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Semi-Quantitative Determination of the Modes of Occurrence Of Elements in Coal: Results from an International Round Robin Project

By

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Introduction

Understanding the modes of occurrence of elements in coal is essential for developing reliable models to predict the behavior of elements during in-ground leaching, weathering, coal cleaning, or combustion. Modeling the behavior of the trace elements is necessary to accurately evaluate the environmental and human health impacts, technological impacts, and economic byproduct potential of coal use. Since the 1950's there has been considerable effort to determine the modes of occurrence of the elements in coal. Most of these efforts resulted in qualitative assessments such as organic-inorganic affinities. During the past 10 years considerable progress has been made in quantifying the modes of occurrence of the elements in coal.

A wide range of techniques is currently used to make these determinations. To generate modes of occurrence information some laboratories rely on analysis of density separates, others use various solvents to selectively leach inorganic constituents and yet others use microbeam instruments such as scanning electron microscopes and electron microprobes. No two laboratories use the same approach or rely on the same assumptions. Under these circumstances is it possible to confidently compare the results of different laboratories? To answer this question, the U.S. Geological Survey (USGS) and eight other laboratories* participated in an international laboratory comparison study of selected coal samples. The International Energy Agency (IEA) has endorsed this inter-laboratory study and has agreed to publish a summary comparing the results. To date, samples of four coals have been distributed to participating laboratories.

Laboratories in four countries were requested to obtain coal samples, grind them, carefully subdivide and distribute the splits of the coal samples to the participating groups. The eastern Canadian thermal coal was ground to 4 mesh and the Wyee, Gascoigne Wood and Illinois #6 were ground to less than 60 mesh. Chemical analysis (Appendix 1A-D) of the coal samples indicates that the splits were homogenous.

Modes of occurrence (chemical speciation) determinations for the four coals are presented in this paper along with the supporting analytical data. The results presented here are essentially the same as those in USGS Open-File Report 99-160 (Palmer and other, 1999) and presented by Willett et al. (1998; 1999) The major difference is the addition of data on the eastern Canadian coal sample.

Information on the ash yield and sulfur content of the four coal samples is given in Table 1. Chemical analysis generated by the USGS and preliminary analyses from seven other participating labs (for three of the four coal samples) are given in Appendix 1. We have not yet received results from the eastern Canadian

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* The University of Kentucky; Energy and Environmental Research Center, University of North Dakota (EERC); Geological Survey of Canada; Imperial College, London, England; University of Sheffield (England); University of Wales (Cardiff, Wales); Consejo Superior de Investigaciones Cientificas (CSIC; Barcelona, Spain); and the Commonwealth Scientific and Industrial Research Organization (CSIRO; Australia).

coal from most of the other participating laboratories. Because the chemistry data are preliminary, only the USGS results are identified.

Table 1. Characteristics of four bituminous coal samples examined in International Laboratory Comparison Study (values in weight percent on an as-received basis)

Sample Source **Country**	**Ash (wt. %)**	**Total Sulfur (wt.%)**
Wyee Australia	23.7	0.36
Gascoigne Wood #2 Great Britain	15.8	1.27
Illinois #6 United States	10.4	3.78
Eastern Canadian Thermal Canada	10.1	3.21

As part of this study each of the participating laboratories have determined trace element modes of occurrence using their own techniques. Three of the labs are using leaching procedures, three labs are using density procedures, and several labs are using SEM and/or microprobe characterization as their primary or secondary method of determining modes of occurrence.

The USGS used a combination of analytical procedures for determining the chemical composition of the samples. These procedures included inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), instrumental neutron activation analysis (INAA), and element specific techniques such as cold vapor atomic absorption (CVAA) for Hg and hydride generation atomic absorption (HGAA) for Se. Mode of occurrence determinations are based on an iterative selective leaching approach that is used in conjunction with scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX), X-ray diffraction (XRD) of the low temperature ash, and electron probe microanalysis (EPMA).

Where possible, USGS data are compared with data generated by the other participating laboratories. Their data include analysis of density separates and XAFS (X-ray absorption fine structure) analysis to determine the speciation of certain elements. This comparison is intended to identify elements for which similar results are obtained by a variety of techniques and those for which there are contradictory results or interpretations. In doing so, this study serves to identify techniques in need of improvement or invalid assumptions.

Methods

Bulk Chemistry

The four coal samples were analyzed by several different techniques. The USGS ash value was determined by ashing the samples at 525 °C. The ash was used for major and trace element determinations using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). The procedures used for ICP-AES involve two different dissolution procedures (Briggs, 1997). A sinter digest is used for the major components Si, Al, Ca, Mg, K, Fe, Ti, P and the trace elements B, BA and Zr. An acid digest is used to determine the concentrations of Na, Be, Co, Cr, Cu, Li, Mn, Ni, Sc, Sr, Th, V, Y, and Zn. The ICP-MS uses the same acid digest solution as the ICP-AES, to determine As, Au, Cd, Cs, Ga, Ge, Mo, Nb, Pb, Rb, Sb, Sn, Tl and U, using procedures described by Meier (1997). Instrumental neutron activation analysis (INAA) of selected whole coal samples was used to determine K, Fe, Na, As, Au, Ba, Br, Co, Cr, Cs, Hf, Ni, Rb, Sb, Sc, Se, Sr, Ta, Th, U, W, Zn, La, Ce, Nd, Sm, Eu, Tb, Yb and Lu, using procedures described by Palmer (1997). The comparison of the INAA results on the whole coal sample and the ICP-AES and ICP-MS results on the ash for those elements that were determined in common increased the quantitative confidence in the values reported. For elements that were determined by more than one method we selected the value for which we had the most analytical confidence. Mercury and Se are determined directly on the coal by cold-vapor atomic absorption analysis and hydride generation atomic absorption, respectively, using procedures described by O'Leary (1997). The analytical technique used for each element is indicated in Appendices 1A-1D. The combination of techniques used by the USGS provides data on a large number of elements with great reliability (Palmer and Klizas, 1997).

Selective Leaching

The sequential selective leaching procedure used in this study is similar to that described by Palmer and others (1993), modified from that of Finkelman and others (1990). Duplicate 5 g coal samples were leached sequentially with 35 ml each of 1N ammonium acetate (CH_3COONH_4), 3N hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48%) and 2N (1:7) nitric acid (HNO_3) in 50 ml polypropylene tubes. Each tube was shaken for 18 hrs using a motorized shaker. Because gas can form during the leaching procedure, it is necessary to enclose each tube in double polyethylene bags, which allows gas to escape, but prevents the release of liquid. After each leaching step, the coal slurries were centrifuged and the resulting solutions were saved for ICP-AES and ICP-MS analysis. The sample was washed at least five times with distilled water, using an ultrasonic cleaner to remove the solvent. After removing the solvent and drying the residual solid, about

0.5 g of this material was removed from each tube for the determination of 28 elements by INAA and the determination of Hg by CVAA analysis.

Chemical data for the leachates and residues were processed to derive the percentages of each element leached by each of the four leaching agents. The calculated percentages were then used as an indirect estimate of the modes of occurrence of 44 elements. By comparing data for the residual fractions with data for the solutions, we estimate a relative error of up to ±20 percent and an absolute error of ±10 percent, for the leached percentages reported.

Scanning Electron Microscopy

Coal-epoxy pellets were prepared for SEM and electron microprobe analysis following the ASTM D2797-85 technique for anthracite and bituminous coal (ASTM, 1993). Four pellets for each of the four coal samples were prepared. The casting procedure impregnates, under pressure, about 7-8 grams of -850 µm coal particles with epoxy. The coal-epoxy mixture is poured into a mold, cured overnight at 60 °C. and ground on a 15 µm diamond platen and 600- grit SiC paper until flat and smooth. Rough polishing is done with 1 µm alumina and final polishing is completed with 0.06 µm colloidal silica. Ultrasonic cleaning between and after the various steps ensures a final product free of extraneous abrasive material.

Polished pellets were examined using a JEOL 840[1] or an ETEC Autoscan[1] scanning electron microscope equipped with an energy-dispersive detector (EDX). Mineral identifications are assigned on the basis of morphology, and major-element composition of grains. Back-scattered electron imaging (BSE) was the primary mode of operation used to characterize the coal samples. EDX analysis provided information on elements having concentrations at the tenths-of-percent level or greater. Typical operating conditions for scanning microscopy are: accelerating potentials of 10-30 kV, magnifications of ~50->10,000 times and working distances of 15, 25, or 39 mm (JEOL) or 15 to 20 mm (ETEC).

Electron Microprobe Analysis

A fully-automated, five spectrometer JEOL JXA 8900R Superprobe[1] was used to quantitatively determine element concentrations in sulfides by the wavelength-dispersive technique. The following elements were measured: Fe, S, Se, Cu, Ni, As, Zn, Cd, and Co. Natural and synthetic standards were used for calculations. Beam current used was 3.0×10^{-8} amps; accelerating voltage was 20 KeV. A minimum beam diameter of about 1-3 micrometers was attained, limiting the minimum grain size for analysis to about 10 micrometers. With the exception of Co, a minimum detection limit of about 100 ppm (0.01 wt. %) was attained for each of the trace elements analyzed in pyrite, using counting times of 60 seconds for peak positions and 30 seconds for upper and lower backgrounds. For Co, the minimum

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[1] Use of trade names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey

detection limit in pyrite is 500 to 600 ppm (0.05-0.06 wt. %), due to an interference with Fe K_β.

X-ray diffraction analysis

To obtain semi-quantitative information on the minerals present in the coals, samples of low-temperature ash (LTA) were pressed into pellets and analyzed using an automated X-ray diffractometer. The low-temperature ash is produced in an oxygen plasma ashing device (Gluskoter, 1965) at temperatures generally determined to be < 200 °C. The X-ray signals were scanned over an interval from 4 to $60^\circ 2\theta$. Counts were collected at an interval of 0.5 seconds per step. The data were processed using a computer program for semi-quantitative mineral analysis by X-ray diffraction (Hosterman and Dulong, 1985).

Results

Bulk chemistry for each of the four samples determined by the USGS and available data from the other laboratories appear in Appendices 1A-1D. Because the data are considered preliminary we have not identified the source of the data other than those of the USGS. The data are determined by 11 different techniques including ICP-AES (ICP), ICP-MS, spark source mass spectrometry (SparkMS), CVAA, atomic fluorescence spectrometry (AFS), HGAA, INAA, PIXE, XRF, graphite furnace atomic absorption analysis (GFAA) and classical flame atomic absorption analysis (AA).

Considering the variety of techniques used, the agreement is generally good. Excluding data obtained by proton induced X-ray emission (PIXE; Column F, Appendix 1), the best agreement was found for Ga, Li, Rb, Sc, Mn, and Ba. For each of these elements, agreement, expressed as the percentage range of total deviation, is within 15 percent for the Wyee, Gascoigne Wood #2, and the Illinois #6 samples. A large group of elements, including As, Be, Cr, Cu, Ga, Ge, Li, Mo, Nb, Ni, Pb, Sb, Sr, Th, Tl, U, V, Se, Cs and B (excluding the anomalous Se, Cs, and B values for Gascoigne Wood #2) have deviation ranges less than 40 percent (excluding PIXE data in column F). Mercury values are within ±40 percent, except for the Wyee coal sample. Cobalt was only within ±40 percent for the Gascoigne Wood #2 sample and Y was only within ±40 percent for the Wyee sample. For Zn, the agreement is poor for each of the samples. Cd had poor agreement for two samples and only one value was above the detection limit for the third coal sample. For Hg and Cd, the poor agreement is a function of the low concentration levels and large uncertainties as detection limits are approached. Where at least 3 values are reported for a given element, USGS data generally fall within the range of the others, or deviate from this range by no more than about 20 percent. Modes of occurrence (leaching) results were not obtained for B, Si, Ga, Ge, and Nb. Inclusion of bulk data for these elements in Appendix 1A-1D is primarily for the purpose of comparing our results with those of other laboratories.

In comparing the USGS values for the four coal samples (Appendix 2), it is evident that the Wyee sample has the highest concentrations of trace-elements which are commonly associated with carbonates (Mn 260 ppm; Sr 100 ppm); whereas the Gascoigne Wood #2 has relatively high concentrations of several transition metals, including Co (6 ppm), Cu (30 ppm), Ni (19 ppm), V (47 ppm) and Cr (35 ppm). The Illinois #6 sample is enriched in B (229 ppm) and contains 2-5 times the Zn of the other coals, which is consistent with the presence of abundant sphalerite. The eastern Canadian thermal coal has the highest concentrations of trace elements associated with sulfide minerals including As (77 ppm), Se (4.8 ppm), Hg (0.18 ppm), Tl (1.2 ppm) and Pb (32 ppm).

