits.

Table 2.44. COC Summary Statistical Data for ACS Crookston Ash (Sampled 1/11/05; n=2)

ACS Crookston (ppm)

COC	Min	Max	Mean	Std Dev	Upper 95% C.I.	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
Be	1.93	1.99	1.96	-	-	55.0	55.0	5.44
B	440	441	441	-	-	6000	3000	582
Co	11.5	12.1	11.8	-	-	600	2000	120
Ni	28.9	30.6	29.8	-	-	560	520	353
Cu	216*[+]	252*[+]	234*[+]	-	-	11.0	100	1610
Zn	162	198	180	-	-	8700	8700	6020
As	76.5*[+#]	83.6*[+#]	80.1*[+#]	-	-	5.00	10.0	58.5
Se	12.6[#]	13.6[#]	13.1[#]	-	-	160	170	5.46
Sr	2510	2570	2540	-	-	18000	NA	77200
Mo	15.8	16.8	16.30	-	-	NA	NA	24.3
Ag	2.08	2.27	2.18	-	-	160	NA	15.9
Cd	3.09	3.46	3.28	-	-	25.0	35.0	17.6
Sn	2.25	2.94	2.60	-	-	9000	15000	11900
Sb	0.38	0.50	0.44	-	-	12.0	14.0	10.9
Ba	8740*[+#]	11000*[+#]	9890*[+#]	-	-	1200	1200	3380
Tl	3.02*[+]	3.66*[+]	3.34*[+]	-	-	3.00	3.00	NA
Pb	48.1	52.8	50.5	-	-	300	400	2100
Cr	31.3	33.6	32.5	-	-	87.0	71.0	73.0
Mn	182	185	183	-	-	3600	1400	NA
V	147*	149*	148*	-	-	30.0	210	2000
Hg	-	-	0.77*[+]	-	-	0.50	0.70	6.58

*exceed the 2006 SRV

[+] exceed the 1999 SRV

[#] exceed the SLV

Table 2.45. Mixing Simulation for Mean Soil with ACS Crookston Ash

ACS Crookston (ppm)

COC	Mean Soil:	w/ 10% Ash (mean)	w/ 10% Ash (95% CI)	w/ 20% Ash (mean)	w/ 20% Ash (95% CI)	2006 SRV (tier 1)	1999 SRV (tier 1)	SLV (typical soil/site)
B	17.6	59.9	-	102	-	6000	3000	582
Ni	25.6	26.1	-	26.5	-	560	520	353
Cu	15.8*	37.6*	-	59.4*	-	11.0	100	1610
As	5.45*	12.9*$^{+}$	-	20.4*$^{+}$	-	5.0	10.0	58.5
Se	0.87	2.09	-	3.31	-	160	170	5.46
Mo	0.63	2.20	-	3.77	-	NA	NA	24.3
Ba	150	1120	-	2100*$^{+}$	-	1200	1200	3380
Cr	21.3	22.4	-	23.6	-	87.0	71.0	73.0
V	25.6	37.8*	-	50.0*	-	30.0	210	2000
Hg	0.03	0.10	-	0.17	-	0.50	0.70	6.58

*exceed the 2006 SRV
$^{+}$exceed the 1999 SRV
$^{\#}$exceed the SLV

Factors Effecting COC in Fly Ashes

A significant factor to COC concentrations is the addition of fuels other than coal. Some plants add petroleum coke, sewage sludge, tires, or wood. Other attributes that affect COC are the type of pollution control devices and the type and operation of boilers.

Coal Source/Fuel Additives

Coal is a sedimentary rock formed from plant matter deposited in anaerobic water and subjected to high temperature and pressure over millions of years. The conditions of plant deposition and formation processes provide the variance seen in coal COC. Coal is grouped into four types or ranks based on amount of carbon: anthracite, bituminous, sub-bituminous, and lignite. All fly ash sources studied currently use sub-bituminous coal from the Powder River Basin (PRB) located in Montana and Wyoming. The greatest advantage of using PRB coal is its low sulfur content (discussed earlier) which allows coal burning plants to meet air quality regulations without extra pollution control measures.

In the past Dairyland Power used a Southern Illinois bituminous coal before switching to PRB coal (Personal Communication, David Lesky, Dairyland Power, 2004). Once the switch to PRB coal was made, these plants reduced antimony and arsenic concentrations to less than 50% of previous ash values. Table 2.46 compares mean COC concentration of ash from Dairyland Power's Genoa, Alma and JPM plants when using Southern Illinois coal compared to ash from

PRB coal. Manganese and selenium were also found to be significantly higher (methods discussed below) in PRB coal ash (except for the Alma plant). Many of the COC were significantly higher in Southern IL coal at one or more of the plants such as Co, Mo, Mn, Pb, Cu, B, As, Ba, and Cd. Illinois coal is bituminous, which is known to contain higher amounts of pyrite (FeS_2) compared to PRB sub-bituminous coals (previously discussed). Pyrite commonly has substitutions within its structure, one prominent substitution is arsenic. This accounts for the elevated arsenic content in IL ash compared to the PRB ash.

To determine significance, a two-sample t significance test was used (Moore and McCabe, 2003). Equation 2.1 was used to calculate t value and Equation 2 was used to calculate the degree of freedom. Probability was estimated using a table that compared the t value and degrees of freedom. Any probability greater than 95% was considered significant.

Equation 2.1. T Calculation $t = \dfrac{\bar{x}_1 - \bar{x}_2}{\sqrt{\dfrac{s_1^2}{n_1} + \dfrac{s_2^2}{n_2}}}$

Equation 2.2. Degrees of Freedom Calculations $df = \dfrac{\left(\dfrac{s_1^2}{n_1} + \dfrac{s_2^2}{n_2}\right)^2}{\dfrac{1}{n_1 - 1}\left(\dfrac{s_1^2}{n_1}\right)^2 + \dfrac{1}{n_2 - 1}\left(\dfrac{s_2^2}{n_2}\right)^2}$

Table 2.46. Dairyland COC with Southern Illinois Coal and Powder River Basin Coal, Data are Mean Values

	Genoa		Alma		JPM	
	S IL Coal[1]	PRB Coal	S IL Coal[1]	PRB Coal	S IL Coal[1]	PRB Coal
COC (ppm)	n=5	n=11	n=5	n=11	n=5	n=14
Sb	4.45	0.15	4.95	0.16	5.04	0.04
As	111	20.4	36.0*	9.91*	55.0*	10.7*
Ba	1260*	2580*	1230	1050	1750*	4940*
Be	5.82	4.34	5.48	2.31	2.44	2.85
B	1200	958	886*	530*	573	621
Cd	2.52	3.42	2.18	2.22	2.84*	1.02*
Cr	64.3	58.6	30.8	28.8	55.6*	81.8*
Co	22.0*	12.5*	14.5*	3.38*	20.4	19.2
Cu	82.5	78.9	42.8*	25.0*	141	174
Pb	95.8	60.6	49.0*	19.1*	38.6	25.1
Mn	81.5	108	78.0*	68.5*	99.3*	232*
Hg	0.32	0.22	0.52	0.22	0.04	0.04
Mo	11.1	7.46	10.1*	4.42*	6.50	5.98
Ni	50.2	32.7	33.8	13.3	28.6*	43.4*
Se	3.50	4.89	4.08	6.00	3.98*	10.2*
Ag	1.42	2.59	1.50	1.23	1.50	1.00
Tl	1.76	1.25	3.83	0.53	0.29	0.16
Zn	138	178	79.2	65.1	65.2	66.0

*Significantly different at 0.05 level.

[1] Source: (Personal Communication, David Lesky, Dairyland Power, 2004)

Another significant impact to COC in fly ash is the addition of fuels other than coal. In the case of King and Riverside 8, petroleum coke is added. Both of these plants have a cyclone boiler in which coal is ground then dropped into the boiler, as apposed to a pulverized coal boiler that crushes coal to a powder then blows the pulverized coal into the boiler. In cyclone boilers, chunks of coal can form a molten material that can stick to the sides of the boiler and reduce efficiency. To prevent this from happening, petroleum coke is added to increase boiler temperatures and prevent the formation of the molten material. The addition of petroleum coke also adds COC to the ash.

Table 2.47 shows the COC content in ashes from Black Dog and High Bridge meand together to represent no fuel additives and King and Riverside 8 ash to show the affect of the addition of 8% petroleum coke. Higher carbon content ash will also have an impact on COC concentrations (discussed in “Boiler Configuration” section). The following COC were found in King and Riverside 8 to be significantly higher (0.05 level) compared to Black Dog and High Bridge: B, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Pb and V. King also contained Sr, Tl, Cr and Mn at significantly higher concentrations. Significance was determined using methods previously discussed (page 49).

Tires and sewage sludge are added to Otter Tail Power’s Big Stone plant. These added fuels will result in increases of COC concentrations (Table 2.47). Higher concentrations of salts are also expected in the ash due to their presence in sewage sludge however salts were not tested in our analysis. Tires contain zinc coated steel belts which will have a direct effect on COC in ash. This difference is very pronounced; zinc concentrations are 92 times larger than the Black Dog and High Bridge ash, and mercury concentrations are 24 times higher. The following COC were found to be significantly higher (0.05 level) compared to Black Dog and High Bridge: B, Ni, Cu, Zn, As, Se, Sr, Cd, Sn, Tl, Pb, Cr and Mn. Significance was determined using methods previously discussed (page 49).

Table 2.47. Fuel Additives Effect on COC in Fly Ash

	Black Dog and High Bridge n=20	King n=8	Riverside 8 n=10	Big Stone n=6
COC (ppm)	PRB Coal	PRB Coal w/ 8% Petroleum Coke	PRB Coal w/ 8% Petroleum Coke	PRB Coal w/ Tires & Sewage sludge
Be	3.40	3.33	3.14	3.52
B	447	967*	649*	1080*
Co	37.1	23.3	24.2*	63.4
Ni	36.4	821*	756*	71.1*
Cu	138	224*	234*	333*
Zn	91.5	172*	146*	8420*
As	11.0	19.0*	17.9*	20.6*
Se	8.84	14.0*	13.5*	17.2*
Sr	2700	3450*	2470	3830*
Mo	6.40	96.3*	93.1*	11.5
Ag	2.85	1.12*	1.28*	2.80
Cd	0.89	1.85*	1.94*	2.45*
Sn	0.67	0.70	0.54	0.44*
Sb	0.13	0.12	0.10	0.18
Ba	4690	4994.20	5310	5480
Tl	0.50	0.81*	0.64	1.00*
Pb	28.7	88.8*	54.6*	74.0*
Cr	63.3	55.5*	64.5	88.8*
Mn	138	262*	134	197*
V	196	1490*	1610*	271
Hg**	0.05	0.68	0.68	1.20

*Significantly different at 0.05 level.
**No enough data to do t-test comparison.

Rapid Energy Center and Hibbard Energy Center burn wood waste in addition to PRB coal. COC found within the wood will be recovered in the fly ash. Wood contains lower concentrations of COC compared to coal. However, the use of wood treatment/sealant will increase COC concentrations. REC ash contained significantly higher Mn, Zn, Cd and Pb, and significantly lower Be, B, Ni, As, Co, Ag, Se, Sr, Mo, Ba, Cr, and V concentrations compared to Black Dog and High Bridge ash. M.L. Hibard ash contained significantly lower Co, Cu, Se, Sr, Be, B, Ni, Ba and V concentrations and significantly higher Zn, Cd, Sn, and Mn. However, both REC and M.L. Hibbard use a traveling grate boiler system and thus COC differences could be from the additional wood or the difference in boiler type.

Table 2.48. Effects of Burning Wood on COC Concentrations in Fly Ash

	Black Dog and High Bridge (n=20)	REC (n=6)	M.L. Hibbard (n=7)
COC (ppm)	PRB Coal	PBR Coal and Wood	PBR Coal and Wood
Be	3.40	1.055*	1.59*
B	447	338*	312*
Co	37.1	5.56*	10*
Ni	36.4	9.31*	32.4*
Cu	138	1412	109*
Zn	91.5	873*	530*
As	10.9	4.50*	31
Se	8.84	2.67*	3.96*
Sr	2700	1180*	1960*
Mo	6.4	5.06*	10.4
Ag	2.85	0.544*	1.69
Cd	0.892	5.97*	2.63*
Sn	0.668	0.902	2.28*
Sb	0.132	0.168	0.167
Ba	4690	1290*	2000*
Tl	0.499	0.43	0.571
Pb	28.7	18*	40.3
Cr	63.3	14.7*	50.4
Mn	138	1390*	1010*
V	196	31.8*	83.0*
Hg**	0.0518	0.0631	0.101

*Significantly different at 0.05 level.
**No enough data to do t-test comparison.

Pollution Control Devices

The largest sink for most COC present in coal is in fly ash, collected by pollution control devices (PCD). COC in coal that does not get deposited in fly ash either leaves though the smoke stacks with flue gas or is captured in bottom ash. Thus when a plant has a smaller concentration of COC it can mean either less COC were present in the fuel or a greater amount of COC were captured in bottom ash or released into the atmosphere with flue gases.

Typically fly ash is collected using one of three types of PCD, electrostatic precipitators (ESP), baghouses, and/or scrubbers. Diagrams in Figure 1.2 show basic functions of PCD. The three PCD result in slight differences in ash collection and thus COC concentration.

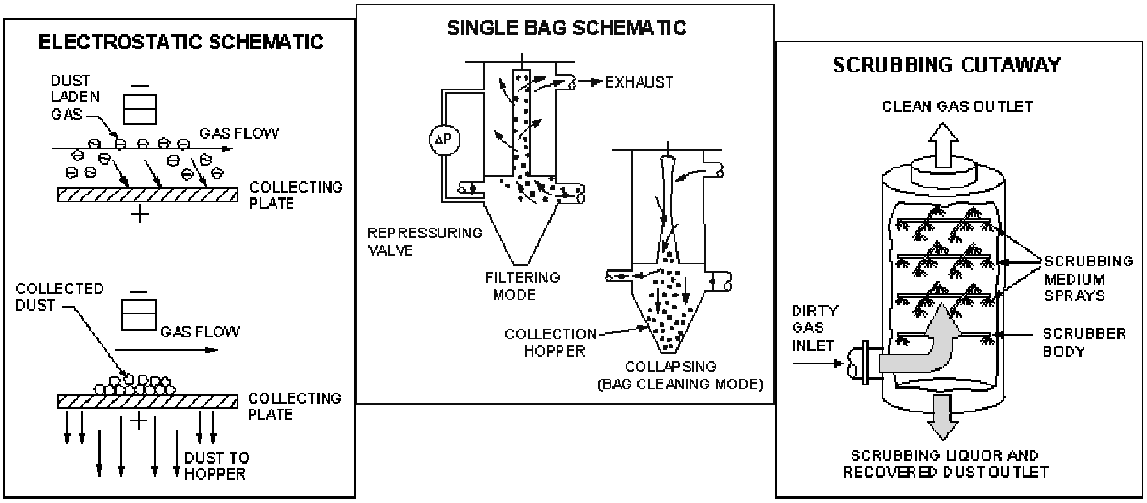

Figure 2.2. Diagram of ESP, Baghouse and Scrubber
(Meridian Engineering and Technology, 1997)

All but three of the sampled plants utilize electrostatic precipitators in their fly ash collection. Electrostatic precipitators work by inducing a negative charge on flue gas (with suspended particles), then passing the flue gas by a positively charged plate were charged ash particles are collected. Black Dog and High Bridge use electrostatic precipitators and will be used to compare other PCD.