Mineralogy of the coal samples is summarized in Appendices 3 and 4. Semi-quantitative estimates of bulk mineralogy are given in Appendix 3, based on X-ray diffraction (XRD) of the LTA. The percentage of total clay minerals (illite, kaolinite and chlorite) in the LTA of the samples ranges from 53 to 75 percent. The Gascoigne Wood #2 LTA has the highest percentage of clay minerals, with 35 percent illite, 30 percent kaolinite and 10 percent chlorite, but the Wyee sample has the highest amount of clays on a whole coal basis due to its higher ash yield. Illite, as determined by XRD, is defined by the peak at 10 Å and may include mixed layered clays. The Canadian, Illinois #6, and Wyee LTA have similar amounts of illite (10-20%), and kaolinite (35-45%), and all lack chlorite. The percentages of quartz in the LTA are about 25 percent for each sample except for the Canadian coal. Pyrite in the LTA ranges from virtually nil in the Wyee to 25% in the Canadian sample. Small amounts of pyrite were found in the Wyee coal by SEM/EDX. Iron in the Wyee coal was found to be present mostly in siderite/carbonates rather than pyrite. Pyritic sulfur values ranged from 0.02 percent in the Wyee to 1.94 percent in the Canadian coal.

SEM examination of pellets prepared from the four coal samples revealed a wide range of accessory phases in the Gascoigne Wood #2 and Wyee coals, and a fairly simple mineralogy for the Illinois #6 and Canadian samples (Appendix 4). These data are useful in helping to interpret the leaching data.

Interpretation of Leaching Data

Leaching data are plotted for each element in Figures 1 to 10. Each graph shows the leaching steps in sequential order for each coal. The graphs show the percent of each element removed at each step and the cumulative percent leached. Interpretation of the results is considered in the section that follows.

For each element in each coal, data for four leachate fractions are generated (Figs. 1-10). The four leachates are intended to reveal as much as possible about the mode of occurrence of elements in coal. The leachates were chosen specifically to attack the most commonly occurring inorganic constituents. The ammonium acetate leach removes loosely bound ions that may be organically associated or ions adsorbed on clays. Ammonium acetate also dissolves some calcite. The HCl-leaching step dissolves carbonates, such as calcite, and monosulfides such as sphalerite, galena, and even chalcopyrite. The HF-leaching step dissolves silicates, including quartz and clay minerals. Note that some silicates, such as zircon, may be resistant to HF-leaching. Leaching with HNO_3 primarily dissolves disulfides such as pyrite, releasing those elements that are pyrite-associated. The sum of these four leaching steps is seldom 100 percent. The difference from 100 percent is due to elements that are shielded from the solvents, in insoluble mineral phases, or are organically bound. The ash yield of the residual leached coal is commonly less than 0.3 weight percent indicating little in the way of shielded and insoluble phases in most coals.

The leaching data are combined with data from XRD, SEM/EDX, and microprobe in making mode of occurrence determinations. Data obtained by XRD are used to determine the relative amounts of major and minor minerals in the coal samples. The electron microprobe gives quantitative elemental concentrations of specific mineral grains. SEM/EDX, and electron microprobe, are used to identify minor and trace minerals. With this information, mass balances can be calculated. Our final interpretations factor in the leaching results, the mass balance information, geochemical principles, and experience obtained from previous leaching experiments. Our interpretations of the element modes of occurrence are summarized in Table 2. Querol and others (1998) and Querol and Huerta (1998) gave similar results for the Wyee, Gascoigne Wood #2, and the Illinois #6 samples based on a synthesis of the USGS data and their analysis of density.

Table 2: Interpretations of modes of occurrence (Units of all numbers are in %). Results for the Wyee, Gascoigne Wood #2, and Illinois #6 samples generally agreed with those of Querol and Huerta (1998) and Huggins (1998), except as noted.

Element	Wyee	Gascoigne Wood #2	Illinois #6	E. Canadian
Li	75 Al-silicate	80 Al-silicate	75 Al-silicate	85 Al-silicate
Be[1]	Al-silicate/organic	Al-silicate/organic	Al-silicate/organic	Al-silicate/organic
Al	90 Al-silicate	90 Al-silicate	90 Al-silicate	85 Al-silicate
Na[2]	30 Al-silicate 50 exchangeable	25 Al-silicate 45 exchangeable	30 Al-silicate 45 exchangeable	25 Al-silicate
K	90 Al-silicate	90 Al-silicate	90 Al-silicate	90 Al-silicate
Rb	50 Al-silicate 35 undetermined	25 Al-silicate 65 undetermined	70 Al-silicate 15 undetermined	75 Al-silicate
Cs	20 Al-silicate 45 undetermined 25 exchangeable	15 Al-silicate 75 undetermined	60 Al-silicate 20 undetermined	80 Al-silicate
Mg[3]	50 carbonate 20 Al-silicate	25 carbonate 30 Al-silicate	15 carbonate 50 Al-silicate	40-55 carbonate 25 Al-silicate

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[1] Querol and Huerta (1998) found nearly all Be in all coals organically associated.

[2] Querol and Huerta (1998) found Wyee: 20% organic and 80% Al-silicate; Gascoigne Wood #2: 45% zeolite, 55% Al silicate; Illinois #6: 25% ionic, 45% organic and 30 % Al silicate.

[3] Querol and Huerta (1998) found Wyee: 100 % Carbonate; Gascoigne Woods #2: 97% carbonate; 3% organic; Illinois #6 20% organic and 80% Al-silicates.

Table 2 (continued)

Element	Wyee	Gascoigne Wood	Illinois #6	E. Canadian
Ca	80-100 carbonate	75-80 carbonate 20-25 organic	70-75 carbonate 25-30 organic	60-70 carbonate
Sr	Organic, carbonate, Al-silicate, phosphate	Organic, carbonate, Al-silicate, phosphate	Organic, carbonate, Al-silicate, phosphate	Organics, phosphate
Ba	Barite	Barite	Barite	
Sc	50 organic 30 Al-silicate	30 organic 65 Al-silicate	25 organic 65 Al-silicate	35 organic 50 Al-silicates
Ti	Ti-oxides and/or Al-silicates	Ti-oxides and/or Al-silicates	Ti-oxides and/or Al-silicates	65 Ti-oxide 35 Al-silicates
V	70 organic 25 Al-silicate	45 organic 55 Al-silicate	35 organic 60 Al-silicate	55 organic 40 Al-silicate
Cr	60 organic 35 Al-silicate	40 organic 50 Al-silicate 10 chromite	65 organic 35 Al-silicate	50 organic 40 Al-silicate
Mn	up to 85 carbonate 10 organic	up to 80 carbonate 20 Al-silicate	up to 60 carbonate 20 sulfide 15 Al-silicate	60-90 carbonate
Fe	80 siderite	35 siderite, 35 silicate 30 pyrite	75 pyrite 10-15 carbonate	60-90 pyrite
Co	75 organic	Organic, Al-silicate, sulfide, carbonate in subequal amounts	Organic, Al-silicate, sulfide, carbonate in subequal amounts	50-70 carbonate 20 pyrite
Ni	35 organic, 30 Al-silicate; rest is subequal sulfide, carbonate	45 organic 20 Al-silicate 20 carbonate	30 sulfide, 35 organic; rest is subequal Al-silicate, carbonate	35-55carbonate 25 pyrite
Cu	35 organic 25 Al-silicate 35 pyrite/chalcopyrite	35 pyrite/chalcopyrite 50 organic 15 Al-silicate	70 pyrite/chalcopyrite 10 Al-silicate	60-80 sulfide
Zn[4]	Mainly sphalerite; Remainder is Al-silicate	Mainly sphalerite Remainder is organic, Al-silicate, pyrite	Mainly sphalerite; Remainder is organic, pyrite	25 organic 15 Al-silicate 45 sulfide
Mo[5]	30 organic 25 Al-silicate 10 sulfide	30 organic 40 Al-silicate 15 sulfide	50 organic 35 Al-silicate 10 sulfide	15 Al-silicate 75 sulfide
Cd	Sphalerite, organic	Sphalerite	Sphalerite	55 organic (?)
As	35 sulfide	55 sulfide	40 sulfide	85 sulfide
Se[6]	45 organic 25 sulfide	50 sulfide 35 organic	70 sulfide 25 organic	65 sulfide 30 organic

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[4] Huggins (1998) found Wyee: organic dominate; Gascoigne Wood #2: illite is the dominant mode of occurrence.

[5] Querol and Huerta, (1998) did not find an Al silicate fraction in any of the coal samples.

[6] Gascoigne-Wood #2: Querol and Huerta (1998) reports 100% pyrite; whereas Huggins (1998) reports only minor pyrite.

Table 2 (continued)

Element	Wyee	Gascoigne Wood	Illinois #6	E. Canadian
Sb	75 organic 15 Al-silicate 10 sulfide	50 organic 25 sulfide 15 silicate	50 organic 25 sulfide 20 Al-silicate	30 organic 45 sulfide
Hg	Mostly sulfide	Dominantly sulfide	Dominantly sulfide	70 sulfide
W	40 organic/W-oxides 30 Al-silicate	50 organic/W-oxides 20 Al-silicate	55 organic/W-oxides 45 Al-silicate	40 organic/W-oxides 30 Al-silicate
Tl	45 Al-silicate 25 sulfide 30 organic	25 Al-silicate 65 sulfide	20 Al-silicate 45 sulfide 20 organic	25 Al-silicate 35 sulfide 30 organic
Pb	55 galena, 15 pyrite, PbSe	60 galena 25 pyrite, PbSe	45 galena 40 pyrite	80 galena
Hf	Dominantly zircon	Dominantly zircon	Dominantly zircon	Dominantly zircon
Ta	65 oxide 25 Al-silicate	65 oxide 15 Al-silicate	65 oxide 25 Al-silicate	55 oxide 30 Al-silicate
Th	Mainly phosphates, oxides, organics	Mainly phosphates, Oxides	Mainly phosphates, oxides	Mainly phosphates
U	45 organic and/or zircon 30 Al-silicate	40 organic and/or zircon 40 Al-silicate	75 organic and/or zircon	45 organic and/or zircon 30 Al-silicate
Y/HREE	Phosphates, organics	Phosphates, organics	Phosphates, organics	Phosphates, organics
LREE	Phosphates	Phosphates	Phosphates	Phosphates

In the sections that follow, results for each element are discussed, largely in order of atomic number with exceptions to allow for grouping of geochemically similar elements. For convenience, elements are also shown in this order in Table 2 and in Figures 1 to 10. For detailed discussions of the leaching results the reader is referred to Palmer and others (1999).

Beryllium (Be)

Thirty to eighty percent of the Be is HF-leachable indicating that a substantial proportion of the Be is in silicates (Fig. 1B). Up to 65 percent of the Be is unleached and is probably associated with the organics. In contrast, Querol and Huerta (1998) found that nearly all of the Be in the three coals they studied is associated with the organics. The results of Querol and Huerta (1998) can be reconciled with the USGS leaching results if organically bound Be is attacked to some extent by HF. Additionally, because of its low atomic weight and low abundance, Be can be difficult to analyze, possibly resulting in conflicting interpretations.

Sodium (Na)

Results obtained for Na by the USGS differ somewhat from those of Querol and Huerta (1998). They found a 20 percent organic-80 percent aluminosilicate Na distribution for the Wyee compared to the USGS interpretation of 30 percent aluminosilicate-50 percent exchangeable ions. Querol and Huerta (1998) found a 45 percent zeolite-55 percent aluminosilicate Na distribution for the Gascoigne Wood #2 compared to USGS results of 25 percent aluminosilicate-45 percent exchangeable ions. Querol and Huerta (1998) found a 25 percent ionic-45 percent organic-30 percent aluminosilicate distribution for the Illinois #6 compared to the USGS results of 30 percent aluminosilicate-45 percent exchangeable ions. The reason for this disagreement is currently under investigation.

Rubidium (Rb) and Cesium (Cs)

In three samples (Wyee, Gascoigne Wood and Illinois #6) there was a substantial HNO_3-leachable fraction of Rb and Cs. This HNO_3-leachable fraction ranged from 15-65 percent for Rb and 20-75 percent for Cs. The mode of occurrence of HNO_3-leachable Rb and Cs is unclear. Sixty to 80 percent of the Rb and Cs in the Illinois #6 and the Canadian samples and lesser proportions (15-50 percent) in the other samples were HF soluble indicating a significant association with silicates. Small to modest amounts of ammonium acetate leachable Cs may be from exchange sites on clays or organics.

Magnesium (Mg)

Leaching data indicate two major modes of occurrence for Mg, in silicates and carbonates, but the data are not as clearly defined as those for some other elements. For the Wyee and Gascoigne Wood coal samples, Querol and Huerta (1998) found a large (97-100 %) carbonate association and did not find the aluminosilicate fraction that the USGS leaching results indicate.

Calcium (Ca)

Palmer et al. (1998) found that calcite is partially soluble in ammonium acetate. The high proportion of ammonium acetate soluble Ca in the Canadian sample may be due to the fine-grained nature of the calcite observed by SEM. Based on comparison with previous leaching results (Palmer and others, 1993; Finkelman and others, 1990), we consider the low percentage of Ca leached from the Canadian sample to be the result of incomplete leaching. The total amounts of Ca leached from the Wyee, Gascoigne Wood #2, and the Illinois #6 samples are also low compared to the results of Querol and Huerta (1998). They found a strong carbonate association for Ca ranging from 71 percent in the Illinois #6 sample to 100 percent in the Wyee. Nevertheless, we interpret our data to indicate a primary carbonate association for Ca.

Strontium (Sr)

Strontium was removed from each of the coals by all four leaching agents with total percentages leached ranging from 55 percent (Canada) to 85 percent (Wyee, Fig. 3C). This leaching behavior indicates that Sr occurs in several phases and that there is no dominant mode of occurrence. Probable modes of occurrence for Sr include the organic association, carbonates, aluminosilicates and phosphates. Multiple modes of occurrence for Sr are inferred also by Querol and Huerta (1998) who found carbonate, silicate and organic associations for Sr in the Illinois #6, and Gascoigne Wood #2 samples, and carbonate and aluminosilicate associations for Sr in the Wyee.

Phosphates were found using the SEM/EDX, especially in the Wyee coal. For example, the phosphate mineral gorceixite ($BaAl_3(PO_4)_2(OH)_5\bullet H_2O$, which generally contains Sr in solid solution, was found in the Wyee coal, attached to a grain of sphalerite (Fig. 11).

Barium (Ba)

Like Sr, all four leaching agents (Fig. 3D) leached Ba from each of the coals. The only exception being ammonium acetate in the Canadian coal. Unlike Sr, we consider the leaching behavior of Ba to be controlled by a single dominant phase (barite), rather than as a minor element in multiple phases. Barite was observed in three of the coals (Appendix 4) and is especially common in the Gascoigne Wood #2.

Although barite is generally assumed to be insoluble, solubility data (Linke 1959) indicate that a few ppm of Ba could be dissolved from barite by solvents used in our leaching process. Based on barite solubility data for the leaching solutions at or near room temperature, the amount of Ba in solution after the ammonium acetate, HCl, and HNO_3 leaching steps is consistent with the dissolution of barite. Fifty to sixty percent of the Ba in each of the coals was leached by HF. Solubility data for barite in HF are not available.

Chromium (Cr)

Like V, Cr shows large (40-65) percentages of unleached element, indicating significant organic fractions (60-65 percent in the Wyee and Illinois #6 samples; Fig. 4d). The HF fraction is again the next most abundant, ranging from 35 percent for the Wyee and Illinois #6, to 50 percent for the Gascoigne Wood #2. The 50 percent silicate Cr fraction found for the Gascoigne Wood #2 is consistent with XAFS (XANES) data of Huggins (1998) that indicate a large part of the Cr in this coal is associated with illite. Some of the unleached Cr could be insoluble chromite rather than Cr in the organics. Chromite was observed in the Illinois #6 and Wyee samples.

Manganese (Mn)

Carbonates were found to be the dominant mode of occurrence for Mn in each of the three coals investigated. This mode is indicated by the sum of HCl and ammonium acetate fractions (see discussion for Ca), which ranges from 60 percent (Illinois #6) to 90 percent (Canada; Fig. 5a). Some of the ammonium acetate-leachable Mn may be loosely-bound ions in the organic matrix rather than Mn in carbonates. These data show that the Wyee coal has up to 85 percent Mn in carbonates, with small amounts of Mn in silicates and organics. The Gascoigne Wood #2 sample has up to 80 percent Mn in carbonates, and 20 percent in silicates (probably illite). The Illinois #6 has up to 60 percent Mn in carbonates, 15 percent in silicates, and 20 percent in sulfide associations, probably pyrite. The Canadian sample has up to 90 percent Mn in carbonates.

Cobalt (Co)

Leaching data for Co are suggestive of multiple modes of occurrence, but leaching totals are quite variable (Fig. 5c). Leaching totals in the Wyee are only 25 percent, suggesting that up to 75 percent of the Co is associated with organics. The other coals have minor HF- and HNO_3-leachable Co, and up to 30 percent associated with organics. In the Canadian sample, 50 percent of the Co is ammonium acetate leachable that we interpret to be in carbonate association. In all four coals small amounts (10-40%) of the Co are present in an HCl soluble phase, possibly a carbonate or monosulfide.

Nickel (Ni)

Nickel was removed in nearly every step of our leaching process (Fig. 5d). For the Wyee coal, 30 percent of the Ni is in the silicates and up to 35 percent is associated with organics. Smaller amounts of Ni are associated with sulfides and carbonates in the Wyee. The Gascoigne Wood #2 and the Illinois #6 have up to 35-45 percent of the Ni associated with organics, 20 percent in an HCl soluble phase and 15 to 20 percent in silicates. The Illinois #6 has twice the proportion of nickel in the sulfide fraction (30%), compared to the Gascoigne Wood #2 (15%). In the Canadian coal, 35 percent of the Ni was leached by ammonium acetate. We interpret this Ni to be in carbonates.

The presence of Ni in pyrite is confirmed by electron microprobe (Appendix 5), and summarized as follows: For the Gascoigne Wood #2 sample, Ni contents in pyrite range from below the detection limit (<100 ppm), to about 0.20 weight percent. An average Ni concentration of 270 ppm (0.027 wt. %) was determined based on 67 pyrite analyses. Using this average concentration, and a pyrite content of 0.7 weight percent (calculated from the pyritic sulfur value), about 10 percent of the Ni in the Gascoigne Wood #2 coal can be accounted for by pyrite. This estimate is in good agreement with the15 percent fraction of Ni in pyrite determined by leaching with HNO_3. For the Illinois #6 coal, microprobe data indicate a concentration range from below the detection limit (<100 ppm) to a maximum of 0.06 weight percent. Typical values are in the 0.00 to 0.02 weight percent range. The probe data are in good agreement with the leaching results, which would require an average Ni concentration in pyrite of about 145 ppm (0.015 wt. %) in order to account for the 30 percent fraction of Ni in pyrite determined by leaching. Pyrite was not sufficiently abundant in the Wyee coal to obtain a representative microprobe analysis, but semi quantitative EDX analysis indicates that some Ni is present in Wyee pyrite. Microprobe data are not available for the Canadian coal sample.

Zinc (Zn)

We observed sphalerite grains in the Wyee, Gascoigne Wood #2, and Illinois #6 samples and consider it to be the dominant mode of occurrence for Zn. As such, we would expect large HCl-leachable fractions for Zn. Surprisingly, these fractions are only in the 20-25 percent range. Illite and pyrite associations are other possible modes of occurrence for Zn as indicated by the leaching data. The presence of minor amounts (< 0.01 to 0.04 wt. %) of Zn in pyrite in the Illinois #6 and Gascoigne Wood #2 samples is indicated by electron microprobe analysis (Appendix 5). However, if 45 percent of the Zn in the Illinois #6 coal were in pyrite, it would require an average Zn content of pyrite in excess of 0.14 weight percent. This appears to be inconsistent with the microprobe data. Likewise, for the Gascoigne Wood #2, if 25 percent of the Zn were in pyrite, it would require an average Zn content of pyrite approaching 0.10 weight percent. Possible explanations for the Zn leaching data include shielding of sphalerite by organics and/or partial solubility of residual sphalerite in HNO_3 (and HF as well).

Cadmium (Cd)

Results of SEM/EDX show that Cd is present in sphalerite in the Gascoigne Wood #2 coal, however, because the amount of Cd in the whole coal is at or below the detection limit, no leaching data were obtained for this sample. For the Wyee coal, cadmium was removed at every step of the leaching process (Fig. 6d). The primary modes of occurrence in the Wyee are a 30 percent HCl-soluble phase (sphalerite) and up to 55 percent Cd associated with organics. The Illinois #6 coal has a 45 percent HNO_3-leachable Cd fraction, the same proportion indicated for the geochemically similar Zn in this coal. In the Canadian sample, more than 50 percent of the Cd was unleached and may be organically associated. The proportion of HCl-leachable Cd in all of the samples seems too low if Cd were dominantly in sphalerite (see discussion for Zn). The fact that the proportion of Cd leached from the three samples for which we have data are all lower than the corresponding proportion of leached Zn, may indicate an organic association for Cd.

However, as many of the Cd values are near the detection limit there is a large uncertainty for Cd.

Arsenic (As)

Leaching data indicate a 35 percent (Wyee) to 55 percent (Gascoigne Wood #2) fraction of arsenic in pyrite, and a 10-40 percent fraction of unleached As, inferred to be organically-associated (Fig. 7a). Lesser amounts of HF- (5-20%) and HCl- (10-35%) leachable As were determined in each of the coals. The portion of HCl-leachable As corresponds well to the 15 percent fraction of arsenate (AsO_4^{3-}) found by Huggins (1998) for the Wyee, Gascoigne Wood #2, and the Illinois #6 samples using XAFS (XANES). Arsenate is generally considered to form by oxidation of arsenic-bearing pyrite. The XAFS data give somewhat smaller organic As fractions than the USGS data (0 percent for Gascoigne Wood #2, < 10 percent for Illinois #6), suggesting that some of the unleached As, especially in the Illinois #6, may actually be in pyrite that was not completely digested, perhaps due to shielding by organic matter. For the Wyee, there is good agreement between the leaching and XAFS data for each of the major As fractions- pyrite, organic, and arsenate.

The presence of As in pyrite is confirmed by electron microprobe (Appendix 5), and summarized as follows: For the Gascoigne Wood #2 sample, As in pyrite ranges from below the detection limit (<100 ppm), to nearly 2 weight percent. An average As value of 0.13 weight percent gives sufficient As to account for all the As in the Gascoigne Wood #2 sample, based on a pyrite content of 0.7 percent (calculated from the pyritic sulfur content), and a whole-coal As value of 9 ppm (Appendix 1-2). An average As content of about 0.2 weight percent was determined for the Gascoigne Wood #2 pyrite, based on 67 microprobe determinations.

For the Illinois #6 coal, microprobe data indicate As contents in pyrite ranging from below 0.01 weight percent to about 0.04 weight percent. These data are consistent with an average concentration of 115 ppm (0.012 wt. percent), required to account for all of the As (3 ppm), based on a pyrite content of 2.6 weight percent. Pyrite was not sufficiently abundant in the Wyee coal to obtain a representative microprobe analysis. Microprobe data for the Canadian coal sample are not available.

Selenium (Se)

The Gascoigne Wood #2, Illinois #6, and the Canadian sample have a significant fraction of Se associated with pyrite (50 to 70%; Fig. 7B) and 25 to 35% associated with the organic fraction. For the Wyee sample, whole-coal Se values and Se values for each of the leachates are near the detection limit (0.5 ppm) resulting in values with very large uncertainties. The Wyee data indicate a 45 percent organic fraction and a 25 percent pyritic fraction for Se. The pyrite and organic associations found for these samples are generally confirmed by other methods, however the proportions indicated are rather variable. For example, XAFS (XANES) data indicate only a minor fraction of pyrite-hosted Se in the Gascoigne Wood #2 (Huggins, 1998), whereas our results show this fraction to be 50 percent, and density separations (Querol and Heurta, 1998) indicate nearly all of the Se is in pyrite.

Antimony (Sb)

Antimony is largely associated with organics, with two of the coals (Illinois #6 and Gascoigne Wood #2) having 50 percent unleached Sb (Fig. 7c). For the Wyee sample, which has the most pronounced organic association of the three coals, up to 75 percent of the antimony may be associated with organics, depending on the amount of ammonium acetate-leachable Sb that is organically-associated. The Canadian coal sample has about 70 percent organically associated Sb. Subsidiary modes of occurrence for Sb include a pyrite association ranging from 10 percent in the Wyee to 25 percent in the Gascoigne Wood #2 and Illinois #6. The silicate fraction accounts for 15 to 20 percent of the Sb in each of the coals.

Mercury (Hg)

Selective leaching data indicate that pyrite is the dominant mineral containing Hg. However, because Hg concentrations in the solid residue of the HNO_3 leach are below the detection limit for CVAA, only minimum fractions can be given for Hg in pyrite in the Gascoigne Wood #2 (>40 %) and Illinois #6 (>55 %) coals (these values are not shown in Fig. 7D). For the Wyee sample, a total of only 40 percent of the Hg was leached by all solvents, suggesting that an unleached 60 percent portion of the Hg is organically associated. Eighty-five percent of the Hg was leached from the Canadian sample, with 70 percent being extracted by nitric acid. Because Hg concentrations in pyrite are below the detection limit for electron microprobe analysis, the presence of Hg in pyrite could not be directly confirmed.

A strong association of Hg with pyrite was found by Querol and Heurta (1998), for the Gascoigne Wood #2 and Illinois #6 coals, and an association with the heavy mineral fraction was found for the Wyee coal. Taken together with the leaching data, and based on our experience with other coals, a strong pyritic association is indicated for Hg. However, the Wyee coal contains very little pyrite (0.02 % pyritic sulfur), thus significant amounts of Hg may be organically associated. The association of Hg with the heavy mineral fraction in the Wyee coal (Querol and Heurta, 1998) indicates that a portion of the unleached Hg may be contained in heavy minerals not dissolved by our procedure.