Less common in our study are baghouses and scrubbers. Baghouses are fabric filters that act like a vacuum cleaner bag to sieve flue gas. Particles larger than the fibers pore size are captured. Scrubbers work by capitalizing on particles absorbance to certain scrubbing materials. At Sherco slake lime ($Ca(OH)_2$) and re-circulated fly ash are used to remove sulfur dioxide (SO_2) gas as it travels though the scrubber then into a baghouse. Sherco is unique in the fact that material injected into the scrubbers will enhance the capture of some COC however, the Ca, SO_3 and SO_4 in lime waste material will dilute the ash, creating lower concentrations of some COC. Ash from Sherco contains high amounts of sulfur and may have expansion problems during ash hydration and thus may not be suitable for soil stabilization.

Baghouses have the ability to capture smaller sized particles compared to ESP (Huang et al., 2004). Smaller particle have a greater surface area, allowing for a greater ability to capture COC (Huang et al., 2004). Riverside 6&7 use a baghouse as its PCD. Big Stone uses an ESP and baghouse combination however due to the addition of tires and sewage sludge comparisons between pollution control devices can not be made. It is expected that a greater recovery of COC will be found in plants with baghouses e.g. Riverside 6&7, compared to plants using ESP such as Black Dog and High Bridge. In Riverside 6&7 Ni, Cu, Zn, Mo, Cr and V were found to be significantly higher (0.05 level) compared to Black Dog and High Bridge (Table 2.49). Boron was found to be significantly lower in Riverside 6&7.

Table 2.49. Comparing COC Effects from Pollution Control Devices

COC (ppm)	Black Dog and High Bridge n=20 ESP	Riverside 6&7 n=10 Baghouse
Be	3.40	3.18
B	447	368*
Co	37.1	21.1
Ni	36.4	46.7*
Cu	138	169*
Zn	91.5	124*
As	11.0	11.8
Se	8.84	10.0
Sr	2700	2890
Mo	6.40	6.51*
Ag	2.85	1.57
Cd	0.89	1.07
Sn	0.67	0.52
Sb	0.13	0.06
Ba	4690	5450
Tl	0.50	0.47
Pb	28.7	31.8
Cr	63.3	91.9*
Mn	138	137
V	196	228*
Hg**	0.05	0.65

*Significantly different at 0.05 level.
**No enough data to do t-test comparison.

Conclusions

The soil and fly ash chemical databases can be used with the MPCA SRV and SLV worksheets to estimate whether an ash/soil mixture exceeds standard criteria for human health risk. The databases are extensive enough for engineers to make initial screening assessments for commonly available fly ash sources in Minnesota, using STUWMPP. In our assessment in STUWMPP we use the SRV values for unrestricted (residential) land use.

The ash generating sources can be placed in three categories depending on maximum amount of ash addition allowed while not exceeding 1999 SRV limits when mean soil data are used (Table 2.51). The SLV criteria are generally not limiting when depth of mixing is ≤ 12 in. and the distance to water table is > 3 ft. Generally the upper limits of allowable ash in a soil mixture is defined by As or Ba SRV limits. Six sources were found to be acceptable using the 1999 SRV limits even with 20% ash in the soil mixture. Eight sources were acceptable for 10% but not 20% mixtures. Four sources produced ash with high enough COC concentrations not to be able to pass the 1999 SRV for 10% mixtures.

Several sources were very close to one or another of the limits, and whether or not the ash would be acceptable at the limit depends on whether the mean ash values or the upper 95% CI values are used. For example, Dairyland Power JPM ash at a 20% mixture exceeded Ba limits when using the 95% confidence interval fly ash value, but not for the mean ash concentrations. Since COC concentrations can vary in soil and ash, we recommend that construction site soil and fly ash source be analyzed for each project.

Table 2.50. Summary of Ash Source Acceptability using 1999 SRV and a Mean Soil Concentration

Acceptable for 20% mixtures	Acceptable for 10% mixtures	Problematic for 10% mixture
Xcel- High Bridge	Xcel- Riverside 6&7	Minnesota Power- H.L. Hibbard
Xcel- Black Dog	Xcel- Riverside 8	Amer Cryst Sug- Moorhead
Xcel- Sherco	Xcel- King	Amer Cryst Sug- East Grand Forks
Dairyland Power- Alma	Otter Tail Power- Hoot Lake Unit 2	Amer Cryst Sug- Crookston
Dairyland Power- Genoa	Otter Tail Power- Hoot Lake Unit 3	
Minnesota Power- REC	Otter Tail Power- Big Stone	
	Dairyland Power- JPM	
	Minnesota Power- BEC	

Our assessment is dependent on the limits set for human health risk. In 2006 MPCA published new SRV limits with very much lowered acceptable concentrations for Cu, As, and V. These new values are less than found in many native soils, which renders the SRV worksheet relatively useless for defining cleanup goals for unrestricted land use. Our data show exceedences of the As and Cu limits even for mean soils. We expect there may be some reassessment of the 2006 goals, at least for As, Cu and V. If restricted use land use is specified, e.g. industrial, the new 2006 limits are not so problematic for defining fly ash limits

For most elements in fly ash, use of fly ash in soil stabilization is unlikely to create a concern for human health risk. Of the 21 COC analyzed, only three COC (As, Ba, and V) exceeded 1999 SRV limits. If the 2006 SRV are used, four COC (As, Ba, V and Cu) can exceed limits. No COC exceeded the SLV thresholds, for typical a typical application scenario. It may be reasonable for future chemical analyses of ash to be limited to As, Ba, and V, or if 2006 SRV limits are used, As, Ba, V and Cu. However, to ensure accurate barium concentrations, sulfur should also be analyzed because the EPA Method 3051 extraction must be modified to get a good estimate of leachable barium when high sulfur concentrations are present.

Chapter 3: Contaminants of Concern in Asphalt Pavement

Old asphalt pavement is commonly broken up into aggregate and used as a base or in new asphalt pavement. Asphalt pavement contains about 95% mineral aggregate and 5% asphalt binder (Kriech et al., 2002). Asphalt binder material contains petroleum that will have some amount of polycyclic aromatic hydrocarbons (PAHs). Some old asphalt pavement contains coal tar, a material that is high in PAHs. Recycling of asphalt pavement in road construction was thought to be a possible exposure pathway of PAHs to humans. Recycling involves breaking up the pavement, thus creating a greater amount of exposed surface area. This study was designed to identify if a potential hazard exists based on the human health risk limits in Minnesota Pollution Control Agency Soil Reference Values and Soil Leaching Values.

The Minnesota Pollution Control Agency has derived clean-up goals for PAHs in contaminated soil that can be used as human health risk guidelines for maximum concentrations that are allowed in soil mixtures. It should be noted that these goals are only guidelines and are not a part of the Minnesota Administrative Code. These goals were developed to give guidelines for the endpoint for the clean-up of polluted soils based on human health risk. Risks associated with contaminants in soils are evaluated by two worksheets, the Soil Reference Value (SRV) worksheet and the Soil Leaching Value (SLV) worksheet.

The SRV worksheet evaluates risk to human health from soil/dust ingestion, dermal contact and inhalation (Minnesota Pollution Control Agency, 1999). Two levels or tiers exist depending on exposure at a contaminated site. Tier 1 assumes a worst case, twenty-four hour per day exposure (residential chronic), and Tier 2 allows users to chose exposure scenarios such as residential chronic, industrial chronic, short-term worker, etc. To be conservative, our evaluation will use the Tier 1 scenario only. The SRV Tier 1 has limits for seven specific PAHs and for benzo(a)pyrene (BaP) equivalency, shown in Table 3.1. The BaP equivalency is a calculation that sums together carcinogenic PAH compounds based on relative potency, using benzo(a)pyrene as a reference value of 1. Twenty-five carcinogenic PAH compounds are involved in the benzo(a)pyrene equivalency calculation for the SRV. These compounds and their potency factors relative to BaP are given in Table 3.2. The BaP equivalency factor is calculated by summing together each species concentration multiplied by its respective potency factor.

Equation 3.1. BaP_{eqv} Calculation

$$BaP_{eqv} = \sum_{i}^{n} P.F._i \times [PAH_i]$$

where: BaP_{eqv} = Benzo(a)pyrene equivalency
P.F. = Potency Factor
n = number of P.F./PAH compounds in calculation
i = individual P.F./PAH compound in calculation

The SLV worksheet evaluates risk posed to groundwater (possible violation of drinking water standards) by leaching, using numerical modeling of pollution transport (Minnesota Pollution Control Agency, 1998b). Two levels or tiers of the SLV exist depending on the knowledge of site conditions. Tier 1 is the default calculation that assumes a worst case scenario with highly permeable soil, thick mixing layer, mixing to the water table, neutral pH, and high rainfall climate. A Tier 2 calculation allows for the input of site specific data for the factors mentioned above. Our assessment will involve a Tier 1 calculation that will represent a worst-case scenario. The SLV contains upper limits for six specific PAHs and benzo(a)pyrene (BaP) equivalency concentrations (Table 3.1). Six carcinogenic PAH compounds are involved in the benzo(a)pyrene equivalency calculation (using Equation 2.1) for the SLV. The six species and their relative potency factors are given in Table 3.2.

Table 3.1. SLV and SRV PAH Upper Limits (Minnesota Pollution Control Agency, 2003; Minnesota Pollution Control Agency, 2005)

PAH	MPCA SRV Tier 1 (mg/kg)	MPCA SLV Tier 1 (mg/kg)
Fluoranthene	1080	295
Pyrene	890	272
Anthracene	7880	942
Naphthalene	10	-
Acenaphthylene	1200	50
Fluorene	1140	47
Quinoline	1.2	-
Benzo(a)pyrene Eqv.	2	10.2

Table 3.2. Potency Factors for Benzo(a)pyrene Equivalency Calculation (Minnesota Pollution Control Agency, 2003; Minnesota Pollution Control Agency, 2005)

PAH for BaP Equivalency	SRV Relative Potency Factor	SLV Relative Potency Factor
Benz(a)anthracene	0.1	0.1
Benzo(b)fluoranthene	0.1	0.1
Benzo(j)fluoranthene	0.1	
Benzo(k)fluoranthene	0.1	0.01
Benzo(a)pyrene	1	1
Chrysene	0.01	0.001
Dibenz(a,j)acridine	0.1*	
Dibenz(a,h)acridine	0.1*	
Dibenz(a,h)anthracene	0.56	
7H-Dibenzo(c,g)carbazole	1*	
Dibenzo(a,e)pyrene	1*	
Dibenzo(a,h)pyrene	10*	
Dibenzo(a,i)pyrene	10*	
Dibenzo(a,l)pyrene	10*	
7,12-Dimethylbenzanthracene	34*	
1,6-Dinitropyrene	10*	
1,8-Dinitropyrene	1*	
Indeno(1,2,3,-d,d)pyrene	0.1	0.1
3-Methylcholanthrene	3*	
5-Methylchrysene	1*	
5-Nitroacenaphthene	0.02*	
1-Nitropyrene	0.1*	
4-Nitropyrene	0.1*	
6-Nitrochrysene	10*	
2-Nitrofluorene	0.01*	

*Our data does not include these species

Literature Review

Polycyclic aromatic hydrocarbons are also known as polycyclic aromatic compounds, polyaromatic hydrocarbons or as polynuclear aromatics. PAHs are a group of over 100 different chemicals consisting of carbon and hydrogen in fused-ring structures. Small amounts of PAHs are common in the environment (Minnesota Pollution Control Agency, 1998a). Most are harmless or mildly toxic, but some PAHs are carcinogenic (Minnesota Pollution Control Agency, 1998a). See Table 3.3 for the Minnesota Pollution Control Agency's list of carcinogenic and non-carcinogenic PAHs.

Polycyclic aromatic hydrocarbons are found in coal and petroleum, but they are also products of incomplete combustion, of either natural or anthropogenic origin. Anthropogenic sources to the environment are more abundant than natural sources and include burning of wood, coal, oil and gas, garbage, or other substances like tobacco or charbroiled meat. The most important natural sources are forest fires and volcanoes (National Research Council, 1983).

Table 3.3. MPCA list of PAHs (Minnesota Pollution Control Agency, 1998a)

Carcinogenic PAHs	Non-Carcinogenic PAHs	Carcinogenic, but unlikely to be found in the environment
Benz(a)anthracene	Phenanthrene	Dibenz(a,h)acridine
Benzo(b)fluoranthene	Pyrene	Dibenz(a,j)acridine
Benzo(j)fluoranthene	Acenaphthene	7H-Dibenzo(c,g)carbazole
Benzo(k)fluoranthene	Acenaphthylene	Dibenzo(a,e)pyrene
Benzo(a)pyrene	Anthracene	Dibenzo(a,h)pyrene
Indeno(1,2,3-cd)pyrene	Benzo(e)pyrene	Dibenzo(a,i)pyrene
Dibenz(a,h)anthracene	Benzo(g,h,i)perylene	Dibenzo(a,l)pyrene
Chrysene	Fluoranthene	5-Methylchrysene
	Fluorene	
	Naphthalene	
	2-Methyl Naphthalene	

Chemical/Physical Properties

PAHs consist of at least two benzene (six-sided with three double bonds) rings but can contain additional fused rings that are not six-sided. Structural diagrams of a few PAHs are given in Figure 2.1. Chemical species with similar molecular weight have many similar properties and therefore general properties are divided into three molecular weight (MW) groupings. Table 3.4

summarizes PAH general properties based on MW. PAHs in the environment exist mostly in the vapor or particulate phases. They have low water solubility, especially high MW species. PAHs have a high affinity for binding to organic carbon in soils (Agency for Toxic Substance and Disease Registry, 1995).

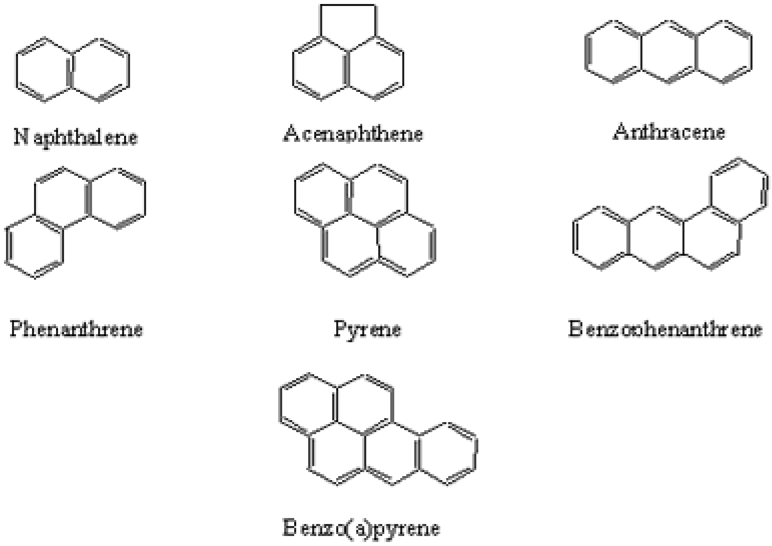

Figure 3.1. Chemical Structures of a Few PAHs (The Hatcher Group, 2005)

Table 3.4. Properties of PAHs

Property	Low MW	Med MW	High MW
Predominant Phase in the Environment[1]	Vapor	Vapor and Particulate	Particulate
Water Solubility[1]	35,000 µg/L -----	to	----- 0.15 µg/L
Henry's Law Const (atm-m^3/mol)[1]	10^{-3} - 10^{-5}	10^{-6}	10^{-5} - 10^{-8}
Koc[2]	10^{3} - 10^{4}	10^{4}	10^{5} - 10^{6}
Vapor Pressure (Pa)[3]	10^{-1} -----	to	----- 10^{-10}
Bioconcentration Factors[1]	lower factor ---	10-10,000	--- higher factor

[1] (Agency for Toxic Substance and Disease Registry, 1995)
[2] (Southworth, 1979)
[3] (Norin and Stroemvall, 2004)

Human Exposure

For U.S. residents, the greatest PAH exposure is through the ingestion of food, but this can vary depending on lifestyle (Agency for Toxic Substance and Disease Registry, 1995). Other important exposure pathways are through active and passive inhalation of the compounds in tobacco smoke, wood smoke and contaminated air, as well as dermal contact with coal tar in cosmetics and shampoos (Agency for Toxic Substance and Disease Registry, 1995). Human daily exposure is estimated to be 0.207 µg from air, 0.027 µg from water, and 0.16 to 1.6 µg from food. These estimates may be as much as twice as high in smokers (Agency for Toxic Substance and Disease Registry, 1995).