Lead (Pb)

A large (45-80%) HCl-leachable fraction, and a smaller (10-40%) HNO_3-leachable fraction was found for Pb in each of the samples (Fig. 8c). These data reflect the primary modes of occurrence for Pb, as monosulfides (galena) and in pyrite, respectively. Galena was observed in the Wyee, Gascoigne Wood #2, and Canadian coals using SEM/EDX. Lead selenide (PbSe; HNO_3-leachable) was found in the Gascoigne Wood #2 and Wyee coals.

Uranium (U)

Leaching data for U show large (40-70%) unleached fractions and a predominance of HF-leachable U (20-40%) (Fig. 9d). The large unleached fractions are indicative of insoluble U-oxides, organically associated U, or zircon. Uraninite was found in the Wyee coal using SEM/EDX. The Gascoigne Wood #2 has the largest HF-soluble fraction (40%), possibly due to a larger proportion of U in zircon (observed by SEM). Additionally, the Wyee coal has an HCl-soluble fraction (20%) and the Gascoigne Wood #2 has an HNO_3-soluble phase (15%). No U-bearing phase was found in the Illinois #6 sample, possibly indicating that its large unleached U fraction (70%) is organically associated.

Yttrium (Y) and Rare Earth Elements (REE)

Leaching data for Y show distinct mode of occurrence patterns for each of the coal samples (Fig. 10A). In the Wyee sample, sub-equal 20-25 percent portions were found by leaching with HCl, HF, and HNO_3, with the remaining 35 percent of the Y has not leached. The 35 percent unleached fraction probably represents organically bound Y. The sum of the HCl and HNO_3 fractions for Y is similar to that determined for the heavy rare earth elements (HREE 30-50%), suggesting that the mineral xenotime (YPO_4), a common accessory phase in coal, may be involved. Xenotime is partially soluble in HCl and HNO_3 and is known to concentrate HREE (Mariano, 1989; Fig. 10B).

For the Gascoigne Wood #2 sample, a 55 percent HNO_3-leachable Y fraction was found, with the remainder as HF-leachable (25 %), HCl-leachable (10%) and unleached (10%). The small unleached fraction indicates that most of the Y is in minerals rather than organics. Like the Wyee sample, the sum of the HCl and HNO_3 fractions for Y (65%) and the HREE (60-70%) are similar. The Illinois #6 sample lacks HNO_3-leachable Y, and instead, consists of a HF-leachable fraction similar to the portion found in the other coals (25%), and a large (75%) unleached portion indicating a strong organic association for Y.

Leaching data for the REE show a great deal of continuity as a result of a progressive increase in their organic association with increasing atomic number (Fig. 10B-D). For the light rare earths (LREE), leaching totals exceed 80 percent, indicating a strong association with mineral phases such as monazite (seen in Wyee, and in Illinois #6 by Dehmer and others, 1998). Leaching totals decrease with increasing atomic number in the lanthanide series, to as little as 25 percent for Lu in the Illinois #6 sample.

Of the four leaching steps, leaching with HCl and with HNO_3 are the most effective in removing the REE. The sum of the HCl and HNO_3 leaching fractions shows a distinct decrease with increasing atomic number, but the trend for the Gascoigne Wood #2 is less pronounced than that for the other two coals (Fig. 10B). Data for the HCl and HNO_3 fractions are shown separately in Figure 10C. The figure shows the falloff in HNO_3 leaching percentages with atomic number to be less pronounced for the Gascoigne Wood #2 than for the other coals, and that REE leaching fractions removed by HCL actually INCREASE in going from light to middle REE. This increase may be due to leaching of apatite, which is known to concentrate middle REE relative to heavy and light REE, on a normalized basis. Apatite was observed in the Gascoigne Wood #2 sample by SEM-EDX.

Sums of HCl and HNO_3 leaching data are again plotted vs. atomic number in Figure 10d. Overall, the data show a gradual increase in organic association of the REE (indicated by the decreasing sums) with increasing atomic number. Querol and Huerta (1998) show a similar pattern for the Illinois #6 sample, but their results for the other two coals are less definitive. In the mineral fractions, our results indicate a predominance of LREE-enriched phases such as monazite vs. other REE-bearing phases. The Illinois #6 sample has the greatest organic association, especially for the HREE. Leaching patterns for the Wyee and Gascoigne Wood #2 coals are similar for the LREE, but the Wyee shows a greater tendency towards organic association of the HREE.

Summary

Splits from four coal samples were analyzed by the USGS and other laboratories in an international interlaboratory comparison of bulk chemistry, mineralogy, and elemental mode of occurrence. For bulk coal chemistry, the USGS uses a multi-technique approach that includes ICP-AES, ICP-MS, INAA, and element specific techniques for Hg and Se. Results obtained by this approach are internally consistent (based on leaching results) and generally in good agreement with those obtained by other labs. The poorest results, expressed as the percentage of variation for a given coal, were found for Hg, Cd, and Zn. Data for Hg and Cd reflect problems associated with determining sub-ppm concentrations of these elements.

Mode of occurrence information presented here for 35 elements and the REE is based primarily on selective leaching data, integration of results obtained by SEM/EDX and XRD (to determine mineralogy), and electron microprobe analysis. For most elements, modes of occurrence determined by the USGS are similar to those found by other laboratories using differing approaches. Where there are differences between laboratories, these are primarily in the relative importance of specific modes.

Interpretation of the selective leaching data is generally straightforward, but some discrepancies were found. For example, significant HNO_3-leachable fractions were found for Rb and Cs. Based on geochemical considerations these elements are not expected to be present in pyrite, and the mode of occurrence of the HNO_3-leachable fraction is unclear. Likewise, leaching data for Zn and Cd show unexpectedly large fractions of these elements leached by HNO_3. Electron microprobe analysis of Zn in pyrite fails to confirm the concentrations of Zn in pyrite indicated by the leaching data. For other elements, (e.g. Ni, As, and Cu) microprobe data for pyrite are consistent with average concentrations in pyrite indicated by leaching results. The combination of selective leaching, microanalysis, SEM/EDX and XRD provides mode of occurrence information on a large range of elements.

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Appendix 1A. - Comparison of Chemical data for Wyee Coal reported by different laboratories

Major elements reported in wt % of ash

Bulk Chemistry Technique	Combined Techniques			ICP only	ICPMS only	Spark MS	PIXE	XRF
Element	USGS	A	B	C	D	E	F	G
Ash %	23.7	23.7	23.1	23.7	23.48	25.9	23.1	23.7
Al_2O_3	21	21.42	22.1	21.8			18.4	21.9
CaO	4.1	3.69	3.66	5.8			2.93	3.7
Fe_2O_3	7.1	6.81	6.56	10.1			4.53	5.8
K_2O	2.6	2.69	2.35	2.4			2.12	
MgO	1.5	1.83	1.37	1.7			0.8	1.6
Na_2O	0.86	0.74	0.82	1				1.0
Si_2O	62			52.8			43.5	57.3
TiO_2	0.89	0.84	0.86	1.7			0.79	0.8
Trace elements reported in ppm on a whole-coal remnant moisture basis								
As	3.0	2.1			2.53	2.8		2.7
B	43	35	48					
Ba	149	140	139	138	136			121
Be	1.4	1.3	9	1.04		1.1		
Cd	0.4	< 0.2	< .2		0.52	0.17		< 0.1
Co	1.9	4	1.5		1.55	2		< 6.8
Cr	10	7	<12.0	10.7	5.55	8		5
Cs	2.3	2.1			1.87			
Cu	14	12	11	9.48	11.3	12	10	12.3
Ga	7.1	6.5	6.2		6.63		8	
Ge	1.1		1.7		1			
Hg	0.05	0.07	0.01			0.04	0.04	< 0.5
Li	11.4	12	6					
Mn	260	254	252			242	133	181
Mo	1.5	0.07	1.2		1.33	1.4		1
Nb	4.7		3.5		3.87			
Ni	3.6	4	2			3	3	4.9
Pb	13	16	11		14.2	11.9	7	11
Rb	25	24			20.5			
Sb	1.1	.66	0.8					0.4
Sc	3.8	3.8		3.3				
Se	< 0.5	0.5	<2.0			0.68		
Sn	2.4		2					
Sr	104	73	100	94.8	84.45		67	91
Th	6.16	6.6	7.8		6.99			
Tl	0.5		0.4		0.54			0.4
U	1.9	1.9	1.7		2.29			0.9
V	19.9	19	11.0	15.4	16.2			36
Y	12.3			11.9	10.36			
Zn	15.1	37	6	16.6	20.29	19	11	16.5

Notes:

A - (Oxides) LTA values were used by converting to percent by weight using the ash value determined by USGS

B - (Oxides) Bulk coal values were converted to percent by weight using their lab's ash value

C - (Elements) Values were converted from ppm in the ash to a bulk coal basis using USGS ash values

D - Values are based on average of two values

G - (Oxides) Bulk coal values were converted to percent by weight using the ash value determined by the USGS

KEY

(See text for description of techniques)

ICP	ICP-MS	SparkMS
CVAA	AFS	Hydride Gen
INAA	PIXE	GFAA
XRF	0.07	

Appendix 1B. - Comparison of Chemical data for Gascoigne Wood #2 reported by different laboratories

Bulk Chemistry	Major elements reported in wt. % of ash							
Technique	Combined Techniques			ICP only	ICPMS only	Spark MS	PIXE	XRF
Element	USGS*	A	B	C	D	E	F	G
Ash %	15.8	15.93	15.8	15.8	16.01	17.5	15.3	15.8
Al_2O_3	24	25.2	26.1	24			21.9	26.4
CaO	2.6	2.29	2.71	2.7			1.68	2.4
Fe_2O_3	8.2	7.96	7.53	9.6			5.73	7.3
K_2O	3.4	3.74	3.40	4.3			3.28	
MgO	1.9	1.48	1.78	1.7			0.87	2.1
Na_2O	1.7	1.45	1.86	0.7				1.7
Si_2O	53			48.3			37.5	5.3
TiO_2	0.98	0.95	1.04	1.6			0.86	0.8
	Trace elements reported in ppm on a whole-coal remnant moisture basis							
As	8.8	8.7			8.4	9	5.0	8.4
B	33.2	33	155					
Ba	237	247	274	246	235			209
Be	1.7	1.7	1.3	1.5		1.5		
Cd	< .13	< 0.20	< .20			0.082		0.1
Co	5.8	8	6	5.1	5.5	6		7.3
Cr	34.8	23	28	25.8	22.3		15	26
Cs	2.4	1.88			0.95			
Cu	30	31	24	25	26.0	28	22	25
Ga	5.7	6.6	5.8		5.6		5	
Ge	4.9		5.3		4.5		2.5	
Hg	0.03	0.07	0.06			.06	0.07	0.8
Li	36.3	35	33					
Mn	110	108	119			108	70	87
Mo	3	?	2.9		2.85	2.9		1.6
Nb	3.2		3.5		3.05			
Ni	19	18	16	17.5		18.1	14	19
Pb	12	14	10		12.5	12	9	9.1
Rb	25.6	25.3			16.4			
Sb	1.8	1.52	1.4					0.7
Sc	4.8	4.57		4.3				
Se	0.87	0.9	<2.0			1.7		
Sn	<1.6		<1.0					
Sr	53.7	36	57	55.1	42.7		49	50
Th	2.8	3	3.6		2.5			
Tl	0.3		0.4		0.4			0.4
U	1.1	1.3	1		1.2			0.9
V	47.4	40	42.0	36.9	40		36	61
Y	5.5			7.1	2.2			
Zn	19.7	39	19	22.1	21.4	22	12	21

Notes:

A - (Oxides) Bulk coal values were converted to percent by weight using their lab's ash value

B- (Oxides) Bulk coal values were used by converting to percent weight using ash value determined by USGS

C - (Elements) Values are based on average of two values except for Li and B (single value) and converted from ppm in the ash to a whole coal basis using USGS ash values

D- Values are based on average of two values

G - (Oxides) Bulk coal values were converted to percent by weight using the ash value determined by the USGS

KEY

(See text for description of techniques)

ICP	ICP-MS	SparkMS
CVAA	AFS	Hydride Gen
INAA	PIXE	GFAA
XRF	?	