PAHs are stored mostly in the kidneys, liver and fat (Agency for Toxic Substance and Disease Registry, 1995). In long-term PAH exposure scenarios, cancer, cataracts, kidney and liver damage, and jaundice may develop. However, in humans most PAHs are released in feces and urine within a few days (Agency for Toxic Substance and Disease Registry, 1995).

In the Environment

In the environment PAHs can volatilize, photolyze, oxidize, biodegrade, bind to suspended particles, or accumulate in aquatic organisms (Agency for Toxic Substance and Disease Registry, 1995). The bulk of PAHs in the environment are tied to organic matter in soil. Sorption of PAHs to soil and sediments increases with increasing soil organic carbon and with increasing surface area of the sorbent particles (Karickfoff et al., 1979).

Air

Most PAHs, whether the result of natural or anthropogenic processes, are released into the air. Residential burning of wood is the largest anthropogenic source, however on a local scale other emission sources can be dominant (Peters et al., 1981; Ramdahl et al., 1982). Urban air contains as much as 5 times higher PAH concentrations (0.15-19.3 ng/m^3) than rural air (0.02-1.2 ng/m^3) (Agency for Toxic Substance and Disease Registry, 1995). Winter concentrations are 5-10 times higher than summer concentrations due to the difference in temperature, sunlight radiation, and an increase in heating emissions (Agency for Toxic Substance and Disease Registry, 1995). An estimated 10,000 to 30,000 tons (8,900- 26,800 metric tons) of PAHs are emitted annually in the U.S. (Baek et al., 1991; EPA, 1998).

Most PAHs in air are associated with particulate matter, with some in the gaseous phase (National Research Council, 1983; Yang et al., 1991). The photo degradation of PAHs in air occurs generally over days to weeks (Agency for Toxic Substance and Disease Registry, 1995). Indoor air has a potentially increased level of PAHs due to tobacco smoke, unvented radiant and convective kerosene space heaters, gas cooking and heating appliances (Chuang et al., 1991; Hoffmann and Hoffmann, 1993; Mumford et al., 1991; National Research Council, 1983; Traynor et al., 1990). However, it is common for outdoor PAH levels to be ten times higher than indoor (Agency for Toxic Substance and Disease Registry, 1995).

Water

The most important source of PAHs in surface water is from the deposition of airborne PAHs (Jensen, 1984). Other sources include municipal waste water discharge (Barrick, 1982), urban storm water runoff (MacKenzie and Hunter, 1979), runoff from coal storage areas (Stahl et al., 1984; Wachter and Blackwood, 1979), effluents from wood treatment plants and other industries (DeLeon et al., 1986; Snider and Manning, 1979; United States Department of Agriculture, 1978), oil spills, and petroleum processing (Giger and Blumer, 1974). In a localized environment any of the above sources can be dominant. Background levels of PAHs in drinking water range from 4 to 24 ng/L (Sorrel et al., 1980). As in air, PAHs are mostly associated with particles and only 1/3 of PAHs in water are in the dissolved phase (Eisler, 1987). The degradation of PAHs in water and soil occurs primarily though microbial metabolism within weeks or months. Losses can also occur through volatilization and sorption to settling particles (Agency for Toxic Substance and Disease Registry, 1995).

Soil

Soil, like water, receives most PAHs from atmospheric deposition after local and long-range transport (Agency for Toxic Substance and Disease Registry, 1995). Other sources include sewage sludge disposal from public treatment plants, automotive exhaust, tire and asphalt wear, irrigation with coke oven effluent, leachate from bituminous coal storage sites, and use of compost-based fertilizers (Perwak et al., 1982; Santodonato, 1981; Stahl et al., 1984; White and Lee, 1980). PAHs can be lost from soil through microbial breakdown, photo oxidation, volatilization, crop uptake and leaching (Smith et al., 1995). Large variations in soil PAH concentrations are shown by data from several publications which were pooled together in an Agency for Toxic Substance and Disease Registry publication (1995) (Table 3.5).

Table 3.5. Soil PAHs Concentrations Found (International Agency for Research on Cancer, 1973; White and Vanderslice, 1980; Windsor and Hites, 1979; Edwards, 1983; Butler et al., 1984; Vogt et al., 1987; Jones, 1987; as shown in Agency for Toxic Substance and Disease Registry publication, 1995)

	Concentration (µg/kg or ppb)		
Compound	Rural Soil	Agricultural Soil	Urban Soil
Acenaphthene	1.7	6	
Acenaphthylene		5	
Anthracene		11-13	
Benz(a) anthracene	5-20	56-110	169-59,000
Benzo(a)pyrene	2-1,300	4.6-900	165-220
Benzo(b)fluoranthene	20-30	58-220	15,000-62,000
Benzo(e)pyrene		53-130	60-14,000
Benzo(g,h,i)perylene	10-70	66	900-47,000
Benzo(k)fluoranthene	10-110	58-250	300-26,000
Chrysene	38.3	78-120	251-640
Fluoranthene	0.3-40	120-210	200-166,000
Fluorene		9.7	
Ideno(1,2,3-c,d)pyrene	10-15	63-100	8,000-61,000
Phenanthrene	30.0	48-140	
Pyrene	1-19.7	99-150	145-147,000

PAHs in Minneapolis, Minnesota Asphalt Pavement

Limited data on PAH concentrations in asphalt pavements are available in the literature. Our experiment set out to expand this limited collection and to give practical comparisons of concentrations in asphaltic pavements. This was done by analyzing entire asphalt pavement instead of binder material alone, which is typically done. By using entire asphalt pavement, a better evaluation of the effects of ground pavement on soil PAH concentrations.

Experiment Design

Sample Collection

The City of Minneapolis collected asphalt pavement cores of varying ages within Minneapolis, Minnesota. A list of all cores collected with age of paving and location is given in Table 3.6. The 2003 core was split into two samples because the core contained two distinct layers. Core diameters were approximately 10 cm (4 inches) and coring depth ranged from 5 cm to 15 cm (2 to 6 inches). In addition, a piece of asphalt pavement that was identified to contain coal tar was collected from Snelling Ave N in Roseville, Minnesota. Samples were sent to Minnesota Department of Transportation, Office of Materials and Road Research to be crushed. Samples were then transported to the University of Minnesota Department of Public Health lab for analysis.

Table 3.6. Asphalt Core Locations

Year Paved	Sampled Street	Between
1918	3rd St S	10th Ave S and 12th Ave S
1924	40th St W	Linden Hills Blvd and Queen Ave S
1930	5th St N	6th Ave N and 10th Ave N
1933	Linden Ave W	Dupont Ave N and Lyndale Ave N
1937	3rd St N	5th Ave N and 7th Ave N
1941	25th St E	36th Ave S and River Pkwy W
1946	5th Ave N	Washington Ave and 4th St N
1953	Grand Ave	48th St W and 34th St W
1962 a	48th St W	Washington Ave S and Vincent Ave S
1962 b	Thomas Ave S	Sheridan Ave S and Lake Harriet Dr
1962 c	Vincent Ave S	48th St W and 47th St W
1966 a	Oliver Ave S	49th St W and 50th St W
1966 b	Queen Ave S	52nd St W and 51st St W
1966 c	Russell Ave S	Lake Harriet Dr and 49th St W
1967	17th Ave NE	Pierce St and Buchanan St
1972	12th Ave S	54th St W and Minnehaha Pkwy
1978	39th St W	Bryant Ave S and Nicollet Ave
1988	Colfax Ave S	Franklin Ave E and 18th St E
1992	Colfax Ave S	34th St W and Lake St W
1996	Aldrich Ave S	26th St W and Frontage S
2000	Columbus Ave S	Franklin Ave E and 18th St E
2003 Top	15th Ave S	21st St E and 26th St E
2003 Bottom	15th Ave S	21st St E and 26th St E

Sample Analysis

Analysis was performed under yellow fluorescent lights to limit PAH photo-degradation. To prevent contamination, glassware was heated to 450 degrees C and held for six hours in a furnace and then allowed to cool to room temperature. Before use, glassware was rinsed with dichloromethane (DCM) and hexane to limit contamination. Sample transfers were accompanied by three rinses with hexane to insure the most complete transfer of sample. Entire ground asphalt pavement cores were analyzed including aggregates.

Approximately a half of gram of crushed asphalt was weighted into a glass fiber filter (to hold asphalt together while allowing for the passage of solvent and PAHs) and placed into a Soxhlet extractor. A surrogate spike was added directly to the sample to track the extraction method efficiencies. The spike compounds were tagged with deuterium to distinguish the surrogate from the compound in the asphalt. Table 3.7 lists the compounds in the surrogate spike and the compounds in the internal standard, which is added before quantification on the GC/MS. Several boiling beads (approximately 10) and approximately 15 grams of sodium sulfate (to absorb water) were added to a 250 mL round-bottom flask. The round-bottom flask was attached to the Soxhlet extractor and two cycles (approximately 100 mL) of DCM were added. DCM solvent was boiled and cycled through the Soxhlet extractor for four hours. This removed all of the black asphaltic material from the crushed pavement and transferred it into the attached round-bottom flask. Heat was removed and after cooling, the DCM solvent (w/ asphaltic material) was transferred to a new 250 mL round-bottom flask leaving behind the beads and sodium sulfate. The sample volume was reduced to about three milliters using a Buchi Rotovapor R-3000, which removed excess solvent. The extract solution contained solid materials which would damage the analytical instrument. To prevent damage to the instrument, the solids were removed using a clean-up column.

Table 3.7. Surrogate and Internal Standard Spikes

Surrogate Standard	Internal Standard
d10-acenaphthene	d8-acenaphthylene
d10-phenanthrene	d10-anthracene
d10-pyrene	d10-fluoranthene
d12-chrysene	d12-benz[a]anthracene
d12-benzo[a]pyrene	d14-dibenzo[ah]anthracene

To create a clean-up column, a glass chromatography column was plugged with glass wool and filled with hexane. Approximately one gram of sodium sulfate was added and allowed to settle. Six grams of two percent activated alumina were added to the column and allowed to settle followed by another gram of sodium sulfate. Four and a half grams of silica were mixed with fifteen milliters of fifteen percent DCM in hexane and then added to the column. Once the silica had settled another gram of sodium sulfate was added to the column. Solvent rinses, to condition the column, consisted of three, ten mL rinses for each of the following solvents: forty percent DCM in hexane, fifteen percent DCM in hexane and hexane. This concluded the preparation and conditioning of the column. Next, the sample was poured into the clean-up column. Followed by three, ten mL rinses of hexane and three rinses with 33.3 mL of forty percent DCM in hexane. The column was allowed to drain completely into a round-bottom flask.

The sample volume was reduced by roto-evaporation to approximately three mL and transferred into a five mL amber vial. The vial was placed under a nitrogen gas stream to further reduce sample volume to approximately 1 mL. Next, the sample was transferred into gas chromatograph (GC) vials and spiked with an internal standard (Table 3.7). PAH concentrations were determined on a Hewlett Packard 5972 gas chromatograph/mass spectrometry equipped with an Equity^{TM}-5 poly (5% diphenyl/95% dimethyl) siloxane capillary column.

The PAH species quantified includes: acenaphthylene, acenaphthene , fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[bjk]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[cd123]pyrene, dibenzo[ah]anthracene, benzo[ghi]perylene and coronene. This list includes the species identified in EPA Method TO-13a, Determination of PAHs in Ambient Air Using Gas Chromatography, Mass Spectrometry. However, Method TO-13a includes naphthalene, which we did not include due to its high volatility and expected low recoveries.

Results

Sample concentrations were adjusted based on surrogate (known spiked amounts) recoveries. A surrogate was never added to the 1962b sample; therefore no adjustments were made to that sample. Surrogate recoveries for each sample are given in the quality assurance/quality control section in Appendix A. In our analysis, separation of benzo[b]fluoranthene, benzo[j]fluoranthene and benzo[k]fluoranthene could not be determined, and instead the sum benzo[bjk]fluoranthene was reported. The SLV BaP equivalency calculation only requires benzo[b]fluoranthene and benzo[k]fluoranthene with potency factors of 0.1 and 0.01 respectively. The higher potency value of 0.1 for the entire benzo[bjk]fluoranthene was used in the SLV BaP equivalency calculation. Fortunately, in the SRV BaP equiv. a potency factor of 0.1 is required for all three species. Therefore the benzo[bjk]fluoranthene could simply be multiplied by the 0.1 potency factor. However, several PAH species involved in the SRV BaP equiv. calculation were not determined. These species are indicated with an asterisk in Table 3.2.

The PAH concentrations for each of the samples are given in Table 3.8. When extraction duplicates were done, the sample with a surrogate spike or the best recovery of the surrogate spike was reported. The Snelling Ave sample, which was known to contain coal tar, contained PAH concentrations significantly higher than in the other asphalt samples. Coal-tar binder, which is high in PAHs, was used in some pavements in the pre-World War Two era. More recently, only petroleum binder, which is much lower in PAHs, has been used. Petroleum asphalt is derived from the distillation of crude oil (Puzinauskas and Corbett, 1978). Coal tar is “a condensation by-product obtained from the high temperature (>1000 C) carbonization of coal during the production of coke” (Puzinauskas and Corbett, 1978).