Appendix 1C. - Comparison of Chemical data for Illinois #6 Coal reported by different laboratories

Bulk Chemistry		Major elements reported in wt. % of ash						
Technique	Combined Techniques			ICP only	ICPMS only	Spark MS	PIXE	XRF
Element	USGS*	A	B	C	D	E	F	G
Ash %	10.4	10.4	10.17	10.4	10.31	12.6	10.1	10.4
Al_2O_3	17	19.41	18.2	17.9			17.1	18.3
CaO	4.5	4.54	4.24	3.4			2.83	3.9
Fe_2O_3	21	19.37	17.9	8.9			11.37	18.1
K_2O	1.7	1.85	1.89	2.2			1.79	
MgO	0.87	1.12	0.82	0.8			1.152	1.0
Na_2O	0.6	.52	0.93	0.8				0.9
Si_2O	48			41.4			36.8	49.6
TiO_2	0.96	1.12	0.82	2			85	0.8
		Trace elements reported in ppm on a whole-coal remnant moisture basis						
As	2.9	2			2.85	3.2		2
B	229		352					
Ba	41.6		46	41.6	42.3			37.4
Be	1.4		1	1.10		1.2		
Cd	.24	.4	.6			.27		0.1
Co	3.4		3.2	2.6	.31	3.9		10.7
Cr	23.9	17	23	18.7	16.1	23	17.0	22
Cs	1	1.1			0.98			
Cu	8.7	8	8	6.76	8.28	9	5	6.2
Ga	3.4		2.9		3.25		4	
Ge	5.2		4.7		4.6		4.0	
Hg	0.05	0.08	0.1			.07	0.09	< 0.7
Li	9.6	9	11					
Mn	36.4	37	40			35	18	24
Mo	6.6	4	5.3		5.41	6.1		3.8
Nb	3.1		2.2		2.18			
Ni	12.5	12	11	11.4		13	8	11.9
Pb	13.5	14	11		13.4	12	7	10
Rb	14.5	12			12.1			
Sb	0.4	0.34	0.4					0.3
Sc	2.5	2.4		2.08				
Se	2.2	1.9	<2.0			2.5		
Sn	<1.0		<1.0					
Sr	28.1	20	26	25.5	23.7		30	23.4
Th	2.2	1.7	2.1		2			
Tl	0.7		0.5		0.67			< 0.4
U	1.3	1.6	1.4		1.81			0.9
V	27	24	33.0	22.88	23.9			38
Y	5.4			5.2	2.45			
Zn	71	103	86	70.2	69.8	63	27	56

Notes:

A - (Oxides) LTA values were used by converting to percent by weight using the ash value determined by USGS

B - (Oxides) Bulk coal values were converted to percent by weight using their lab's ash value 10.17%

C - (Elements) Values were converted from ppm in the ash to a bulk coal basis using USGS ash values

D - Values are based on average of two values; Ash value 10.31

G - (Oxides) Bulk coal values were converted to percent by weight using the ash value determined by the USGS

KEY

(See text for description of techniques)

ICP	ICP-MS	SparkMS
CVAA	AFS	Hydride Gen
INAA	PIXE	GFAA
XRF	AA	

Appendix 1D. - Comparison of Chemical data for Eastern Canadian Thermal Coal determined by different labortories

Bulk Chemistry — Major elements reported in wt. % on an ash basis

	Comb. Techniques	ICPMS only	XRF
Element	USGS	D	G
Ash %	10.1	7.47	10.1
Al_20_3	18		13.2
Ca0	2.9		2.6
Fe_20_3	34		36.5
K_2O	1.6		1.0
MgO	1.3		1.8
Na_2O	1.0		1.7
Si_2O	37		30.9
TiO_2	0.77		0.8

Trace elements reported in ppm on a whole-coal remnant moisture basis

Element	USGS	D	G
As	77	54	67
B	12.1		
Ba	43.4	27.9	63
Be	0.9	0.95	
Cd	0.2	0.1	2
Co	3.3		
Cr	13.1	7.1	12
Cs	0.9	0.68	
Cu	10.1	9.1	14
Ga	2.8	2.4	
Ge	2.3	1.8	
Hg	0.18		
Li	14.1	9.8	
Mn	150	96	143
Mo	5.5	4.2	5
Nb	2	1.1	
Ni	9.9		12
Pb	32	28	54
Rb	9.7	6	
Sb	1.3	1.1	1.6
Sc	1.7	1.2	
Se	4.8		
Sn		0.28	
Sr	31.3	23.8	35
Th	1.4	1.1	
Tl	1.2	0.75	13
U	0.4	0.29	
V	15.2		20
Y	3	2.5	
Zn	36.4	25.5	45

(See text for description of techniques)

ICP	ICP-MS	SparkMS
CVAA	AFS	Hydride Gen
INAA	PIXE	GFAA
XRF	AA	

Notes:

D - Values are based on average of three values

G - (Oxides) Bulk coal values were converted to percent by weight using the ash value determined by the USGS

Appendix 2. Comparison of ash and chemical data reported by USGS.

[Data on whole coal remnant moisture basis, in ppm except as noted]
John H. Bullock Jr., Analyst (ICP, ICP-MS and CVAA)

Graph Number		Wyee Coal	Gascoigne Wood #2	Illinois #6	Canada
	Ash (%)	23.7%	15.8%	10.4%	10.1%
1	Li	11.4	36.3	9.6	14.1
2	Be	1.4	1.7	1.4	0.91
3	Al (%)	2.6%	2.0%	0.94%	0.96%
4	Na	1500	2000	500	750
5	K	5100	4500	1500	1300
6	Rb	25	25.6	14.5	9.7
7	Cs	2.3	2.4	0.98	0.94
8	Mg	2100	1800	550	790
9	Ca	7000	2900	3300	2100
10	Sr	104	53.7	28.1	31.3
11	Ba	149	237	41.6	43.4
12	Sc	3.8	4.6	2.5	1.7
13	Ti	1300	930	600	470
14	V	19.9	47.4	27.0	15.2
15	Cr	10	34.8	23.9	13.1
16	Mn	260	110	36.4	150
17	Fe (%)	1.2%	0.91%	1.5%	2.4%
18	Co	1.9	5.8	3.4	3.3
19	Ni	3.6	19	12.5	9.9
20	Cu	14	30.0	8.7	10.1
21	Zn	15.1	19.7	71	36.4
22	Mo	1.5	3	6.6	5.5
23	Cd	0.42	<0.13	0.24	0.20
24	As	3.0	8.8	2.9	77
25	Se	< 0.5	0.87	2.2	4.8
26	Sb	1.1	1.8	0.41	1.3
27	Hg	0.05	0.03	0.05	0.18
28	W	2.04	0.69	0.36	0.73
29	Tl	0.47	0.32	0.69	1.2
30	Pb	13	12	13.5	32
31	Hf	2.4	2.3	0.48	0.43
32	Ta	0.35	0.23	0.14	0.14
33	Th	6.2	2.8	2.2	1.4
34	U	1.9	1.1	1.3	0.43
36	La	13.9	11.9	4.8	6.2
36	Ce	25.3	19.7	8.9	10.8
36	Nd	9	7.6	3.3	< 6.0
36	Sm	2.8	2.1	0.98	1.1
36	Eu	0.44	0.4	0.2	0.22
36	Tb	0.37	0.22	0.13	0.14
36	Yb	1.3	0.84	0.52	0.4
36	Lu	0.19	0.12	0.067	0.06
35	Y	12.3	5.5	5.4	3.0
	B	43.0	33.2	229	12.1
	Si (%)	6.9%	3.9%	2.3%	1.7%
	Ga	7.1	5.7	3.4	2.8
	Ge	1.1	4.9	5.2	2
	Nb	4.7	3.2	3.1	2.0

Appendix 3. Low Temperature Ash Yields and Mineralogy

[Minerals Determined by X-ray diffraction. All values in percent of the low temperature ash] Frank T. Dulong, Analyst

Mineral	Wyee	Gascoigne Wood #2	Illinois #6	E. Canadian
Quartz	30	20	25	11
Feldspars	10	< 1	< 1	ND
Carbonates	< 5	<5	5	< 1
Illite	20	35	10	17
Kaolinite	35	30	45	36
Chlorite	ND	10	ND	ND
Pyrite	ND	< 5	15	25
Anatase	NR	NR	NR	7
% LTA Ash	25.6	17.1	13.4	13.9

ND = Not detected
NR = Not reported

Appendix 4. Minor and trace phase mineralogy observed by SEM

[Mineral indications are based on elemental composition of grains determined with an energy dispersive X-ray system and morphology]

Coal Sample	Observed Minerals
Wyee	
	Monazite (rare earth phosphate)
	Ilmenite
	Pyrite
	Uraninite
	Chalcopyrite
	Galena
	Gypsum
	Barite
	Crandallite Group (Sr)
	Rutile
	Mo, Pb, Cu, Sb Sulfide
	Chromite
	Argentite
	Lead Selenide
	Cassiterite
Gascoigne Wood #2	
	Pyrite
	Gypsum
	Barite
	Rutile
	Sphalerite (Cd)
	Zircon (Hf)
	Amphibole
	Fe, Ni, Cu Sulfide
	Lead Selenide (in Pyrite)
	Galena
	Apatite
Illinois #6	
	Pyrite
	Sphalerite (Cd)
	Fe Oxide
	Chromite
	Barite
Eastern Canadian	
	Galena
	Calcite
	Rare Earth Phosphate
	Zircon
	Ti Oxide
	Apatite

Appendix 5A. Element compositions of pyrite grains in Gascoigne-Wood #2 sample as reported by USGS

[Determinations are made by analysis of individual grains in electron microprobe; values are presented in percent]

Grain Number	Se	Cu	Ni	As	Zn	Cd	Co*	Fe	S	Total	Size and Form (micrometers)
10	< .01	< .01	< .01	.10	< .01	< .01	< .01	47.40	49.40	96.95	70 x 120 subhedral
11	< .01	< .01	< .01	.12	< .01	< .01	.02	47.40	49.57	97.17	
12	< .01	< .01	< .01	.12	< .01	< .01	.01	46.99	49.94	97.10	
13	< .01	< .01	< .01	.10	.01	< .01	.02	47.53	50.33	98.04	
14	< .01	.02	< .01	.49	.01	< .01	.01	47.00	51.22	98.80	75 x 90 composite subhedral
15	.02	< .01	< .01	.35	.01	< .01	.01	48.01	52.41	100.85	
16	< .01	< .01	< .01	.26	.01	< .01	.02	47.92	51.71	99.96	
17	< .01	.01	< .01	.35	< .01	< .01	.01	47.44	51.01	98.88	
18	< .01	.03	< .01	.08	.01	< .01	.02	47.51	53.58	101.27	50 x 120 subhedral
19	< .01	< .01	< .01	.07	< .01	< .01	.02	47.12	53.46	100.73	
20	< .01	.02	.00	.50	.03	< .01	.01	48.25	52.54	101.40	60 x70 subhedral wi. euhedral overgr.
21	< .01	.01	.01	.07	< .01	< .01	< .01	48.20	52.64	100.99	
22	< .01	.02	.04	.30	< .01	< .01	.01	48.65	45.63	94.70	
23	< .01	.01	.05	.06	< .01	< .01	.02	46.90	52.38	99.45	
24	< .01	.04	.08	.16	.02	< .01	.01	47.68	50.83	98.87	60 x 60 subhedral
25	.02	.04	.12	.19	.03	< .01	.02	47.42	50.99	98.88	
26	.02	.04	.15	.30	< .01	< .01	.02	47.38	51.90	99.86	
27	.01	.04	.09	.19	.04	< .01	.03	47.30	51.52	99.25	
29	< .01	< .01	< .01	.17	.01	< .01	.01	47.69	49.31	97.24	75 x 80 subhedral
30	< .01	< .01	< .01	.15	< .01	< .01	.01	47.67	52.79	100.67	
33	.01	.04	< .01	.25	< .01	< .01	.02	46.61	51.15	98.12	60 x 100 composite subhedral
34	< .01	.03	< .01	.23	< .01	< .01	< .01	46.72	51.13	98.16	
35	< .01	.02	< .01	.22	< .01	< .01	< .01	47.02	51.14	98.45	
36	< .01	.01	< .01	.01	.01	< .01	.01	47.88	52.66	100.62	50 x 60 composite subhedral
37	.04	< .01	< .01	.09	< .01	< .01	.01	45.47	49.13	94.79	
38	< .01	.00	< .01	.19	.01	< .01	< .01	46.85	51.23	98.33	
39	.01	.02	.03	.01	.01	< .01	.01	47.13	47.01	94.28	30 framboid
42	< .01	.03	< .01	.40	< .01	< .01	< .01	47.26	50.63	98.37	70 x 70 composite subhedral
43	< .01	.02	< .01	.83	< .01	< .01	.01	46.40	50.07	97.38	

Appendix 5A.- continued.

Grain Number	Se	Cu	Ni	As	Zn	Cd	Co	Fe	S	Total	Size and Form (micrometers)
44	< .01	< .01	< .01	.21	.01	< .01	.01	47.81	52.70	100.79	35 x 60 subhedral
45	< .01	.04	.00	.40	.01	< .01	.01	47.10	52.19	99.79	
46	.01	< .01	.01	.02	< .01	< .01	.01	47.85	52.37	100.31	15 framboid
47	< .01	.02	.05	.01	.01	< .01	< .01	48.22	52.22	100.58	17 framboid
48	< .01	.03	< .01	.14	.01	< .01	.01	45.48	48.89	94.61	70 x 100 composite subhedral
49	< .01	.06	.08	.22	.03	< .01	< .01	47.10	50.47	98.01	
50	< .01	.01	.04	.12	.00	< .01	.01	47.31	51.00	98.54	
51	< .01	.03	.00	.11	.01	< .01	< .01	46.59	50.26	97.06	
53	< .01	< .01	.01	1.92	.01	< .01	.02	47.51	50.19	99.71	55 x 65 subhedral
54	< .01	< .01	< .01	.88	< .01	< .01	< .01	48.00	51.06	99.99	
55	< .01	.01	.01	.06	< .01	< .01	.01	48.55	51.98	100.67	80 x 90 subhedral
56	< .01	< .01	.11	.13	.01	< .01	.02	48.28	50.91	99.50	
57	< .01	.01	< .01	.69	.01	< .01	.02	48.23	51.44	100.43	
58	< .01	< .01	< .01	.38	.02	< .01	< .01	48.69	51.84	100.99	
59	< .01	< .01	.01	.30	< .01	< .01	< .01	48.43	50.53	99.31	
60	< .01	< .01	< .01	.24	< .01	< .01	.01	48.29	51.53	100.12	40 x 75 composite subhedral
61	< .01	< .01	< .01	.20	< .01	< .01	.01	48.01	51.88	100.16	
62	< .01	.01	< .01	.10	< .01	< .01	< .01	48.46	52.97	101.59	
63	< .01	< .01	.01	.01	.02	< .01	.01	48.99	51.55	100.65	50 anhedral (round)
64	< .01	< .01	.01	.01	.02	< .01	.02	48.41	50.83	99.35	
65	< .01	.01	.01	.01	.03	< .01	< .01	48.35	50.38	98.84	
66	< .01	< .01	< .01	.35	.01	< .01	.01	47.56	51.44	99.42	35 x 60 subhedral
67	< .01	< .01	.01	.27	< .01	< .01	.01	48.42	51.59	100.35	
68	< .01	.01	< .01	.30	.03	< .01	< .01	48.20	50.73	99.31	
70	< .01	.02	.03	.01	.01	< .01	.01	47.49	48.66	96.28	20 framboid
71	< .01	.03	.04	.01	.02	< .01	.01	48.49	51.68	100.34	40 x 40 subhedral
72	< .01	.03	.06	.01	.02	< .01	.01	48.33	50.85	99.37	
73	< .01	.04	.03	.00	.01	< .01	.01	48.35	50.97	99.45	

Appendix 5A.- continued.

Grain Number	Se	Cu	Ni	As	Zn	Cd	Co*	Fe	S	Total	Size and Form (micrometers)
77	< .01	.02	.03	< .01	.01	< .01	.01	48.88	51.32	100.32	25 framboid
78	< .01	.07	.05	.01	.04	< .01	.01	47.95	51.46	99.62	30 framboid
79	< .01	.10	.05	.02	.01	< .01	< .01	47.80	50.82	98.83	
80	.01	.02	.21	.06	< .01	< .01	.03	47.06	49.74	97.18	30 x 35 composite subhedral
81	< .01	.02	.19	.09	< .01	< .01	.02	47.49	50.30	98.15	
82	.00	.01	< .01	.24	.02	< .01	.01	47.75	49.98	98.05	25 x 45 subhedral
83	.03	.03	< .01	.21	< .01	< .01	.01	47.65	50.48	98.46	
84	.02	.03	.07	.06	< .01	< .01	.01	48.60	50.31	99.15	45 x 95 composite subhedral
85	.01	.04	.06	.10	.01	< .01	.01	48.55	50.66	99.48	
86	.02	.03	.06	.08	< .01	< .01	.00	48.67	51.46	100.37	

* ~0.05 wt. % contribution of Fe interference has been subtracted from Co values.

Appendix 5B.Element compositions of pyrite grains in Illinois #6 sample as reported by USGS.

[Determinations are made by analysis of individual grains in electron microprobe; values are presented in percent]

Grain Number	Se	Cu	Ni	As	Zn	Cd	Co*	Fe	S	Total	Size and Form (micrometers)
88	< .01	.01	< .01	.01	0.01	< .01	0.00	48.26	50.27	98.60	80 x 130 plumose
90	< .01	< .01	< .01	< .01	< .01	< .01	.01	46.63	48.29	94.98	80 x 100 plumose
91	< .01	.01	< .01	< .01	.01	< .01	< .01	48.56	52.00	100.63	50 x 60 composite subhedral
93	.01	< .01	< .01	.01	.01	< .01	< .01	48.30	51.04	99.42	100 x 100 composite subhedral
94	< .01	< .01	< .01	.01	.01	< .01	< .01	48.68	51.51	100.25	
95	.01	< .01	< .01	< .01	.01	< .01	< .01	48.45	52.14	100.66	
96	< .01	< .01	< .01	< .01	.02	< .01	< .01	48.54	52.43	101.04	
99	< .01	< .01	< .01	< .01	.02	< .01	< .01	47.39	46.64	94.11	125 x 125 subhedral
100	< .01	< .01	.01	< .01	.01	< .01	< .01	47.86	53.59	101.52	
101	< .01	< .01	< .01	< .01	< .01	< .01	< .01	48.72	53.77	102.54	
102	.01	.02	< .01	< .01	< .01	< .01	.01	47.47	52.16	99.73	70 x 80 composite subhedral
103	< .01	.04	< .01	< .01	< .01	< .01	< .01	47.32	52.07	99.48	
104	< .01	.01	.02	.04	.01	< .01	.02	47.25	51.92	99.31	
105	< .01	.01	< .01	.01	< .01	< .01	.01	48.41	52.16	100.64	70 x 130 subhedral
106	.01	< .01	< .01	.01	< .01	< .01	< .01	48.64	52.28	100.99	
107	< .01	< .01	< .01	< .01	< .01	< .01	< .01	48.63	52.51	101.19	
108	< .01	.01	< .01	.01	.01	< .01	< .01	48.62	53.02	101.72	
109	< .01	< .01	< .01	.01	.01	< .01	< .01	48.18	53.27	101.53	
110	< .01	< .01	.01	< .01	.04	< .01	< .01	47.55	51.47	99.12	40 framboid in cluster
111	< .01	.01	.01	< .01	.01	< .01	< .01	47.68	51.59	99.34	
112	< .01	< .01	< .01	< .01	< .01	< .01	< .01	47.92	52.52	100.49	
113	.01	< .01	< .01	< .01	.02	< .01	< .01	47.82	52.89	100.79	35 framboid
114	< .01	< .01	< .01	.01	< .01	< .01	< .01	47.16	52.09	99.30	
115	.01	< .01	< .01	.01	.02	< .01	< .01	48.10	51.41	99.59	35 x 45 composite subhedral
116	< .01	< .01	< .01	.01	.01	< .01	< .01	47.83	52.22	100.12	
117	< .01	< .01	.03	< .01	.01	< .01	< .01	48.26	52.14	100.50	30 framboid in cluster
118	.01	< .01	.02	< .01	< .01	< .01	.01	48.90	53.34	102.33	

* ~0.05 wt. % contribution of Fe interference has been subtracted from Co values.

Appendix 5B - continued.

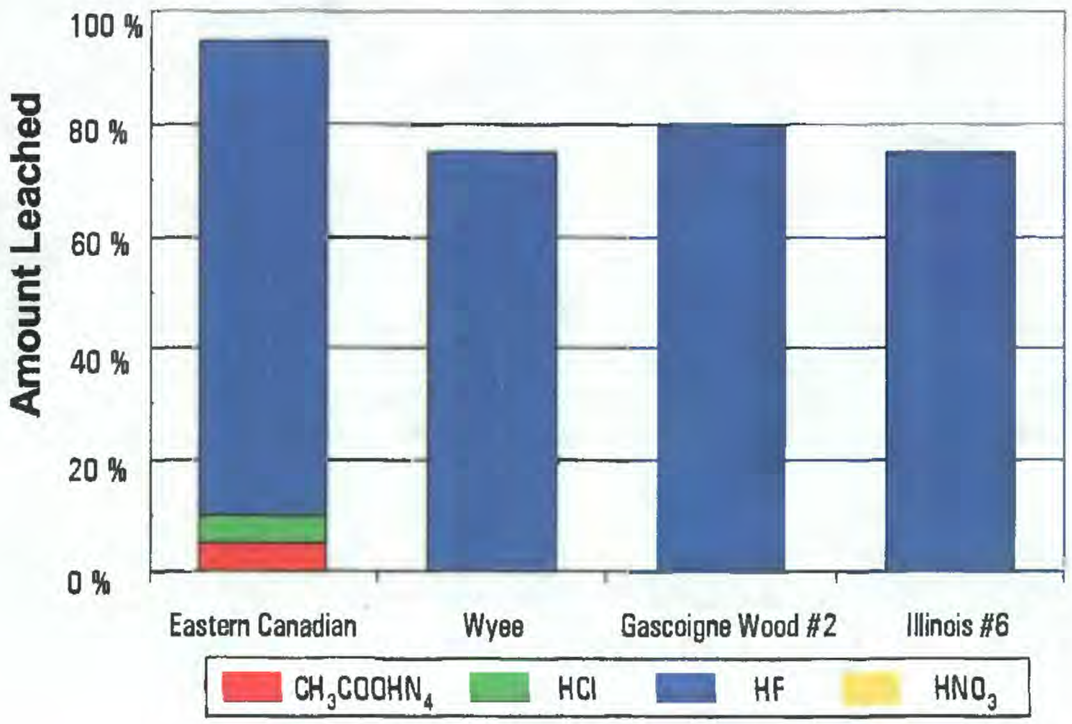
[Determinations are made by analysis of individual grains in electron microprobe; values are presented in percent]

Grain Number	Se	Cu	Ni	As	Zn	Cd	Co*	Fe	S	Total	Size and Form (micrometers)
119	.01	< .01	< .01	< .01	.01	.00	< .01	48.30	51.80	100.18	25 framboid in cluster
120	< .01	< .01	< .01	< .01	< .01	< .01	< .01	48.14	51.71	99.91	
121	< .01	.02	< .01	.01	.01	< .01	< .01	47.86	51.84	99.78	90 x 150 composite anhedral/subhedral
122	< .01	< .01	< .01	< .01	.01	< .01	< .01	48.52	52.74	101.33	
123	< .01	.02	< .01	.01	.01	< .01	< .01	46.92	51.14	98.15	
125	< .01	< .01	< .01	< .01	.01	< .01	< .01	48.02	53.25	101.32	60 x 80 composite subhedral
126	< .01	< .01	< .01	< .01	.02	< .01	< .01	47.52	51.45	99.04	
130	< .01	.05	.06	< .01	.01	< .01	< .01	46.97	50.84	97.98	100 x 120 composite
131	< .01	.08	< .01	.02	.01	< .01	< .01	47.25	50.98	98.38	
132	< .01	.07	.01	.01	.03	< .01	< .01	46.63	51.16	97.97	
133	.01	.05	.01	.01	.01	< .01	< .01	46.39	51.53	98.05	
134	.01	.01	< .01	< .01	.02	< .01	< .01	48.20	51.87	100.16	20 x 50 subhedral (cleat?)
135	.01	< .01	< .01	.01	.01	< .01	.02	47.84	52.97	100.91	
136	< .01	.01	< .01	< .01	.01	< .01	.01	48.66	51.75	100.48	70 x 85 composite
137	< .01	< .01	< .01	.01	< .01	< .01	.00	48.18	52.95	101.19	
138	< .01	< .01	< .01	.00	.02	< .01	.01	48.35	51.38	99.81	
139	< .01	< .01	< .01	< .01	.01	< .01	< .01	47.25	50.31	97.63	
140	< .01	< .01	.02	.03	.03	< .01	.01	47.93	50.07	98.14	30 framboid in cluster
141	< .01	< .01	.03	.01	.02	< .01	.01	46.89	50.82	97.82	
142	< .01	< .01	.01	.01	< .01	< .01	< .01	47.59	51.70	99.34	15 framboid
144	< .01	< .01	< .01	.01	.02	< .01	< .01	47.61	48.81	96.50	100 x 175 composite
146	< .01	< .01	< .01	.01	< .01	< .01	< .01	46.13	50.18	96.37	55 x125 subhedral
147	.01	< .01	< .01	.01	.01	< .01	< .01	45.99	50.15	96.22	
150	< .01	.02	.01	< .01	.02	< .01	< .01	43.73	50.21	94.05	