Table 3.8. PAHs Concentrations in Asphalt Pavement Cores

PAH (mg/kg)	1918	1924	1930	1933	1937	1941	1946	1953
acenaphthylene	0.00747	0.0296	0.159	0.0530	1.04	0.690	0.137	0.00555
acenaphthene	3.42	4.16	4.06	4.26	4.12	4.15	3.74	3.81
fluorene	0.143	0.288	0.379	0.0213	0.176	7.02	0.125	0.00202
phenanthrene	1.37	3.64	3.60	1.40	0.973	20.7	1.76	0.904
anthracene	0.165	0.412	0.439	0.122	0.435	6.85	0.287	0.176
fluoranthene	0.182	1.35	0.373	1.08	1.82	14.3	1.79	0.588
pyrene	0.672	2.98	1.29	1.67	2.40	11.5	3.04	0.670
benz[a]anthracene	0.142	2.36	0.547	0.435	1.45	3.16	2.41	0.222
chrysene	1.20	1.65	2.45	1.67	2.31	4.44	1.55	0.551
benzo[bjk]fluoranthene	0.434	1.43	1.03	0.728	4.45	3.04	1.73	0.229
benzo[e]pyrene	0.820	1.73	1.85	1.04	2.16	1.84	1.41	0.270
benzo[a]pyrene	0.534	1.01	0.822	1.01	2.28	1.80	0.921	0.295
perylene	0.317	0.440	0.277	0.190	1.16	0.125	0.166	0.336
indeno[cd123]pyrene	0.206	0.509	0.0749	0.365	0.111	0.448	1.84	0.255
dibenzo[ah]anthracene	0.168	0.541	<0.00181	<0.00181	0.0616	0.0910	1.06	0.192
benzo[ghi]perylene	0.369	1.60	0.145	1.10	0.402	0.472	1.47	0.791
coronene	<0.000175	1.31	0.0312	0.144	0.106	1.18	<0.000175	2.05
SRV BaP equiv.	1.31	3.67	1.01	1.18	3.16	2.88	5.87	1.16
SLV BaP	0.781	1.98	0.990	1.16	2.95	2.56	2.58	0.558
Total:	10.2	25.4	17.5	15.3	25.5	81.9	23.4	11.4

Table 3.8. PAHs Concentrations in Asphalt Pavement Cores (continued)

PAH (mg/kg)	1962a	1962b*	1962c	1966a	1966b	1966c	1967	1972
acenaphthylene	<0.000482	0.207	0.0209	0.00617	<0.000482	<0.000482	0.0492	0.0369
acenaphthene	3.60	0.203	3.68	3.33	3.97	3.63	4.17	3.83
fluorene	0.127	1.23	0.193	0.113	0.237	0.167	0.154	0.200
phenanthrene	1.66	6.58	1.14	0.584	1.61	0.766	1.42	3.06
anthracene	0.167	1.80	0.104	0.0560	0.203	0.108	0.112	0.251
fluoranthene	0.229	3.53	0.472	0.316	0.328	0.302	0.548	2.33
pyrene	0.618	0.0616	0.770	0.528	0.739	0.504	1.62	2.49
benz[a]anthracene	<0.000700	0.365	0.350	<0.000700	<0.000700	<0.000700	1.50	0.978
chrysene	0.907	0.0570	1.75	0.916	1.61	0.897	3.61	2.51
benzo[bjk]fluoranthene	0.140	0.372	0.528	0.431	0.701	0.490	0.343	1.93
benzo[e]pyrene	1.22	0.0168	1.98	1.08	1.88	1.10	1.46	2.06
benzo[a]pyrene	0.168	0.526	0.655	0.184	0.241	0.389	0.337	1.18
perylene	0.366	0.211	0.419	<0.000860	1.02	0.227	0.0519	0.555
indeno[cd123]pyrene	0.402	0.258	0.594	0.427	0.860	0.515	0.469	2.02
dibenzo[ah]anthracene	0.346	0.0990	0.234	<0.00181	0.456	0.186	0.491	1.13
benzo[ghi]perylene	0.854	0.487	1.50	<0.000590	2.29	0.905	1.60	3.88
coronene	0.394	0.0749	1.32	0.396	0.445	0.997	0.217	5.27
SRV BaP equiv.	1.65	1.03	1.78	0.279	2.28	1.26	2.62	6.31
SLV BaP equiv.	0.570	0.724	1.04	0.271	0.855	0.677	1.06	2.80
Total:	11.2	16.1	15.7	8.37	16.6	11.2	18.2	33.7

*Surrogate recovery not available, therefore sample was not adjusted based on surrogate recovery

Table 3.8. PAHs Concentrations in Asphalt Pavement Cores (continued)

PAH (mg/kg)	1978	1988	1992	1996	2000	2003a	2003b	Snelling Ave, Coal
acenaphthylene	0.0207	0.136	0.00591	<0.000482	<0.000482	<0.000482	<0.000482	20.7
acenaphthene	4.15	4.09	4.07	3.97	4.25	4.25	4.22	3.82
fluorene	0.0459	0.363	0.0805	0.107	0.141	0.119	0.0672	48.5
phenanthrene	0.965	6.12	3.38	3.23	2.95	1.47	0.749	144
anthracene	0.0614	1.10	0.829	0.452	0.306	0.107	0.0540	90.3
fluoranthene	0.273	1.01	4.95	1.06	1.02	0.310	0.156	142
pyrene	0.893	6.76	5.32	1.49	2.37	1.09	0.974	131
benz[a]anthracene	<0.000700	7.10	2.87	0.994	0.916	0.401	<0.000700	123
chrysene	1.12	14.3	3.90	2.46	2.07	2.17	0.812	114
benzo[bjk]fluoranthene	1.30	2.40	4.93	1.39	1.22	0.851	0.207	209
benzo[e]pyrene	1.58	4.32	3.31	3.22	3.49	1.97	0.707	46.6
benzo[a]pyrene	1.50	3.83	3.35	2.11	3.81	1.04	0.168	82.9
perylene	0.561	1.17	1.21	0.824	1.66	0.415	0.159	17.7
indeno[cd123]pyrene	<0.00162	0.965	3.70	<0.00162	<0.00162	0.452	0.162	116
dibenzo[ah]anthracene	<0.00181	<0.00181	1.54	<0.00181	<0.00181	0.684	0.201	54.4
benzo[ghi]perylene	0	2.83	5.69	0.514	<0.000590	2.18	0.953	83.5
coronene	0	2.17	2.23	<.000175	<.000175	2.97	0.121	9.72
SRV BaP equiv.	1.64	5.02	10.8	2.37	4.04	4.04	1.04	352
SLV BaP equiv.	1.63	4.89	6.04	2.35	4.02	1.90	0.407	182
Total:	12.5	58.7	51.4	21.8	24.2	20.5	9.71	1440

Discussion

It is expected that petroleum-based binders contain PAHs due to the intrinsic existence of PAHs in petroleum. The PAH species and concentrations are dependent on the source of petroleum (Puzinauskas and Corbett, 1978). For example a South Louisiana crude oil contains 1.2 mg/kg of benzo[a]pyrene and 23 mg/kg chrysene but a Kuwaiti crude oil contains 0.5 mg/kg benzo[a]pyrene and 6.9 mg/kg for chrysene (International Agency for Research on Cancer, 1989). Concentrations of PAHs vary even within the same oil field (Puzinauskas and Corbett, 1978). Therefore it is difficult to assign PAH concentrations to asphalt materials. This is especially true when considering that petroleum refining practices, asphalt mixtures and road construction practices can vary and effect PAH concentrations. We assumed that the greatest range in these factors would be captured by sampling asphalt material from a large range in age of construction.

Sampled roads ranged in ages from 1918 to 2003. Obviously an active road paved in 1918 will have undergone maintenance including new asphalt lifts. Unfortunately it is not common to record the date when a new lift is added. This means that sample year is only reflective of the year the road was originally paved and does not consider added lifts, which will add some variation in PAH concentrations. Possibly the largest factor in our sample PAH concentration variation is the method of extracting the entire asphalt core including the aggregate. It is suspected that theses factors are to account for the variation seen within the samples.

Table 3.9 gives the range and mean obtained for all samples except for the coal tar sample at Snelling Ave., which is reported in a separate column. Coal tar is the byproduct of making coke from coal. Coal tar contains approximately 50% PAHs or more by weight (Mahler, 2003; U.S. Dept Health and Human Services, 2002). If a pavement contains coal-tar binder, PAH concentrations will be much higher compared to petroleum asphalt (Kriech, 1999). This was shown in the Snelling Ave. coal tar sample. The total sum of PAHs for the coal tar sample were more than sixty times the mean total PAHs from the other samples. Benzo[bjk]fluoranthene was 148 times larger compared to the mean petroleum binder samples. Coal tar has a strong odor and in general a sticker texture. The 1941 sample was suspected to contain some coal tar due to its scent and sticker texture. As expected, the 1941 sample contained higher concentrations of PAHs compared to the other samples. It was much less than the Snelling Ave sample, which suggest that other petroleum based asphalt lifts were present.

For all except the Snelling Ave sample, PAH concentrations were below SRV and SLV upper limits for individual PAH species. The Snelling Ave sample exceeded the fluorene 47 mg/kg SLV limit, with a sample concentration of 48.5 mg/kg. It is surprising that such large concentrations of PAHs present in the coal tar sample were still within acceptable limits. However BaP equivalency concentration shows a much different perspective. The SRV BaP equivalency upper threshold is 2 mg/kg, while the mean of the samples contain a 2.89 mg/kg concentration and the maximum SRV BaP equivalency value was found to be 10.8 mg/kg. The coal tar sample was well above the upper limit with a concentration value of 352 mg/kg. The 10.2 mg/kg SLV BaP equivalency threshold was less of an issue for the petroleum based asphalt with mean value of 1.86 mg/kg and a maximum value of 6.04 mg/kg. The Snelling Ave sample exceeds the SLV BaP equivalency with a value of 182 mg/kg.

Table 3.9. Sample Range in PAH Concentrations

PAH (mg/kg)	SRV Tier 1 (mg/kg)	SLV Tier 1 (mg/kg)	Min*	Max*	Mean*	Snelling Ave. coal tar
acenaphthylene	-	-	<0.000482	1.04	0.113	20.7
acenaphthene	1200	50	0.203	4.26	3.79	3.82
fluorene	1140	47	0.00202	7.02	0.500	48.5
phenanthrene	-	-	0.584	20.7	3.05	144
anthracene	7880	942	0.0540	6.85	0.635	90.3
fluoranthene	1080	295	0.156	14.3	1.67	142
pyrene	890	272	0.0616	11.5	2.20	131
benz[a]anthracene	-	-	<0.000700	7.10	1.14	123
chrysene	-	-	0.0570	14.3	2.39	114
benzo[bjk]fluoranthene	-	-	0.140	4.93	1.32	209
benzo[e]pyrene	-	-	0.0168	4.32	1.76	46.6
benzo[a]pyrene	-	-	0.168	3.83	1.22	82.9
perylene	-	-	<0.000936	1.66	0.516	17.7
indeno[cd123]pyrene	-	-	<0.00162	3.70	0.637	116
dibenzo[ah]anthracene	-	-	<0.00181	1.54	0.325	54.4
benzo[ghi]perylene	-	-	<0.000590	5.69	1.31	83.5
coronene	-	-	<0.000175	5.27	0.932	9.72
SRV benzo[a]pyrene	2	-	0.280	10.8	2.89	352
SLV benzo[a]pyrene	-	10.2	0.271	6.04	1.86	182
Total:	-	-	8.37	81.9	23.5	1440

*excluding Coal Tar sample

Petroleum (binder) asphalt PAH concentrations available in the literature are compared to our Minneapolis samples in Table 3.10. Our sample PAH concentrations are expected to be lower than what is found in the literature because our samples digestions were diluted by aggregate. Larger ranges in PAH concentrations were found in the Minneapolis samples compared to that found in the literature. As previously mentioned this could be a result of mixing several layers of asphalt, extracting and analyzing entire pavement, and in one case the possible presence of coal tar. In general, PAH concentrations in the literature fit into the range found in our samples.

Table 3.10. PAH Concentrations in Asphalt

Material:	MPCA SLV (Tier 1)[1] (mg/kg)	MPCA SRV (Tier 1)[2] (mg/kg)	Range in Minneapolis Sampled Asphalt (mg/kg)	Mean of 7 European Asphalts[4] (mg/kg)	Mean of 12 U.S. Asphalts[4] (mg/kg)	Range of 6 Asphalt Pavements[5] (mg/kg)
Fluoranthene	295	1080	0.156 - 14.3	0.48	0.4	<1
Pyrene	272	890	0.616 - 11.5	0.66	1.4	<1 - 9.1
Benz(a)anthracene			<0.00181 – 7.10	0.52	2.9	<1 - 2
Chrysene			0.057 – 14.3	1.69	2.8	<1 - 12
Benzo(e)pyrene			0.0168 – 4.32			
Benzo(b)fluoranthene			0.140- 4.93*		0.8	<1 - 1.5
Benzo(k)fluoranthene				0.06	b.d.l.	<1
Benzo(a)pyrene			0.168 – 3.83	0.76	1.8	<1 - 3.7
Benzo(ghi)perylene			<0.000590 – 5.69	2.19	b.d.l.	<1 - 2.4
Dibenz(ah)anthracene			<0.00181 – 1.54	0.22	0.6	<1
Indeno(1,2,3-cd)pyrene			<0.00162 – 3.70	b.d.l.	b.d.l.	<1
Phenanthrene			-	3.3	2.4	<1 - 30
Anthracene	942	7880	0.0540 – 6.85	0.13	b.d.l.	<1 - 1.5
Naphthalene		10	-		1.9	<1
Acenaphthylene	50	1200	<0.000482 – 1.04		b.d.l.	<1
Fluorene	47	1140	0.00202 – 7.02		1.4	<1 - 1.8
Acenaphthalene			-		b.d.l.	<1
Acenaphthene			0.203 – 4.26			
Quinoline		1.2	-			
SRV Benzo(a)pyrene Eqv	-	2	0.280 – 10.8	0.96	2.5	4.9/ 4.2
SLV Benzo(a)pyrene Eqv	10.2	-	0.271 – 6.04	0.81	2.2	4.2/ 4.1

[1](Minnesota Pollution Control Agency, 1998b); [2](Minnesota Pollution Control Agency, 1999); [3](Brandt and De Groot, 2001); [4](Kriech, 1991); [5](Kriech, Kurek, et al., 2002)
b.d.l. = below detection limit
*benzo(bjk)fluoranthene

No single literature source contained data for all twenty-five species used in the SRV BaP calculation; therefore BaP equivalencies in Table 3.10 were calculated from available data only (not including values below detection limit). Using the upper limit concentrations given in the "range for 6 asphalts" data from Kreich et al. (2002), as shown in Table 3.10, and assuming the concentration of the non-detects is zero the calculated value is 4.2 mg/kg. If PAHs that were below detection limit were given a value of 1 mg/kg (the detection limit), the BaP equivalency would be 4.9 mg/kg. Both calculations exceed the 2 mg/kg SRV recommended limit. However, if the asphalt material is mixed with a material that contains very few PAHs, such as soil or aggregate rock to provide additional aggregate for the base (a common practice), the mixture would most likely be below the SRV limit even for asphalt with high BaP contents. When coal tar is involved the risk increases, to a level that is likely to be unacceptable.

Literature data for coal tar show PAH values that are as much as two-thousand times higher than petroleum asphalts. These values are much higher than the SLV and SRV maximum limits. Differences found from the Snelling Ave sample in the literature can be explained by the extraction methods. In the literature PAH concentrations were found by first extracting the binder material, then extracting and calculating the PAH concentrations based on binder material. Therefore our samples appeared to contain much less PAHs due to the aggregate present. Coal-tar binder is no longer used in U.S. highway paving but it is still a common ingredient in sealants (Howard Marks, National Asphalt Assoc., 2005, personal communication). These sealants presently are not used on streets or roads in Minnesota, but occasionally coal tar is found under old roads during renovation, as with the Snelling Avenue sample.

Table 3.11. Coal-Tar Asphalt PAH Concentrations

PAH	MPCA SLV (tier 1)[1] (mg/kg)	MPCA SRV (tier 1)[2] (mg/kg)	Snelling Ave., St Paul Sampled Coal Tar (mg/kg)	European Coal Tar[5] (mg/kg)	Low Temp U.S. Coal Tar[5] (mg/kg)	High Temp Coal Tar[5] (mg/kg)
Fluoranthene	295	1080	142	36000	7900	12000
Pyrene	272	890	131	27200	3100	2400
Benz(a)anthracene			123	20400	2600	5000
Chrysene			114	11200	1500	4900
Benzo(b)fluoranthene			209		1600	2700
Benzo(k)fluoranthene				6010	860	1300
Benzo(a)pyrene			82.9	15170	2100	2300
Benzo(ghi)perylene			83.5	3530	780	140
Dibenz(ah)anthracene			54.4	127	800	140
Indeno(1,2,3-cd)pyrene			116		520	650
Phenanthrene			144	25700	6500	5300
Anthracene	942	7880	90.3	7310	2100	2300
Naphthalene		10			21000	5.4
Acenaphthylene	50	1200	20.7		2700	200
Fluorene	47	1140	48.5		7000	240
Acenaphthalene					2100	54
SRV Benzo(a)pyrene Eqv	-	2	352	17800	3100	3400
SLV Benzo(a)pyrene Eqv	10.2	-	182	17300	2600	3200

[1](Minnesota Pollution Control Agency, 1998b); [2](Minnesota Pollution Control Agency, 1999), [5](Kriech, 1991)

Leaching of PAHs from asphalt pavement is not expected to be significant, due to low solubility of PAHs. A MnDOT and MDH study of runoff from asphalt stockpiles found PAH concentrations nearly all at or below detectable limits (Sadecki, 1996). Kriech et al. (2002) found that among three asphalt pavements subject to the EPA's Toxicity Characteristic Leaching Procedure (TCLP), PAH concentrations of < 0.1 mg/L were found, except for one pavement with 0.18 mg/L naphthalene. Results of other leachate studies using TCLP, synthetic precipitation leaching procedure (SPLP), an acid water leach and deionized water leaching, showed all, or almost all PAH concentrations below detection levels (Brantley, 1999; Townsend, 1998; Kriech, 1990; Norin, 2004). With better detection limits, Brandt was able to detect PAHs from asphalt using an acid water leachate test at ng/L levels. Naphthalene was found at greatest concentrations with a range of 35 to 371 ng/L, and benzo(a)pyrene ranged from below detection to 0.3 ng/L (Brandt, 2001). A list of the leachate data with detection limits low enough to show actual values is given in Table 3.12.

The Minnesota Department of Health has a drinking water standard only for benzo(a)pyrene, at 0.2 µg/L or 200 ng/L (Minnesota Department of Health, 2002). The highest benzo(a)pyrene value given in the leachate data in Table 3.12 was 0.3 ng/L, however most of the values were reported below detection limit.

Although our work is focused on human health risk we also compared the data in Table 3.12 with the proposed Minnesota Pollution Control Agency (2005) chronic standard (CS) limits for five PAH concentrations in surface water for aquatic health. A CS is defined as “the highest water concentration of a toxicant to which organisms can be exposed indefinitely without causing chronic toxicity” (Minnesota Pollution Control Agency, 2005). All reported data are below the CS concentrations except for anthracene data from a Swedish study (Norin et al., 2004). That study compared leachate from a two-year-old asphalt storage pile with a recently crushed asphalt. These piles produced anthracene concentrations of 500 ng/L and 100 ng/L respectively. These anthracene concentrations are well above the surface water CS for anthracene (35 ng/L) but are not reflective of the concentrations that might leach from asphalt mixed with soil because soil would absorb much of the PAH from solution. However, if coal tar sealants are used, as is common for parking lots, runoff can include up to 10.2 mg/L PAH (Mahler, 2005).

Table 3.12. PAH Concentrations in Leachate

Material:	Surface Water[1]	Conventional Middle East penetration bitumen[2]	Conventional Heavy Venezuelan penetration bitumen[2]	Conventional Heavy Venezuelan penetration bitumen[2]	Multiphalte® bitumen[2]	Asphalt stored 2 yrs, Harryda, Sweden[3]	Asphalt not stored, Harryda, Sweden[3]
Method:		pH 4 water leachate	pH 4 water leachate	pH 4 water leachate	pH 4 water leachate	pH 4 water leachate	pH 4 water leachate
	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
Fluoranthene	1900	0.4	1.7	0.8	1	100	100
Pyrene		0.4	3.9	1.4	4	100	100
Benz(a) anthracene		0.1	1.4	0.45	b.d.l.	b.d.l.	b.d.l.
Chrysene		0.3	5.3	0.83	b.d.l.	b.d.l.	b.d.l.
Benzo(b)fluoranthene		b.d.l.	0.4	0.14	b.d.l.	b.d.l.	b.d.l.
Benzo(k)fluoranthene		b.d.l.	0.2	0.14	b.d.l.	b.d.l.	b.d.l.
Benzo(a)pyrene		b.d.l.	0.1	0.3	b.d.l.	b.d.l.	b.d.l.
Benzo(ghi)perylene		b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Dibenz (ah)anthracene		b.d.l.	b.d.l.	b.d.l.	b.d.l.	40	200
Indeno(1,2,3-cd)pyrene		b.d.l.	b.d.l.	b.d.l.	b.d.l.	20	40
Phenanthrene	3600	4.1	180	47	82	1800	700
Anthracene	35	0.1	12	5	28	500	100
Naphthalene	65000	35	371	51	168	28000	9200
Fluorene		2.1	42	7	44	2100	500
Acenaphthene	20000	1.3	17	5	11	3000	700
Coronene		0.03	0.05	0.09	b.d.l.		

[1] (Minnesota Pollution Control Agency, 2005); [2] (Brandt, 2001); [3] (Norin, 2004)
b.d.l. = below detection limit

Conclusion

Asphalt pavement concentrations of PAHs appear not to be problematic when recycling asphalt as aggregate under road. However coal tar pavements may be of concern. Our data show coal tar is not often found in asphalt streets, at least in Minneapolis, even for streets that date back to 1918. The BaP equivalency concentrations can exceed the SRV limits for some streets but this may not limit the reuse of these asphalts as aggregate or in the incorporation into the base during cold in-place recycling. The dilution with soil or other aggregate materials will decrease PAH concentrations below the SRV limits. The asphalt concentrations do not exceed SLV limits which suggest leaching should not be a problem. Leaching of PAHs might be a problem for parking lots, driveways and airport runways where coal tar sealants have been used.

Chapter 4: Conclusion

The Minnesota Pollution Control Agency Soil Reference Value (SRV) and Soil Leaching Value (SLV) worksheets provide easily calculated risk-based guidance concerning human health risk posed by waste construction materials under roads. The SRV worksheet calculates limits that minimize risk resulting from direct human contact with contaminants of concern (COC) in soil. The SLV worksheet calculates upper limits that will minimize the potential for contamination of groundwater. If the concentrations of COCs are known for soil and a waste material it is easy to calculate the concentration in mixtures and compare to SRV and SLV limits. We successfully used this approach in a previous project where we developed a computer based tool, Screening Tool for the Utilization of Waste Materials in Paving Projects (STUWMPP), for setting risk-based limits for assessment of fly ash use in soil.

The SRV limits vary with assumed exposure scenario. In our evaluations we used the SRV limits for residential exposure (unrestricted land use), which assume the most human contact with soil compared to other scenarios. This generates the lowest SRV concentrations. The industrial and short-term worker scenarios assume less contact and generate higher SRV concentrations. Concentration limits calculated assuming residential exposure are very highly protective for waste application under a pavement and even are protective if base materials containing waste are placed in a residential setting during future reconstruction, or abandonment.

We used the 1999 SRV risk assessment that was in place when the project was initiated. More recently, 2006, MPCA reassessed the SRV limits based on the most recent USEPA risk data. This resulted in a very significant reduction in the SRV limits for some elements, including copper and arsenic. The residential exposure SRV concentrations for copper decreased from 100 ppm to 11 ppm and for arsenic from 10 ppm to 5 ppm. These new concentration limits are within the range for unpolluted soils in Minnesota, which implies that many soils in Minnesota are problematic for residential use. If the new limits remain in force for residential land use scenario, addition of any material containing more than 11 ppm copper or 5 ppm arsenic could be considered to be problematic. The 2006 SRV limits may still be useful for assessment of risk of waste materials containing more copper and arsenic if the exposure scenario changes from residential to worker or industrial exposure. In this case the more permissive short-term worker or industrial exposures could be used.

The SLV limits vary with the potential leaching to groundwater. Thus, the limits are greater for finer textured soils with deeper groundwater than for coarse soils with shallow groundwater. Also, for many COCs leaching is pH dependent, decreasing at higher pH. The SRV limits assume infiltration of rainwater in bare soil. When applied to materials used under a pavement the SRV limits area very highly protective, even allowing for the possibility of removal of the pavement in the future.

In the determination of inorganic elemental concentrations in fly ash and soil, high temperature acid digestion using EPA 846 methods 3050 or 3051 is sufficient for the assessment of potential environmental or human health risk. More rigorous digestion, like the EPA 846 method 3052, which is used to determine the total concentrations, is not necessary. In fly ash sources that contain > 20,000 ppm (2%) sulfur the extraction of barium is incomplete due to the formation of barium sulfate in the digestion vessels. For high sulfur ash it is necessary to repeat the extraction using a 10-fold reduction in sample size to determine barium.

Concentrations of the COC were determined for 14 high clay sub-soils that are typical of soils that could benefit from stabilization with fly ash. The data show a wide range of concentrations of many of the COCs. These soils were sampled in areas where there was minimal likelihood of human disturbance and we conclude the variation is natural variation in the soils. Comparison of the arsenic concentrations (mean = 5.4, range = 1.7 ppm to 9.6 ppm) shows that the mean value is greater than the 2006 residential SRV. The maximum value measured is close to the residential limit of 10 ppm for the 1999 SRV worksheet. Comparison of the copper concentrations (mean 15.8, range = 10.5 ppm to 22.4 ppm) shows that all except the lowest concentration is above the 2006 limit.

Eighteen fly ash generating plants were sampled periodically over periods of 2 to 7 weeks. The data for the COC show that the concentrations vary greatly depending coal source, addition of auxiliary fuels, type of burner, and type of pollution control devices. Generally ash from eastern bituminous coals is more problematic for soil stabilization because of higher arsenic compared to western coals. However, all the ash generators we sampled are currently burning sub bituminous coal from the Powder River Basin (PRB) in Wyoming and Montana. The cleanest ash sources were from pulverized coal injection burners with Wyoming PRB coal, with or without wood as an added fuel. Among these ash sources the cleanest was the Xcel Sherco 3 plant, which uses lime scrubbing to remove SO_2 from the stack gases. The lime dilutes the minor elements. However, this ash source is not acceptable for soil stabilization due to the high sulfur content, which causes unwanted expansion in stabilized soils. Cyclone boilers require a higher heat value fuel than PRB sub bituminous coal and another fuel must be added such as petroleum coke. This can increase concentrations of some elements. Vanadium and nickel are higher in the King and Riverside 8 ash due to the addition of petroleum coke. Cyclone boilers also produce a high carbon ash, which removes mercury from the flue gas increasing the Hg concentration in the ash. The Ottertail Power Big Stone plant adds waste tires and sewage sludge into the fuel mix, which produces an ash that is more than 5 times higher in zinc than any of the other ash sources. The American Crystal Sugar plants burn Montana PBR coal using traveling grate boilers. This fly ash is higher in arsenic as compared to most PBR coal burning plants.

Generally the COC have higher concentrations in ash than in soils and the addition of any amount of ash will increase concentrations of COC when ash is added to stabilize a soil. We evaluated ash/soil mixes of 10% and 20%, representing a realistic range of fly ash application rates for soil stabilization. In these calculations we added ash to a soil with mean concentrations of COC. The SLV limits were calculated for a silty clay soil with a pH 7 and a distance to water table of 3 ft. The shallow water table assumption was used to illustrate a worst case situation. The results showed that strontium, silver, tin and antimony and lead, are never problematic for the ash sources we sampled. The most problematic elements were arsenic, barium, vanadium, and copper, but copper is problematic only if the 2006 residential limits are used. We found that SRV, and not SLV limits, set the upper concentration for ash addition. When the 1999 SRV limits were used, our calculations suggest that 6 of the ash sources could be used at 20% and 8 of the sources can be used at greater than 10% but not at 20%. Only the American Crystal Sugar ash sources and the Minnesota Power Hibbard plant ash cannot be used in 10% mixtures. This is due to high arsenic contents.

Asphalt pavement concentrations of PAHs in Minneapolis streets appear not to be problematic for placement of recycled pavement under roads except when coal tar has been used. Coal tar appears to be rare in the streets of Minneapolis even for roads that date back to 1918 and it is rather easy to detect because it is sticky and has unique odor. The benzo(a)pyrene (BaP) equivalency concentrations can exceed the residential SRV limits for some streets but this should not limit the reuse of these asphalts as aggregate or in the incorporation into the sub-base during recycling. The dilution with soil or other aggregate materials will decrease PAH concentrations below the residential SRV limits. The asphalt PAH concentrations do not exceed SLV limits, which suggest leaching should not be a problem. The Minneapolis data suggest that, in general, asphalt incorporation into aggregate or sub-base in Minnesota will not cause problems due to PAH contents unless coal tar has been used in the asphalt.

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Appendix A: Quality Control/Quality Assurance of Soil and Fly Ash Data

Quality control (QC)/quality assurance (QA) activities included a digestion blank run with every set of extractions. Plus, a sample extraction duplicate was run with every other set of extractions. If no duplicate was analyzed, then a standard material was included with the digestion set. Digestion blank solutions contained only the digestion acid mixture.

Table A.1 gives the mean concentrations measured in the digestion blank solution for fly ash digestions and for a soil digestion. Coefficients of variation are given for each element for the fly ash blanks. Elements with the largest coefficient of variation are Cr (240%), Ag (117%), Co (116%), Ni (110%), Se (105%), As (101%), and Be (101%). To understand if background/blank COC concentration are an issue for COC in fly ash, we calculated the percentage the mean blank concentration is of the mean ash COC concentration. Almost all blank COC concentrations were less than 2% of the mean ash COC concentration. However, percentages were higher for the elements: Ni (2.33%), Ag (23.2%), Sn (35.5%), Sb (32.9%), Tl (9.23%), Cr (5.83%). All COC are found at concentrations less than the SRV or SLV limits. Considering that only Cu, As, V and Ba are elements that are close to SRV limits for ash/soil mixtures these results are acceptable.

The soil digestion blank proved similar to the ash blanks. However, due to the smaller quantities found in soil compared to ash, blank percentage of mean soil values are higher. This is especially pronounced in Ag (33.1%), Sn (18.6%), B (17.4%), Cu (16.5%), Mo (9.76%) and Ni (8.58%). Copper is an element that posses a problem when using the 2006 SRV, however the amount present in the sample blank is not enough to account for the surpassed limits. The other COC are far from the SRV or SLV limits.

Table A.1. COC Concentrations in Blank Solutions

COC (ppm)	Ash Blank Mean	Coefficient of Variance	Ash Blank % of the mean ash	Soil Blank	Soil Blank % of mean soil
Be	0.0258	101 %	0.861 %	0.00273	0.457 %
B	7.91	51.4 %	1.35 %	3.06	17.4 %
Co	0.0270	116 %	0.133 %	0.0059	0.0434 %
Ni	3.17	110 %	2.33 %	2.2	8.58 %
Cu	2.60	0.722 %	1.72 %	2.6	16.5 %
Zn	1.46	192 %	0.301 %	2.78	5.65 %
As	0.0637	101 %	0.332 %	0	0
Se	0.153	105 %	1.66 %	0	0
Sr	0.466	45.8 %	0.0156 %	0.3	0.621 %
Mo	0.226	63.1 %	1.13 %	0.0615	9.76 %
Ag	0.377	117 %	23.2 %	0.68	33.1 %
Cd	0.0262	85.3 %	1.4 %	0.0209	5.51 %
Sn	0.350	75.8 %	35.5 %	0.132	18.6 %
Sb	0.0486	109 %	32.9 %	0.0066	7.14 %
Ba	0.698	29.5 %	0.0157 %	0.672	0.448 %
Tl	0.0680	130 %	9.23 %	0.0142	3.58 %
Pb	0.192	60.3 %	0.516 %	0.19	1.90 %
Cr	3.43	240 %	5.83 %	1.4	6.57 %
Mn	0.372	67.6 %	0.132 %	0.3	0.0444 %
V	1.80	3.78 %	0.861 %	1.8	7.04 %

Ash Standards were analyzed with every other digestion set. The ash standard is a certified reference material (CRM) 001-100 (Lot#AZ01) of fly ash provided by Resource Technology Corp. (RTC). The fly ash comes from a power plant in the Eastern part of the United States. It was chose as the standard because RTC provided certified values of trace metal concentration when using EPA Method 3051. Other standard providers only offer trace metal concentrations based on total values only. Table A.2 gives the mean concentrations measured in the ash standard solution. Coefficients of variation for the ash standard material were relatively low (given in Table A.2). Elements with the largest coefficient of variation are Sb (38.8%), Ag (34.3%), B (31.6%) and Sn (27.4%).