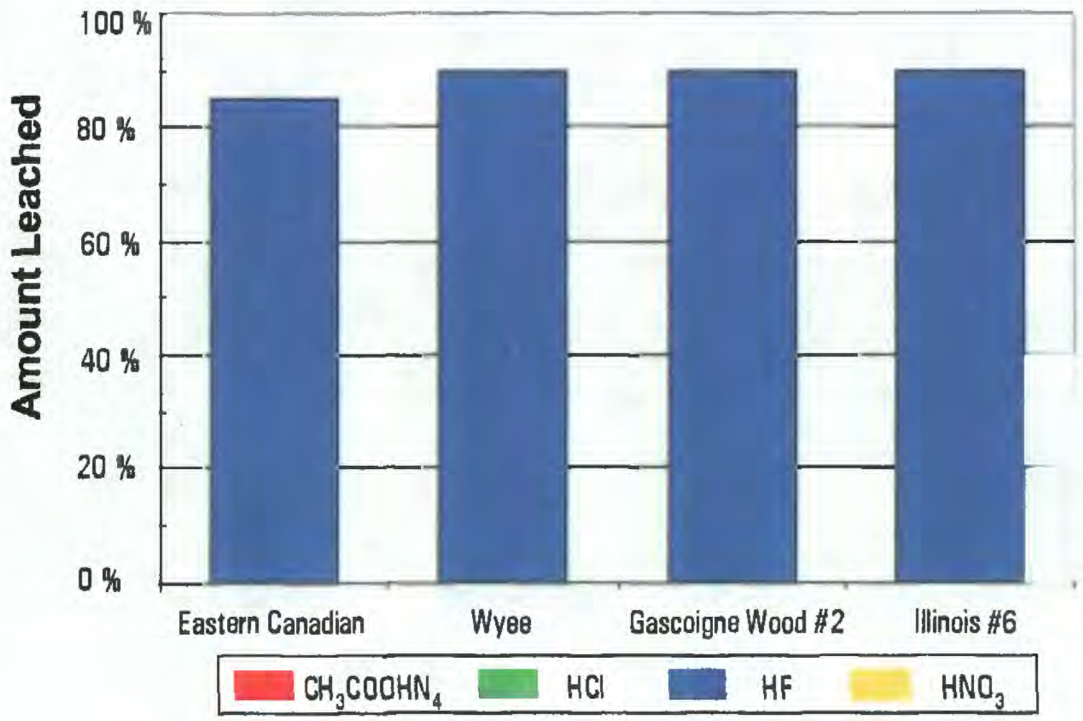
* ~0.05 wt. % contribution of Fe interference has been subtracted from Co values.

Figure 1 - Lithium (A); Beryllium (B); Aluminum (C)

1A. Lithium



1C. Aluminum



1B. Beryllium

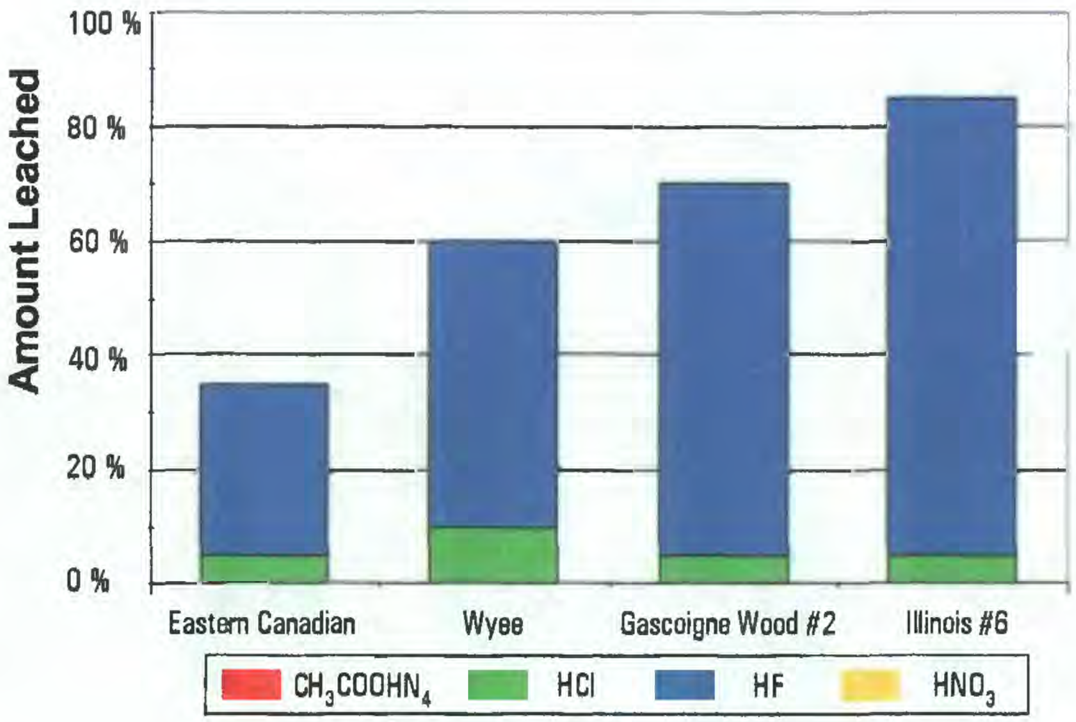
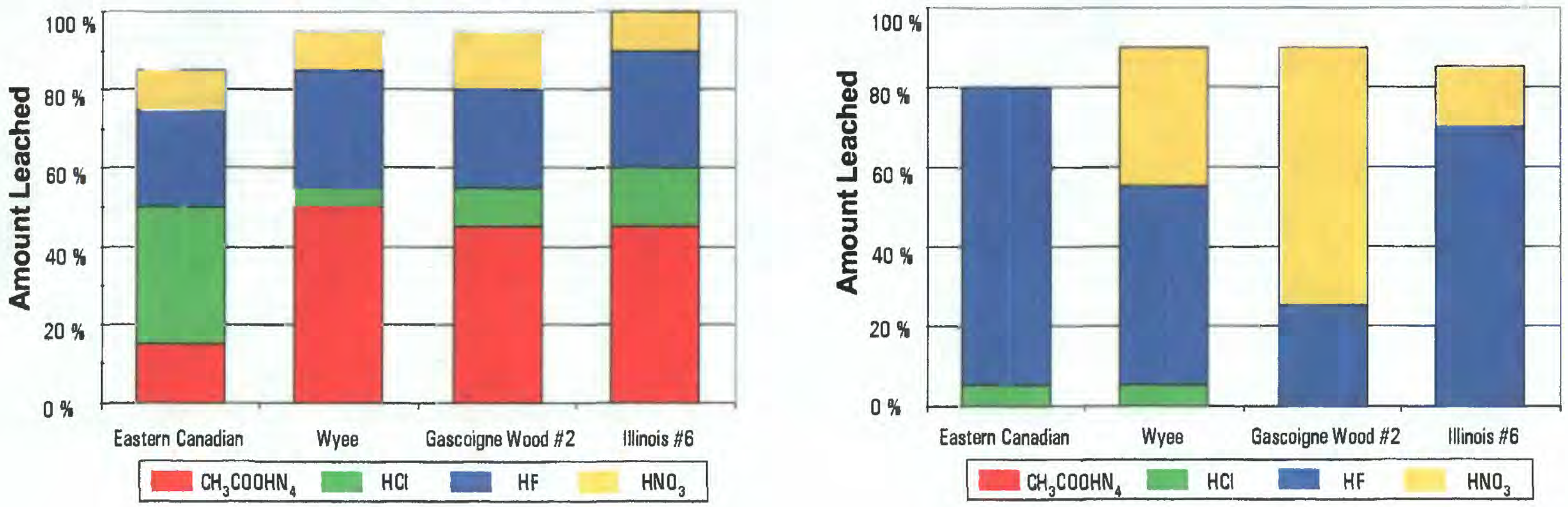


Figure 2 - Sodium (A); Potassium (B); Rubidium (C); Cesium (D)

2A. Sodium

2C. Rubidium



2B. Potassium

2D. Cesium

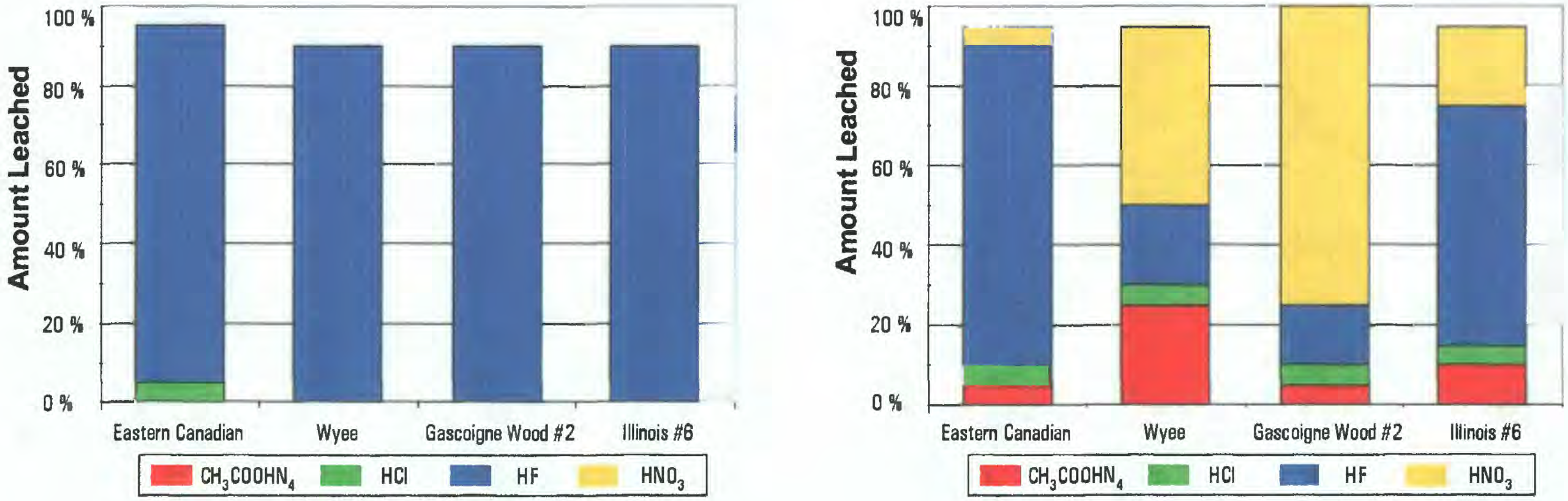
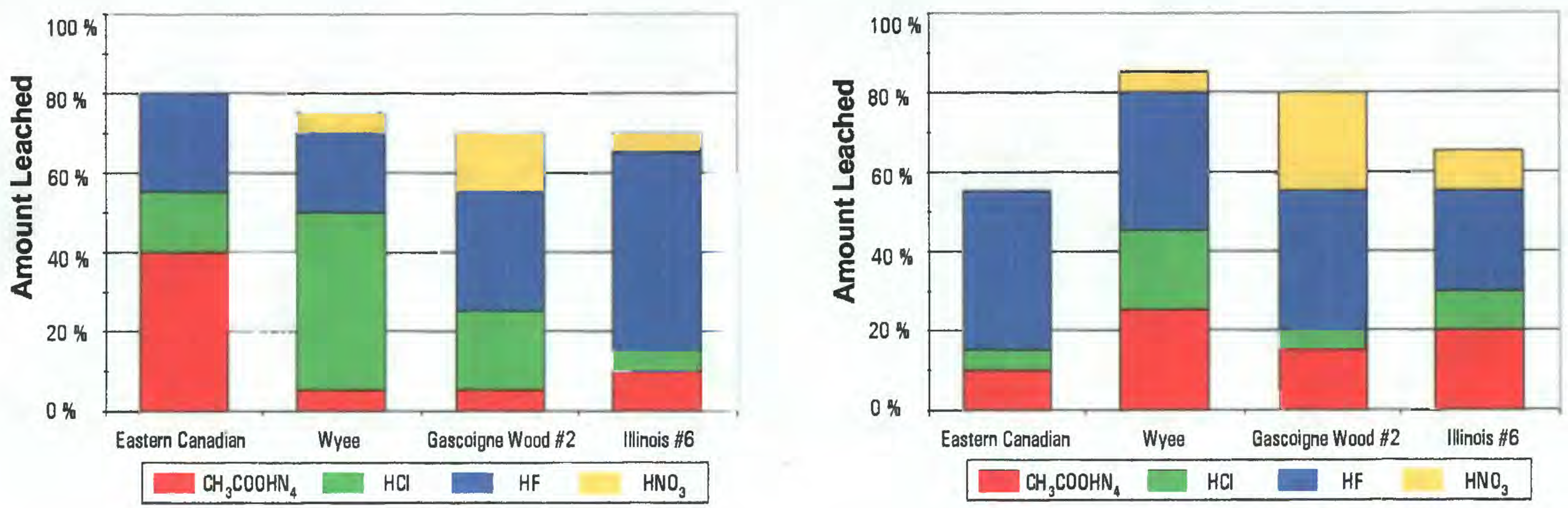


Figure 3 - Magnesium (A); Calcium (B); Strontium (C); Barium (D)