Table A.2. Ash Standard Mean and Standard Deviation

COC (ppm)	Mean Analytical Value	Ash Standard Coefficient of Variation
Be	0.755	15.0 %
B	30.1	31.6 %
Co	16.0	10.1 %
Ni	23.5	7.97 %
Cu	43.2	4.57 %
Zn	63.9	3.58 %
As	53.1	5.70 %
Se	3.16	12.4 %
Sr	944	5.19 %
Mo	20.4	5.91 %
Ag	0.689	34.3 %
Cd	0.841	4.64 %
Sn	0.810	27.4 %
Sb	0.101	38.8 %
Ba	482	4.57 %
Tl	0.382	11.1 %
Pb	25.8	6.10 %
Cr	30.5	5.26 %
Mn	327	3.26 %
V	97.5	4.31 %

Concentrations determined were reasonably close to actual certified values from RTC (Table A.3). Unfortunately RTC provides only four COC values as checks for the ash standard. Concentrations determined from our analysis were on mean higher than the certified values. This indicates that our digestion was more rigorous, yielding higher values, thus producing more conservative values for evaluation of human health risk.

Table A.3. Comparison of Ash Standard Mean to Certified Value

COC (ppm)	Certified Value	Mean Analytical Value	% Relative Difference
Ni	19.8	23.5	16.9 %
Cu	40.7	43.2	5.90 %
Ba	428	482	11.8 %
Cr	29.1	30.5	4.56 %

Similar findings were produced using the soil reference material (CRM) 001-100 (Lot#CF003) of non-polluted soil provided by Resource Technology Corp (RTC). However, more COC were given to make comparisons with. All COC quantified, besides Ni, Cd and Pb were higher than certified values. Once again, this demonstrates a more rigorous digestion.

Table A.4. Comparison of Soil Standard to Certified Value

COC (ppm)	Certified Value	Mean Analytical Value	% Relative Difference
Be	0.7	0.714	2.04 %
Co	9.3	15.2	48.1 %
Ni	8	7.56	5.62 %
Cu	9.7	9.79	0.913 %
Zn	112.3	115	2.34 %
As	2	2.9	17.7 %
Se	0.3	1.28	124 %
Cd	0.53	0.264	67 %
Ba	204.3	207	1.3 %
Pb	17.3	14.6	17.1 %
Cr	9	11.9	27.5 %
Mn	557.3	564	1.23 %
V	17.4	26.9	42.9 %

For runs without a standard, a sample digestion duplicate was analyzed. Table A.5 gives percentage differences for all digestion duplicates. Percentage differences were calculated by dividing the difference in COC concentrations between the samples by the mean of the two samples. Silver, Sn and Sb consistently showed the most variance between sample duplicates. The Big Stone ash sample duplicate was more variable compared to the other sample duplicates. This could potentially be a result of the heterogeneous fuel Big Stone uses (coal, tires, sewage sludge). However, these elements are far below SRV/SLV limits and thus we don’t anticipate any issues with them.

Table A.5. Relative Differences Between Sample Duplicates

COC (ppm)	King	King	Rvsd 6& 7	Rvsd 8	High Bridge	Black Dog	Black Dog	Big Stone
Be	9 %	1 %	3 %	1 %	0 %	2 %	5 %	23 %
B	1 %	3 %	3 %	0 %	2 %	1 %	1 %	30 %
Co	16 %	3 %	2 %	3 %	3 %	2 %	2 %	14 %
Ni	14 %	9 %	5 %	5 %	3 %	6 %	1 %	5 %
Cu	13 %	2 %	4 %	3 %	1 %	7 %	11 %	5 %
Zn	11 %	5 %	5 %	3 %	2 %	22 %	13 %	1 %
As	3 %	5 %	3 %	4 %	5 %	3 %	0 %	15 %
Se	12 %	1 %	2 %	3 %	3 %	3 %	10 %	23 %
Sr	11 %	1 %	4 %	2 %	1 %	1 %	6 %	4 %
Mo	7 %	0 %	2 %	0 %	7 %	3 %	6 %	25 %
Ag	96 %	23 %	9 %	48 %	66 %	100 %	75 %	94 %
Cd	5 %	0 %	3 %	3 %	4 %	1 %	5 %	3 %
Sn	54 %	53 %	3 %	25 %	136 %	78 %	88 %	148 %
Sb	78 %	29 %	13 %	31 %	152 %	58 %	84 %	95 %
Ba	11 %	5 %	7 %	32 %	5 %	4 %	4 %	123 %
Tl	82 %	2 %	2 %	14 %	85 %	35 %	54 %	36 %
Pb	9 %	1 %	2 %	1 %	3 %	1 %	0 %	5 %
Cr	22 %	7 %	4 %	5 %	1 %	13 %	1 %	5 %
Mn	12 %	3 %	4 %	3 %	2 %	8 %	15 %	3 %
V	11 %	0 %	3 %	1 %	1 %	7 %	5 %	0 %

Table A.5 Relative Differences Between Sample Duplicates (continued)

COC (ppm)	U2 Hoot Lake	U3 Hoot Lake	M.L. Hibbard	REC	ACS	Genoa	Alma
Be	1 %	1 %	8 %	2 %	4 %	4 %	3 %
B	2 %	3 %	1 %	3 %	5 %	1 %	3 %
Co	0 %	14 %	9 %	4 %	4 %	2 %	16 %
Ni	2 %	19 %	8 %	8 %	3 %	2 %	12 %
Cu	1 %	12 %	9 %	6 %	2 %	4 %	3 %
Zn	0 %	13 %	1 %	1 %	1 %	1 %	10 %
As	4 %	8 %	11 %	4 %	1 %	3 %	0 %
Se	1 %	1 %	3 %	5 %	2 %	9 %	9 %
Sr	2 %	8 %	11 %	2 %	3 %	2 %	1 %
Mo	11 %	75 %	9 %	6 %	42 %	3 %	1 %
Ag	7 %	9 %	77 %	36 %	51 %	39 %	34 %
Cd	1 %	3 %	7 %	5 %	0 %	1 %	3 %
Sn	8 %	58 %	-2 %	42 %	50 %	5 %	29 %
Sb	27 %	54 %	27 %	34 %	53 %	27 %	30 %
Ba	13 %	20 %	55 %	1 %	3 %	1 %	3 %
Tl	1 %	4 %	22 %	120 %	5 %	10 %	0 %
Pb	2 %	13 %	0 %	3 %	6 %	7 %	14 %
Cr	2 %	13 %	34 %	14 %	2 %	1 %	11 %
Mn	1 %	13 %	5 %	19 %	3 %	1 %	0 %
V	6 %	4 %	1 %	10 %	1 %	2 %	2 %

For soil digestions, two samples were run in duplicates. Percentage differences between the two samples are given in Table A.6. Soils are more variable in composition so it is expected that larger relative differences are found compared to the ash duplicates.

Table A.6. Relative Differences Between Sample Duplicates

COC (ppm)	Faribault	Nobles
Be	4.42 %	9.80 %
B	22.0 %	42.7 %
Co	0.0608 %	8.87 %
Ni	0.0209 %	17.5 %
Cu	2.07 %	1.33 %
Zn	0.678 %	7.87 %
As	0.862 %	7.13 %
Se	14.9 %	10.3 %
Sr	1.18 %	0.305 %
Mo	6.78 %	22.6 %
Ag	30.7 %	47.7 %
Cd	0.0136%	0.542 %
Sn	47.6%	40.3 %
Sb	74.4%	59.3%
Ba	0.662%	9.89%
TI	17.4%	13.6%
Pb	3.31%	1.14%
Cr	4.84%	34.1%
Mn	1.00%	12.4%
V	2.91%	25.3%

Appendix B: Soil and Fly Ash Data

Table B.1. Sub-soil COC Concentrations

COC (mg/kg)	Grant	Blue Earth	Marshall	Rock	Swift	Polk	Clay
Hg	0.0237	0.0265	0.00770	0.0294	0.0179	0.0228	0.0409
Be	0.542	0.641	0.398	0.602	0.561	0.602	0.637
B	24.1	14.1	16.7	6.57	24.6	17.8	17.5
Co	12.0	23.4	18.4	17.3	10.2	10.6	12.0
Ni	29.0	29.5	18.7	26.5	15.6	22.9	28.0
Cu	18.7	16.2	11.5	15.4	15.1	18.0	20.6
Zn	45.3	58.2	41.7	41.9	42.2	42.6	68.9
As	7.53	4.65	1.89	6.18	1.67	6.35	4.63
Se	1.24	1.07	0.665	0.733	1.11	0.754	0.654
Sr	103	29.9	24.9	27.9	30.7	80.8	35.7
Mo	1.70	0.401	0.267	0.449	0.642	0.324	0.285
Ag	1.79	0.797	0.511	0.501	1.45	0.869	0.913
Cd	0.521	0.323	0.236	0.174	0.497	0.376	0.492
Sn	1.42	0.528	0.375	0.226	1.50	0.655	0.658
Sb	0.231	0.0719	0.0410	0.0151	0.232	0.0963	0.119
Ba	160	196	83.4	155	112	96.3	153
Tl	0.732	0.341	0.207	0.225	0.624	0.396	0.438
Pb	8.52	11.9	5.52	9.59	9.57	9.46	11.8
Cr	15.0	27.0	20.4	20.5	14.7	15.9	18.7
Mn	680.	919	453	622	219	468	932
V	26.0	30.5	18.8	25.4	12.5	28.0	21.6

Table B.1. Sub-soil COC Concentrations (continued)

COC (mg/kg)	Scott	Chippewa	Waseca	Lac Qui Parle	Faribault	Jackson	Nobles
Hg	0.0221	0.0244	0.0147	0.0224	0.0404	0.0481	0.0265
Be	0.464	0.339	0.663	0.607	0.691	0.740	0.879
B	10.7	8.74	22.7	20.1	13.9	32.2	17.1
Co	19.1	12.9	11.1	11.4	16.4	7.53	7.90
Ni	20.7	18.9	27.6	24.7	28.7	37.4	30.7
Cu	10.5	12.1	13.5	15.5	16.0	15.1	22.4
Zn	36.9	33.4	53.6	44.3	69.4	52.1	58.2
As	8.77	5.19	3.63	4.87	4.67	6.70	9.56
Se	0.589	0.663	1.07	0.948	1.08	0.774	0.848
Sr	36.5	43.4	26.6	107	26.5	36.4	67.0
Mo	0.851	0.809	0.663	0.595	0.550	0.874	0.414
Ag	0.562	0.474	1.52	0.717	0.564	12.5	5.64
Cd	0.242	0.319	0.309	0.435	0.366	0.470	0.554
Sn	0.490	0.396	1.19	1.06	0.422	0.799	0.207
Sb	0.0528	0.0485	0.177	0.0627	0.0461	0.0834	0.0187
Ba	138	90.1	163	186	222	210	136
Tl	0.287	0.278	0.513	0.359	0.382	0.408	0.371
Pb	9.36	8.43	8.66	10.5	13.2	10.3	13.0
Cr	14.3	12.4	27.5	12.9	27.5	44.0	27.7
Mn	594	497	472	715	1350	945	587
V	18.2	16.0	24.8	17.5	38.1	36.6	43.9

Table B.2. Fly ash COC Concentrations

COC (mg/kg)	ACS Crookston	ACS Crookston	ACS EGF	ACS EGF	ACS Moorhead	ACS Moorhead
Date sampled	1/11/05 1100	1/11/05 1530	1/11/05 0930	1/11/05 1400	1/10/05 1000	1/10/05 1600
Be	1.99	1.93	2.40	1.87	1.93	1.47
B	441	440	398	423	430	340
Co	12.1	11.5	12.0	11.2	13.0	10.5
Ni	30.6	28.9	29.1	31.3	32.3	29.3
Cu	252	216	199	190	243	255
Zn	198	162	132	119	196	220
As	83.6	76.5	68.4	75.8	99.1	87.6
Se	12.6	13.6	12.5	13.3	11.4	9.22
Sr	2510	2570	3000	3750	2530	1830
Mo	15.8	16.8	21.3	20.2	15.0	24.9
Ag	2.08	2.27	2.18	1.34	1.52	1.43
Cd	3.46	3.09	2.24	3.03	3.60	3.58
Sn	2.25	2.94	3.79	3.45	1.61	5.59
Sb	0.383	0.502	0.795	0.606	0.299	1.07
Ba	11000	8740	12300	12100	10200	9020
Tl	3.66	3.02	2.44	2.90	2.88	3.06
Pb	52.8	48.1	30.4	45.7	54.3	44.8
Cr	33.6	31.3	31.3	34.1	38.0	32.3
Mn	185	182	189	206	206	165
S	99200	85600	58200	53200	80100	91200
V	149	147	162	172	150	126
Hg	0.770		0.757		0.794	

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	HEC	HEC	HEC	HEC	HEC	HEC	HEC
Date sampled	11/01/04	11/23/04	12/05/04	12/13/04	12/18/04	12/22/04	12/28/04
Be	1.23	1.55	2.14	1.91	2.00	1.17	1.16
B	221	379	365	281	385	259	297
Co	8.17	10.9	11.2	11.9	10.9	7.96	9.20
Ni	24.2	43.9	19.5	46.9	36.0	25.3	31.1
Cu	65.0	141	52.0	129	120	105	149
Zn	141	793	259	612	697	543	666
As	4.36	50.9	14.3	20.6	18.2	35.3	73.5
Se	0.908	4.67	3.27	3.31	3.75	5.06	6.74
Sr	2230	2010	1370	2330	2190	1830	1730
Mo	5.49	13.5	7.04	10.6	11.2	6.34	19.0
Ag	1.92	2.25	1.60	1.75	2.68	1.08	0.575
Cd	0.660	3.73	2.38	3.67	2.57	2.61	2.82
Sn	1.51	2.97	1.33	2.11	2.56	2.44	3.02
Sb	0.216	0.227	0.0973	0.129	0.241	0.132	0.129
Ba	3420	2130	988	1960	1880	2110	1470
Tl	0.387	0.903	0.405	0.521	0.716	0.521	0.546
Pb	14.4	63.3	28.0	52.7	45.3	38.5	39.7
Cr	26.0	75.7	23.8	51.5	70.0	42.5	63.0
Mn	636	1760	607	1220	1060	898	903
V	67.7	92.5	49.4	107	96.9	81.0	86.3

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	BEC	BEC	REC	REC	REC	REC	REC	REC
Date sampled	1/12/05	1/15/05	10/18/04 0700; 40% coal	10/18/04 0930; 40% coal	10/18/04 1200; 35% coal	10/18/04 1600; 35% coal	10/25/04 1030; 80% coal	10/25-11/01/04; 63% coal
Be	3.54	3.21	0.916	0.784	0.700	1.02	1.71	1.21
B	872	795	342	352	357	272	419	284
Co	13.4	12.1	5.26	5.36	5.30	5.81	5.77	5.86
Ni	35.8	33.4	8.73	8.56	8.75	10.8	9.61	9.48
Cu	141	107	143	160	183	116	139	111
Zn	69.8	56.0	943	1330	1600	649	431	286
As	24.2	28.9	3.55	4.92	5.44	3.58	5.89	3.65
Se	12.9	11.9	2.48	3.05	3.44	1.88	3.12	2.03
Sr	5460	5130	930	890	894	884	2050	1440
Mo	14.9	25.1	4.88	5.04	5.39	4.67	8.58	5.34
Ag	0.967	1.06	0.406	1.28	0.386	0.196	0.216	0.782
Cd	1.04	1.03	7.75	8.96	10.1	3.85	3.10	2.01
Sn	0.987	1.70	0.826	1.47	1.01	0.598	0.716	0.795
Sb	0.0588	0.0928	0.140	0.272	0.225	0.085	0.144	0.141
Ba	5620	5800	1170	1020	1130	1190	1520	1710
Tl	0.861	0.895	1.91	0.732	0.539	0.212	0.289	0.377
Pb	27.8	27.0	16.1	20.7	23.7	10.8	28.1	8.56
Cr	52.9	51.1	13.3	12.1	13.7	19.5	13.9	15.9
Mn	497	516	1550	1590	1540	1200	1140	1330
V	168	165	27.7	23.3	23.0	29.5	48.2	39.4

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	Genoa	Genoa	Genoa	Genoa	Genoa	Genoa	Genoa
Date sampled	2/16/05 0700	2/21/05 0715	3/01/05 0700	3/07/05 0700	3/07/05 1015	3/07/05 1120	3/07/05 1330
Be	3.62	4.06	3.55	3.87	4.08	4.68	5.27
B	817	897	784	877	877	1000	1190
Co	10.7	12.5	11.6	12.1	13.0	13.8	13.8
Ni	27.1	33.3	30.9	31.7	34.0	36.1	30.5
Cu	70.8	82.8	72.6	75.5	80.3	83.9	77.0
Zn	116	184	131	147	167	171	172
As	16.4	18.3	16.6	20.6	20.1	20.8	23.7
Se	5.07	5.02	4.26	4.76	4.73	5.50	5.46
Sr	1310	1440	1330	1340	1370	1430	1330
Mo	7.06	7.50	6.76	7.37	7.86	8.17	7.61
Ag	1.96	1.73	1.14	0.862	2.30	8.43	2.48
Cd	1.85	3.05	2.07	2.54	2.82	3.01	3.64
Sn	1.41	0.756	0.724	0.701	1.52	1.45	0.817
Sb	0.221	0.103	0.0808	0.0819	0.232	0.244	0.131
Ba	2410	2780	2570	2650	2680	2680	2510
Tl	1.26	1.20	1.14	1.16	1.49	1.60	1.33
Pb	36.2	56.2	40.7	49.4	54.3	59.2	65.8
Cr	54.1	65.7	56.4	58.6	60.9	63.5	55.5
Mn	100	114	104	104	112	113	103
V	139	157	138	148	147	149	144

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	Genoa 3/07/05 1410	Genoa 3/07/05 1430	Genoa 3/08/05 0715	Genoa 3/14/05 0730
Be	5.12	5.45	3.80	4.20
B	1110	1190	849	944
Co	13.1	13.4	11.4	12.7
Ni	30.8	39.9	30.7	35.0
Cu	78.0	79.8	79.9	87.2
Zn	212	197	211	252
As	24.0	24.2	19.4	20.6
Se	5.13	4.77	4.60	4.52
Sr	1310	1350	1370	1400
Mo	7.32	8.55	6.86	6.98
Ag	2.05	1.49	9.82	3.46
Cd	4.82	4.27	4.52	5.10
Sn	0.719	0.660	1.26	0.809
Sb	0.101	0.0952	0.241	0.113
Ba	2440	2520	2560	2620
Tl	1.15	1.22	1.25	1.00
Pb	80.1	73.5	71.0	80.5
Cr	55.3	57.6	55.8	61.0
Mn	108	107	106	113
V	140	148	143	146

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	JPM 2/16/05 0630	JPM 2/16/05 0830	JPM 2/16/05 0915	JPM 2/16/05 1000	JPM 2/16/05 1115	JPM 2/16/05 1215	JPM 2/16/05 1300
Be	2.65	2.79	3.15	3.13	3.12	2.94	2.44
B	646	606	585	587	568	588	508
Co	18.8	19.4	20.2	20.4	20.3	20.1	16.8
Ni	48.0	42.8	40.1	41.5	39.9	41.8	42.4
Cu	180	180	159	161	159	173	152
Zn	59.3	65.3	76.5	82.1	84.6	74.6	64.8
As	10.0	10.4	10.9	10.6	10.9	11.0	8.98
Se	9.87	10.2	9.15	9.07	8.77	10.2	8.01
Sr	3380	3370	3000	2990	2970	3210	2600
Mo	5.30	6.32	6.64	6.44	6.41	2.06	5.00
Ag	1.21	0.756	1.69	0.976	0.856	0.650	1.00
Cd	0.984	0.990	0.989	0.977	1.02	1.01	0.892
Sn	0.291	0.212	0.679	0.295	0.259	0.180	0.323
Sb	0.0387	0.0362	0.0861	0.0457	0.0344	0.0132	0.0366
Ba	5170	5250	5130	5170	5030	5120	3990
Tl	0.145	0.1303	0.261	0.183	0.156	0.127	0.133
Pb	24.5	24.6	26.2	27.1	26.7	26.3	21.3
Cr	81.9	81.8	79.5	83.0	80.8	88.1	76.4
Mn	239	225	179	191	197	217	209
V	214	224	214	216	217	202	197

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	JPM 2/17/05 0630	JPM 2/18/05 0500	JPM 2/23/05 wk	JPM 3/02/05 wk	JPM 3/09/05 wk	JPM 3/15/05 wk	JPM 3/22/05 wk
Be	2.87	2.81	2.90	2.74	2.54	2.94	2.87
B	583	605	597	725	741	654	695
Co	18.8	19.3	19.6	18.4	18.2	19.1	19.3
Ni	49.0	50.1	46.0	40.1	40.2	43.4	41.7
Cu	166	170	168	191	185	196	195
Zn	70.8	71.6	71.1	49.0	46.3	53.3	54.6
As	9.86	10.7	11.3	11.2	9.90	11.9	12.1
Se	10.0	10.7	11.1	12.1	11.7	10.9	11.2
Sr	3140	3190	3140	3640	3650	3390	3470
Mo	6.20	6.23	4.41	7.13	7.07	7.17	7.34
Ag	0.823	0.612	29.2	0.949	1.83	0.950	0.659
Cd	1.03	1.05	1.02	1.16	1.01	1.59	1.11
Sn	0.265	0.284	0.699	0.348	0.665	0.387	0.505
Sb	0.0364	0.0311	0.0594	0.0581	0.109	0.0559	0.0522
Ba	4830	4650	5080	4680	5280	5010	4810
Tl	0.117	0.102	0.240	0.132	0.207	0.130	0.111
Pb	25.3	24.7	25.4	25.1	24.1	25.3	25.1
Cr	84.9	70.5	86.7	80.5	78.4	89.2	84.0
Mn	264	299	266	399	261	226	241
V	212	217	204	234	220	230	235

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	Alma 2/16/05 1045	Alma 2/16/05 1230	Alma 2/17/05 NG	Alma 2/18/05 0900	Alma 2/18/05 1300
Be	2.52	2.23	1.67	1.98	2.11
B	605	546	488	561	502
Co	3.54	3.27	2.14	2.59	3.12
Ni	13.3	11.3	7.26	9.91	12.0
Cu	26.2	24.5	18.8	21.3	23.0
Zn	92.5	84.1	63.3	77.3	81.6
As	10.5	9.41	8.84	10.1	9.87
Se	6.29	5.86	4.91	5.89	5.46
Sr	1050	999	840	903	965
Mo	4.70	4.21	3.69	4.20	5.60
Ag	1.88	1.16	0.537	0.475	2.81
Cd	3.07	2.93	2.77	2.92	2.70
Sn	1.19	0.747	0.664	0.635	1.45
Sb	0.231	0.131	0.181	0.126	0.314
Ba	1120	1090	917	988	1050
Tl	0.651	0.426	0.354	0.350	0.758
Pb	24.5	22.3	18.7	21.0	24.6
Cr	26.2	23.3	17.3	20.2	24.8
Mn	62.5	65.0	57.6	64.9	64.2
V	52.4	48.8	39.1	46.3	48.3

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	Alma 2/21/05 1000	Alma 2/23/05 wk	Alma 3/01/05 wk	Alma 3/09/05 wk	Alma 3/15/05 wk	Alma 3/21/05 wk
Be	1.94	2.06	2.07	2.68	3.39	2.80
B	511	506	524	594	508	481
Co	2.77	2.68	2.43	4.43	5.78	4.39
Ni	10.2	8.80	9.10	23.9	23.0	17.1
Cu	21.9	20.4	18.7	27.1	41.8	31.6
Zn	83.0	76.8	40.1	33.7	42.7	40.5
As	9.86	9.43	9.54	10.4	10.1	10.9
Se	5.35	5.49	5.89	6.91	6.89	7.08
Sr	943	886	755	706	907	701
Mo	4.20	4.18	3.73	4.58	4.72	4.81
Ag	0.820	2.21	0.623	1.51	0.790	0.713
Cd	3.49	2.82	1.35	0.817	0.719	0.784
Sn	0.825	1.44	0.833	0.891	0.508	0.621
Sb	0.143	0.238	0.167	0.0911	0.0648	0.0657
Ba	998	937	933	1070	1390	1060
Tl	0.466	0.59	0.393	0.684	0.530	0.624
Pb	25.6	20.4	11.5	13.3	14.6	13.8
Cr	21.8	20.1	26.8	39.1	52.7	44.0
Mn	63.6	65.8	71.1	78.2	88.3	72.0
V	46.9	43.1	43.1	59.0	79.2	66.8

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	King 11/19/04 0930	King 11/19/04 1000	King 11/19/04 1030	King 3/4/05
Be	3.32	3.25	3.28	3.10
B	1020	1010	958	885
Co	24.5	24.1	24.6	20.5
Ni	769	737	756	886
Cu	232	227	231	209
Zn	198	193	198	140
As	19.8	20.0	18.5	17.6
Se	14.1	13.9	12.8	13.0
Sr	3730	3610	3580	3250
Mo	89.4	88.3	84.8	97.4
Ag	1.57	1.11	0.873	0.737
Cd	1.81	1.79	1.95	1.71
Sn	1.12	0.572	0.375	0.353
Sb	0.147	0.122	0.0755	0.0725
Ba	3410	3770	2500	3810
Tl	0.852	0.764	0.730	0.744
Pb	120	120	113	71.0
Cr	60.5	58.9	58.9	50.4
Mn	302	294	297	228
V	1350	1340	1360	1520

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	King	King	King	King
Date sampled	3/8/05	3/11/05	3/15/05	3/18/05
Be	3.29	3.32	3.63	3.44
B	978	880	986	1010
Co	21.6	23.3	24.4	23.0
Ni	823	958	834	809
Cu	215	214	225	235
Zn	151	164	170	160
As	18.2	17.4	19.5	21.3
Se	13.8	13.7	14.8	16.0
Sr	3390	3150	3410	3520
Mo	93.2	111	101	104
Ag	1.46	0.789	0.933	1.49
Cd	1.72	1.84	1.93	2.05
Sn	0.799	0.460	0.632	1.33
Sb	0.149	0.102	0.110	0.200
Ba	3810	3520	3660	3690
Tl	0.835	0.766	0.801	1.02
Pb	70.9	66.5	73.5	75.5
Cr	51.9	54.2	56.2	53.2
Mn	254	228	240	251
V	1470	1750	1580	1530

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	Riverside 8 10/28/04 0730	Riverside 8 10/29/04 0730	Riverside 8 10/29/04 1200	Riverside 8 10/30/04 0645	Riverside 8 10/30/04 1020
Be	3.23	2.89	2.85	2.83	3.02
B	691	553	587	595	654
Co	23.7	22.1	21.5	23.2	24.2
Ni	680	728	682	782	774
Cu	244	215	210	223	237
Zn	138	116	113	123	132
As	19.5	15.3	15.4	17.6	17.8
Se	15.4	11.7	11.4	13.0	13.5
Sr	2630	2430	2310	2360	2500
Mo	95.1	82.3	79.7	90.8	92.9
Ag	0.994	0.766	1.64	1.12	0.957
Cd	1.73	1.69	1.67	1.77	1.92
Sn	0.630	0.238	0.774	0.395	0.268
Sb	0.156	0.0470	0.142	0.0845	0.0635
Ba	3600	2440	3300	2540	2350
Tl	0.699	0.509	0.606	0.545	0.578
Pb	57.1	45.4	45.4	49.6	54.7
Cr	63.7	57.1	53.9	57.3	62.3
Mn	137	128	125	128	138
V	1570	1430	1420	1600	1600

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	Riverside 8-6 10/28/04 0730	Riverside 8-7 mean 11/01/04 0700	Riverside 8-8 11/08/04 0720	Riverside 8-9 11/15/04 0545	Riverside 8-10 11/22/04 0700
Be	3.26	2.87	3.01	3.67	3.81
B	717	711	577	695	710
Co	24.4	25.4	22.4	26.0	29.0
Ni	693	850	816	784	775
Cu	246	250	234	245	237
Zn	139	169	144	185	203
As	18.5	19.2	16.8	19.8	19.5
Se	13.9	15.4	12.8	13.9	13.7
Sr	2640	2380	2490	2490	2460
Mo	92.1	104	96.3	99.0	98.9
Ag	0.851	1.48	0.944	2.67	1.39
Cd	1.78	2.12	2.22	2.26	2.21
Sn	0.419	0.645	0.608	1.17	0.291
Sb	0.0923	0.113	0.0699	0.141	0.0794
Ba	3210	2650	2370	3770	3220
Tl	0.668	0.710	0.511	0.865	0.711
Pb	58.9	54.3	52.2	66.0	62.4
Cr	64.1	68.6	75.5	72.6	70.2
Mn	139	128	144	138	136
V	1570	1810	1760	1680	1620

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	Riverside 7	Riverside 7	Riverside 7	Riverside 7	Riverside 7
Date sampled	4/18/05	4/19/05	4/19/05	4/19/05	4/19/05
Be	3.08	3.01	3.02	3.43	3.28
B	353	348	344	394	377
Co	21.6	22.9	22.3	22.1	21.5
Ni	51.1	48.5	49.9	49.5	47.4
Cu	172	172	171	173	171
Zn	124	136	136	131	125
As	11.9	13.4	12.5	11.9	11.9
Se	10.2	11.0	10.0	10.4	9.85
Sr	2940	2800	2830	2940	2890
Mo	6.47	7.31	6.97	6.99	6.53
Ag	1.99	1.77	1.48	3.34	1.66
Cd	1.05	1.25	1.25	1.04	0.990
Sn	0.599	0.538	0.501	1.08	0.446
Sb	0.0798	0.0763	0.0723	0.178	0.0587
Ba	5780	5500	5510	5600	4940
Tl	0.516	0.515	0.496	0.707	0.458
Pb	36.3	36.1	37.9	32.1	31.3
Cr	102	91.2	96.1	96.6	95.3
Mn	151	136	143	145	142
V	235	243	240	239	234

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	Riverside 7	Riverside 7	Riverside 7	Riverside 7	Riverside 7
Date sampled	3/14/05	3/24/05	4/1/05	4/8/05	4/14/05
Be	3.47	3.08	2.79	3.17	3.44
B	375	492	404	373	343
Co	19.2	22.6	19.4	19.2	20.6
Ni	41.9	48.7	41.8	41.5	46.7
Cu	171	162	178	167	155
Zn	110	119	96.8	125	142
As	10.8	12.0	10.2	11.3	12.3
Se	9.57	10.3	9.15	9.54	10.0
Sr	2920	2810	2890	2960	2560
Mo	6.13	6.69	6.12	5.79	6.13
Ag	1.33	1.08	1.48	1.40	1.97
Cd	0.961	1.10	2.18	0.969	0.979
Sn	0.300	0.417	5.29	0.236	0.521
Sb	0.0429	0.0414	0.0808	0.0476	0.0755
Ba	5580	5280	5870	5460	4950
Tl	0.378	0.433	0.369	0.366	0.458
Pb	31.7	33.6	23.2	27.4	28.6
Cr	89.6	89.4	82.3	84.5	91.3
Mn	144	138	122	131	123
V	228	214	217	217	217

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	Sherco	Sherco
Date sampled	11/1/04	11/15/04
Be	2.06	2.30
B	854	808
Co	6.76	5.87
Ni	17.6	15.9
Cu	46.2	43.8
Zn	36.0	33.9
As	6.58	10.8
Se	4.72	4.28
Sr	3520	3160
Mo	6.97	7.25
Ag	0.694	0.547
Cd	0.533	0.580
Sn	1.88	1.88
Sb	0.0936	0.101
Ba	959	1290
Tl	0.267	0.319
Pb	28.1	28.7
Cr	29.8	28.9
Mn	430	465
V	60.8	61.1

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	High Bridge 11/16/05	High Bridge 11/25/04	High Bridge 12/01/04	High Bridge 12/07/04	High Bridge 12/20/04
Be	3.51	3.29	3.06	3.48	3.38
B	387	381	364	418	420
Co	18.0	18.1	19.6	18.1	18.7
Ni	34.6	34.3	39.2	35.7	35.0
Cu	145	143	147	147	152
Zn	86.2	77.2	106	81.1	85.0
As	9.66	9.18	10.6	10.5	10.2
Se	7.85	7.68	7.79	8.71	7.96
Sr	2780	2790	2660	2940	2900
Mo	6.11	6.10	6.18	6.25	6.34
Ag	1.63	1.39	1.27	2.57	1.32
Cd	0.908	0.826	0.908	0.827	0.790
Sn	0.466	0.387	0.544	0.911	0.352
Sb	0.115	0.0871	0.0467	0.178	0.0774
Ba	4780	5080	4840	4820	5310
Tl	0.356	0.304	0.300	0.505	0.292
Pb	29.8	28.1	30.0	25.9	26.5
Cr	66.8	61.3	64.3	65.0	61.7
Mn	136	132	126	131	136
V	215	205	208	205	208

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	High Bridge 12/17/04 0710	High Bridge 12/17/04 0820	High Bridge 12/17/04 0945	High Bridge 12/17/04 1100	High Bridge 12/17/04 1215
Be	3.32	3.41	3.24	3.44	3.33
B	354	400	387	401	402
Co	16.6	17.7	17.1	18.2	18.2
Ni	23.4	31.9	30.4	32.3	32.9
Cu	43.2	139	136	140	141
Zn	63.9	80.3	88.0	85.4	80.8
As	8.88	10.4	9.78	9.94	10.1
Se	7.96	8.37	7.66	8.16	8.52
Sr	946	2820	2780	2780	2820
Mo	5.87	6.49	6.05	6.09	6.36
Ag	3.29	3.26	1.36	1.20	1.79
Cd	0.860	0.861	0.799	0.852	0.874
Sn	1.12	1.25	0.542	0.421	0.704
Sb	0.357	0.211	0.0869	0.0450	0.119
Ba	488	4940	4310	4880	4960
Tl	0.647	0.595	0.319	0.282	0.415
Pb	28.8	28.1	26.1	27.8	27.4
Cr	31.5	59.2	56.8	60.2	60.1
Mn	331	128	124	129	129
V	97.2	203	200	200	201

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	Black Dog	Black Dog	Black Dog	Black Dog	Black Dog
Date sampled	4/26/05	4/26/05	4/26/05	4/27/05	4/27/05
Be	3.75	3.17	3.52	2.84	3.98
B	551	442	471	392	539
Co	201	188	19.0	17.9	21.9
Ni	38.8	40.0	36.1	39.0	42.6
Cu	138	141	135	144	151
Zn	94.3	102	98.4	96.2	102
As	12.0	11.1	13.0	11.2	12.4
Se	8.93	8.18	10.1	9.00	10.4
Sr	2680	2760	2750	2670	2830
Mo	6.77	6.26	6.84	6.26	6.92
Ag	17.1	4.52	1.85	1.21	6.23
Cd	0.940	0.96	0.940	0.920	0.990
Sn	1.09	0.44	1.34	0.290	0.720
Sb	0.210	0.13	0.250	0.040	0.160
Ba	4720	4850	4970	4680	5080
Tl	0.75	0.59	0.790	0.480	0.690
Pb	31.4	32.7	29.6	31.6	32.6
Cr	72.4	70.3	69.5	67.8	66.3
Mn	126	127	122	121	123
V	197	199	200	203	195

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	Black Dog	Black Dog	Black Dog	Black Dog	Black Dog
Date sampled	3/24/05	3/28/05	4/12/05	4/22/05	4/27/05
Be	3.97	2.94	3.15	3.85	3.43
B	661	494	520	477	484
Co	26.5	21.2	26.9	20.3	19.9
Ni	41.9	38.5	43.5	38.7	38.9
Cu	147	138	157	138	130
Zn	115	71.2	102	105	110
As	11.9	10.7	12.1	11.8	12.6
Se	11.1	9.39	9.57	8.91	10.5
Sr	2860	2720	2860	2820	2900
Mo	5.93	6.82	7.37	6.44	6.52
Ag	2.25	1.13	1.27	1.24	1.02
Cd	0.920	0.870	0.950	0.940	0.920
Sn	0.280	0.700	0.430	0.840	0.540
Sb	0.060	0.110	0.060	0.170	0.120
Ba	4980	4920	5130	4970	5010
Tl	0.500	0.520	0.540	0.570	0.540
Pb	28.1	22.3	25.5	29.1	32.0
Cr	71.0	60.2	63.3	69.4	69.5
Mn	129	147	133	117	107
V	203	188	196	201	195

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	Big Stone 2/3/05 1200	Big Stone 2/4/05 1200	Big Stone 2/4/05 pm	Big Stone 2/14-18/05	Big Stone 2/21-25/05	Big Stone 3/4/05
Be	3.95	3.73	3.42	4.06	2.96	3.00
B	1190	1150	1070	1250	897	908
Co	64.0	72.4	69.4	65.1	55.0	54.6
Ni	71.6	71.7	72.3	73.2	70.9	67.0
Cu	335	348	335	343	322	318
Zn	7390	8270	8380	8360	8650	8430
As	23.2	22.3	24.8	18.6	17.7	17.2
Se	20.4	18.2	34.9	18.3	15.2	14.0
Sr	3900	3770	3810	3960	3710	3850
Mo	14.6	13.8	12.6	8.93	8.36	10.5
Ag	4.87	2.48	1.83	2.43	3.32	1.85
Cd	2.46	2.51	2.42	2.50	2.50	2.32
Sn	1.19	0.480	0.418	0.361	0.545	0.382
Sb	0.315	0.211	0.173	0.106	0.151	0.116
Ba	5640	5480	5470	6080	3800	6380
Tl	1.24	1.03	0.913	0.858	1.01	0.928
Pb	79.9	82.3	75.7	76.0	67.9	62.2
Cr	90.8	91.8	88.9	89.5	85.9	86.0
Mn	225	212	215	179	176	174
V	281	281	275	269	261	257

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	U2 Hoot Lake 1 2/01/05 1050	U2 Hoot Lake 2 2/02/05 0930	U2 Hoot Lake 3 2/03/05 0950	U2 Hoot Lake 4 2/04/05 1115	U2 Hoot Lake 5 2/05/05 1015
Be	3.03	2.34	4.07	3.81	3.47
B	366	281	470	415	430
Co	14.6	11.5	15.8	14.8	15.2
Ni	32.8	26.8	31.5	28.9	31.2
Cu	149	113	142	124	133
Zn	91.0	62.5	80.6	71.6	83.1
As	23.5	18.6	23.4	20.7	24.6
Se	11.4	6.31	9.45	8.44	11.3
Sr	6360	5710	6810	5930	5760
Mo	4.49	6.12	7.09	6.28	8.55
Ag	2.33	1.31	2.23	1.63	1.68
Cd	0.835	0.781	0.953	0.845	0.914
Sn					
Sb	0.219	0.0854	0.197	0.0859	0.0666
Ba	5780	5810	7520	5980	6060
Tl	1.20	0.742	1.01	0.624	0.737
Pb	22.1	16.9	18.6	16.1	19.5
Cr	58.3	53.3	57.8	53.4	56.1
Mn	296	249	279	265	286
V	201	183	207	188	211

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	U2 Hoot Lake 6	U2 Hoot Lake 7	U2 Hoot Lake 8 avg	U2 Hoot Lake 9	U2 Hoot Lake 10
Date sampled	2/06/05 0830	2/07-11/05	2/14-18/05	2/21-25/05	2/28-3/04/05
Be	3.37	5.00	2.87	2.75	2.47
B	396	495	596	578	547
Co	14.7	17.8	14.6	13.6	11.3
Ni	31.2	37.3	33.9	30.5	27.3
Cu	123	154	138	126	124
Zn	71.0	82.0	71.7	63.7	54.8
As	20.5	20.7	33.6	33.7	35.0
Se	9.20	10.3	13.2	11.9	10.0
Sr	5640	7030	4650	4370	5340
Mo	7.44	4.86	24.6	25.9	18.3
Ag	1.47	2.38	1.54	1.64	1.41
Cd	0.819	0.953	0.946	0.968	0.907
Sn				0.680	0.760
Sb	0.0463	0.204	0.101	0.150	0.114
Ba	5530	5850	3810	7750	8790
Tl	0.633	1.02	0.807	0.804	0.785
Pb	17.4	19.8	19.5	19.4	19.0
Cr	55.6	56.8	57.2	50.7	47.6
Mn	273	263	250	215	257
V	197	199	276	239	206

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg)	U3 Hoot Lake 1	U3 Hoot Lake 2	U3 Hoot Lake 3	U3 Hoot Lake 4	U3 Hoot Lake 5
Date sampled	2/01/05 1030	2/02/05 1600	2/03/05 1400	2/04/05 1150	2/05/05 1150
Be	4.24	3.28	3.43	3.45	2.62
B	533	416	438	435	326
Co	18.1	13.1	13.8	15.3	12.2
Ni	37.6	26.6	29.1	35.1	31.9
Cu	170	120	132	128	87.9
Zn	92.0	53.5	62.1	73.6	58.1
As	24.1	17.0	20.2	21.6	15.7
Se	12.3	7.22	8.03	9.34	7.20
Sr	6920	6800	6810	5580	4190
Mo	2.18	6.92	7.58	7.87	7.04
Ag	2.47	1.44	2.62	1.56	1.96
Cd	1.02	0.650	0.764	0.820	0.757
Sn					
Sb	0.200	0.108	0.0701	0.0496	0.198
Ba	4570	7560	6560	3970	3900
Tl	1.17	0.634	0.604	0.538	0.768
Pb	22.0	14.9	16.4	15.5	11.5
Cr	58.5	43.7	49.0	57.7	57.8
Mn	249	210	223	249	273
V	189	176	194	197	160

Table B.2. Fly Ash COC Concentrations (continued)

COC (mg/kg) Date sampled	U3 Hoot Lake 6 avg 2/06/05 0730	U3 Hoot Lake 7 2/07-11/05	U3 Hoot Lake 8 2/14-18/05	U3 Hoot Lake 9 2/21-25/05	U3 Hoot Lake 10 2/28-3/04/05
Be	3.44	4.73	2.67	2.53	2.52
B	419	474	503	499	551
Co	14.1	17.1	14.4	12.5	12.8
Ni	31.2	34.4	33.1	29.4	31.8
Cu	118	143	125	110	131
Zn	63.7	72.5	67.0	50.4	54.2
As	17.0	19.4	28.4	22.1	31.1
Se	7.64	10.4	10.9	8.43	10.3
Sr	5600	7030	4690	3630	5060
Mo	5.38	4.01	17.5	12.4	12.5
Ag	1.50	2.48	1.67	1.30	1.33
Cd	0.728	0.860	0.872	0.715	0.850
Sn					
Sb	0.0739	0.190	0.130	0.0687	0.0892
Ba	4890	5960	3820	3620	4010
Tl	0.513	0.985	0.712	0.515	0.654
Pb	14.4	19.0	18.7	14.7	18.4
Cr	54.1	55.9	57.0	45.7	49.0
Mn	241	246	252	194	260
V	176	183	215	178	189

Appendix C: Quality Assurance/Quality Control for Asphalt Pavement Data

Quality Assurance and quality control was practiced during the extraction and analysis of PAHs. Instrument detection limits are given in Table C.1. Surrogate recoveries for each of the analyzed samples are given in Table C.2. The 1962b, 1946 dup, 1953 dup, and the 1988 dup samples never received a surrogate spike and no data were available to adjust for recoveries. Various surrogate recoveries were calculated. The difficultly of the extraction, which included a filtration cleanup. Part of the surrogate spike could have possibly been captured on the solids filtered out during the clean-up column procedure. This is consistent with the general lower recoveries for higher molecular weight PAHs like chrysene and benzo(a)pyrene.

Table C.1. Instrument Detection Limits

PAH	Detection Limit (mg/kg)
acenaphthylene	0.000482
acenaphthene	0.000658
fluorene	0.000491
phenanthrene	0.0000957
anthracene	0.000297
fluoranthene	0.000533
pyrene	0.000860
benz[a]anthracene	0.000700
chrysene	0.00106
benzo[bjk]fluoranthene	0.00246
benzo[e]pyrene	0.000593
benzo[a]pyrene	0.00163
perylene	0.000936
indeno[cd123]pyrene	0.00162
dibenzo[ah]anthracene	0.00181
benzo[ghi]perylene	0.000590
coronene	0.000175

Table C.2. Surrogate Spike Recoveries

Surrogate Spike (%recovered)	1918	1924	1930	1933	1937	1941	1946	1946 dup*	1953	1953 dup*
d10-acenaphthene	66%	90%	53%	69%	90%	68%	102%	NA	54%	NA
d10-phenanthrene	73%	78%	56%	67%	99%	69%	112%	NA	56%	NA
d10-pyrene	87%	68%	72%	71%	121%	99%	95%	NA	60%	NA
d12-chrysene	73%	44%	62%	33%	106%	43%	54%	NA	55%	NA
d12-benzo[a]pyrene	51%	30%	34%	25%	52%	11%	11%	NA	41%	NA

*No surrogate spike added.

Table C.2. Surrogate Spike Recoveries (continue)

Surrogate Spike (%recovered)	1962a	1962b*	1962c	1966a	1966b	1966c	1967	1972	1978
d10-acenaphthene	102%	NA	56%	34%	69%	63%	69%	148%	65%
d10-phenanthrene	53%	NA	54%	33%	62%	60%	65%	128%	46%
d10-pyrene	51%	NA	50%	30%	61%	52%	58%	110%	37%
d12-chrysene	26%	NA	33%	23%	38%	31%	26%	75%	13%
d12-benzo[a]pyrene	10%	NA	10%	13%	11%	15%	23%	46%	3%

*No surrogate spike added.

Table C.2. Surrogate Spike Recoveries (continue)

Surrogate Spike (%recovered)	1988	1988 dup*	1992	1996	2000	2000 dup	2003a	2003b	Snelling Ave, Coal Tar
d10-acenaphthene	42%	NA	86%	81%	78%	66%	105%	124%	36%
d10-phenanthrene	46%	NA	78%	63%	61%	46%	95%	116%	31%
d10-pyrene	68%	NA	74%	79%	45%	51%	112%	104%	29%
d12-chrysene	54%	NA	63%	22%	10%	7%	63%	92%	23%
d12-benzo[a]pyrene	49%	NA	37%	5%	1%	0%	44%	81%	10%

*No surrogate spike added.

Four sets of sample extraction duplicates are given in Table C.3. Most of these values were not adjusted based on surrogate recoveries since many were not surrogate spiked. However, the 2000 samples sets are adjusted based on surrogate recoveries given in Table C.2. The reproducibility from the duplicates varied. Extractions involved analyzing 0.5 gram of the entire asphalt core including aggregate, which can result in a large sample to sample variability in aggregate content, with variable dilution of the asphalt binder. Another large contribution to error is the variation in recovery due to retention of analytes in the insoluble fraction retrained in the filtration process during cleanup. This is most problematic for the larger molecular weight compounds.