3A. Magnesium

3C. Strontium



3B. Calcium

3D. Barium

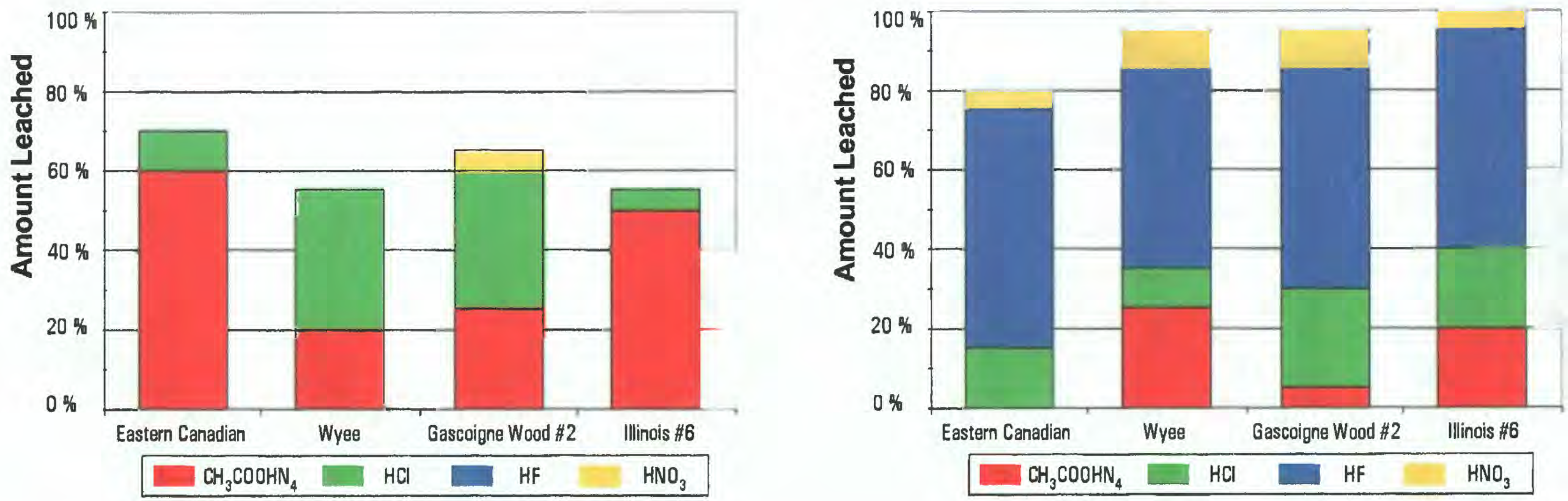
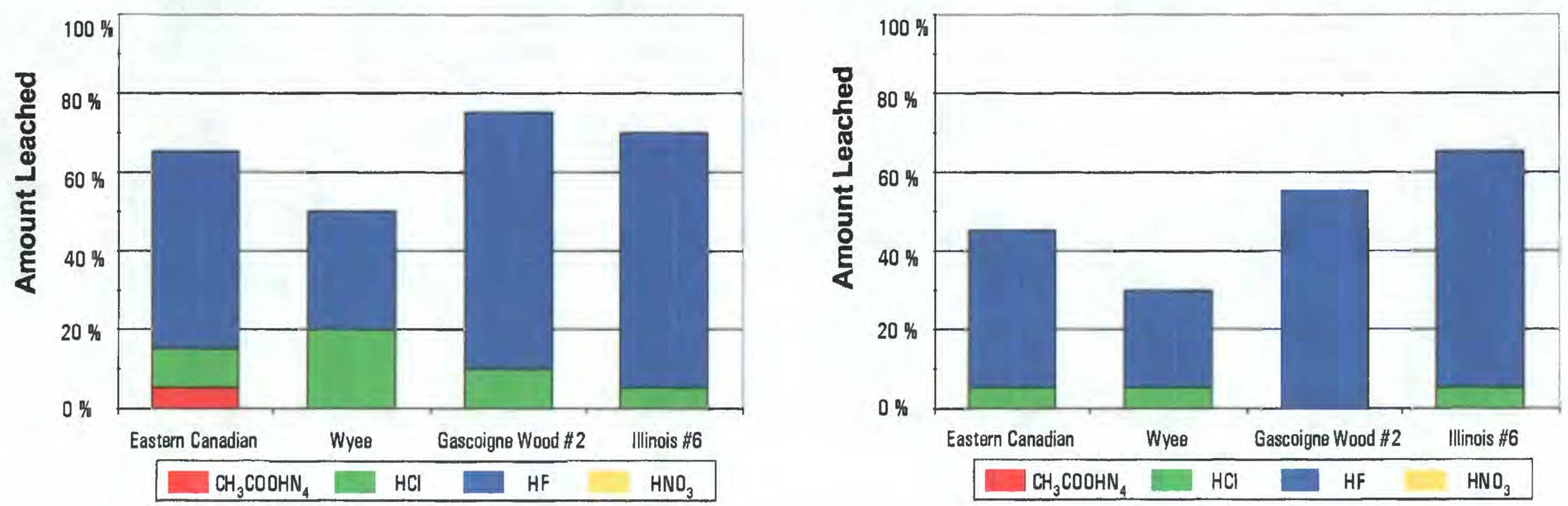


Figure 4 - Scandium (A); Titanium (B); Vanadium (C); Chromium (D)

4A. Scandium 4C. Vanadium



4B. Titanium 4D. Chromium

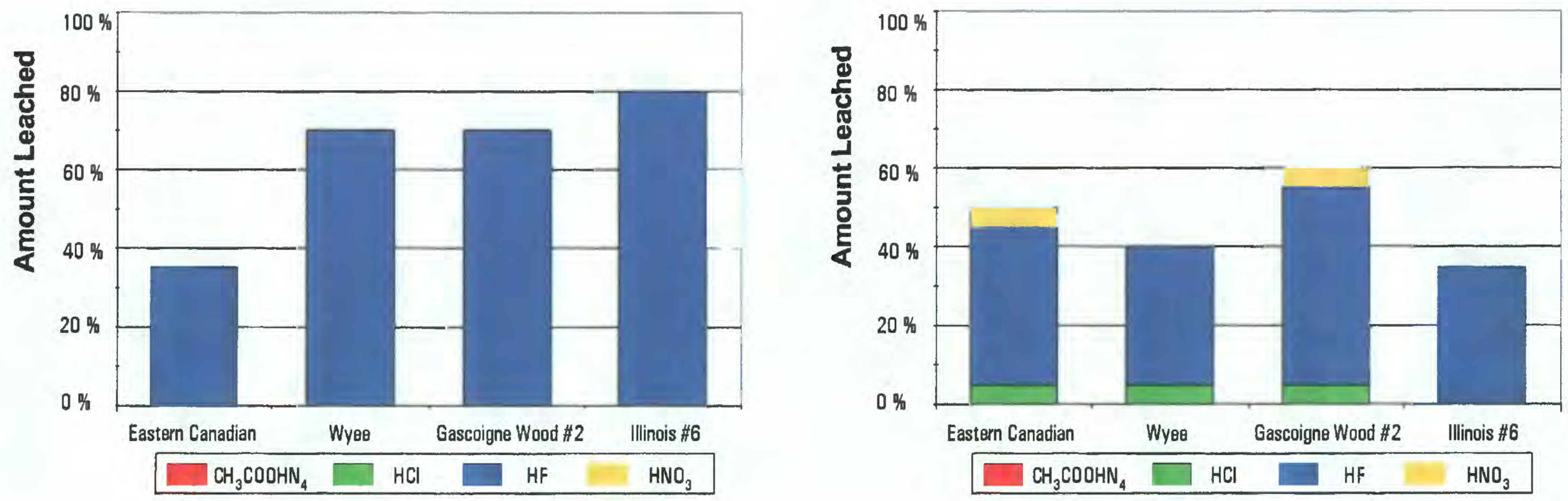
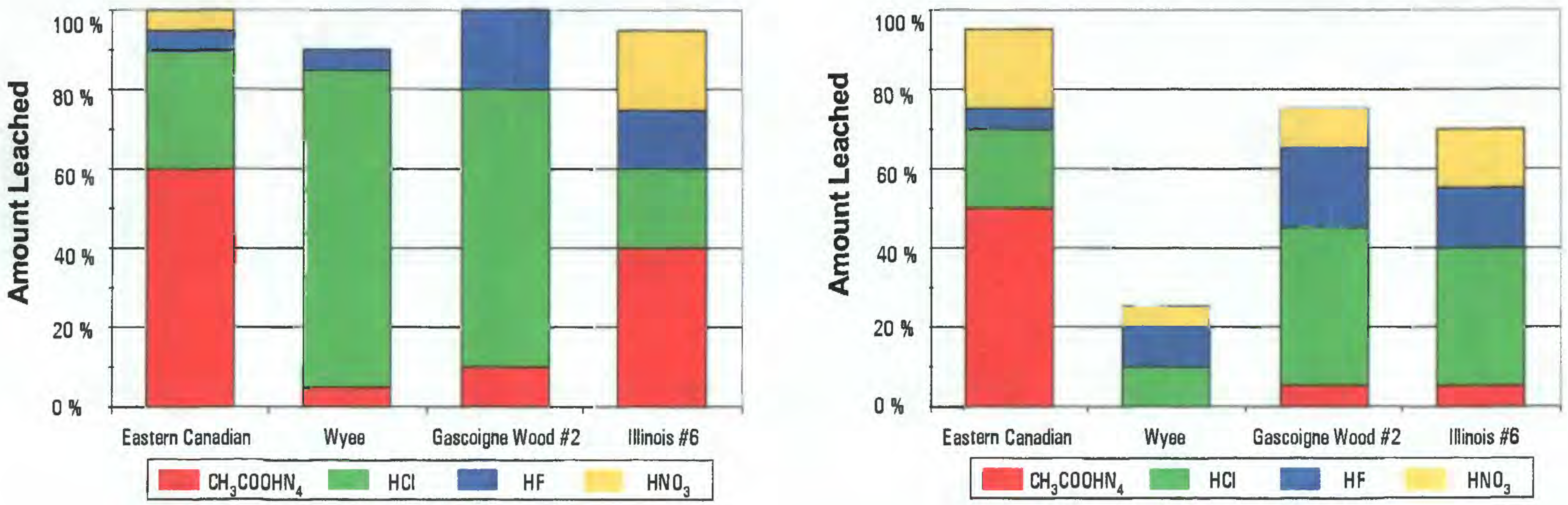


Figure 5 - Manganese (A); Iron (B); Cobalt (C); Nickel (D)

5A. Manganese

5C. Cobalt



5B. Iron

5D. Nickel

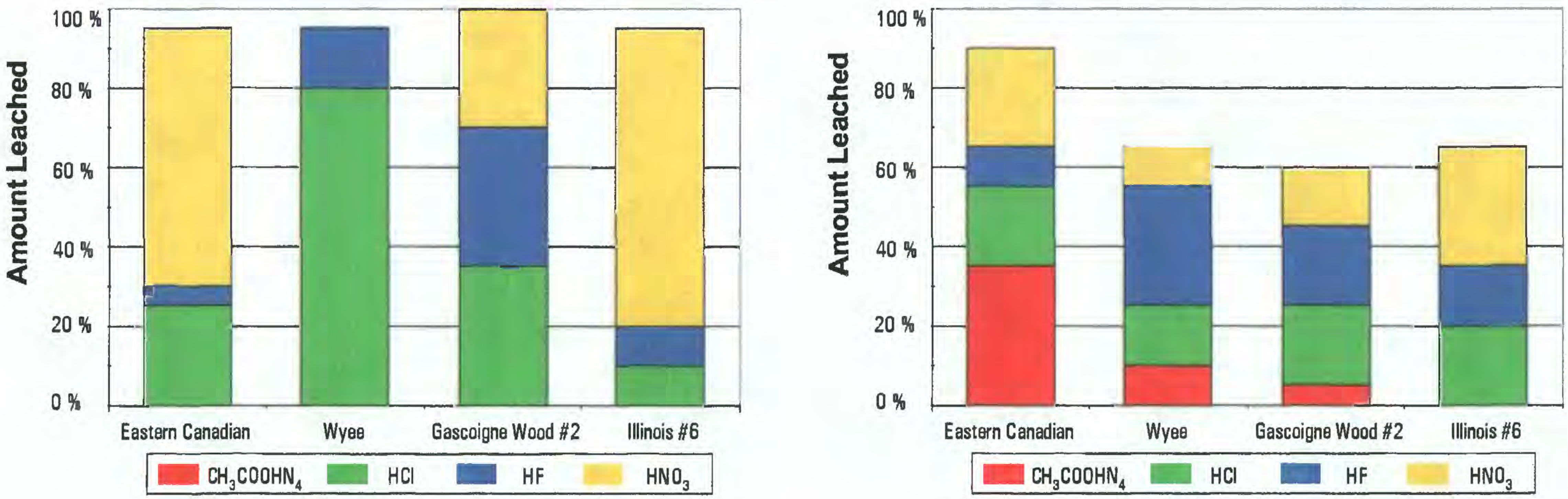
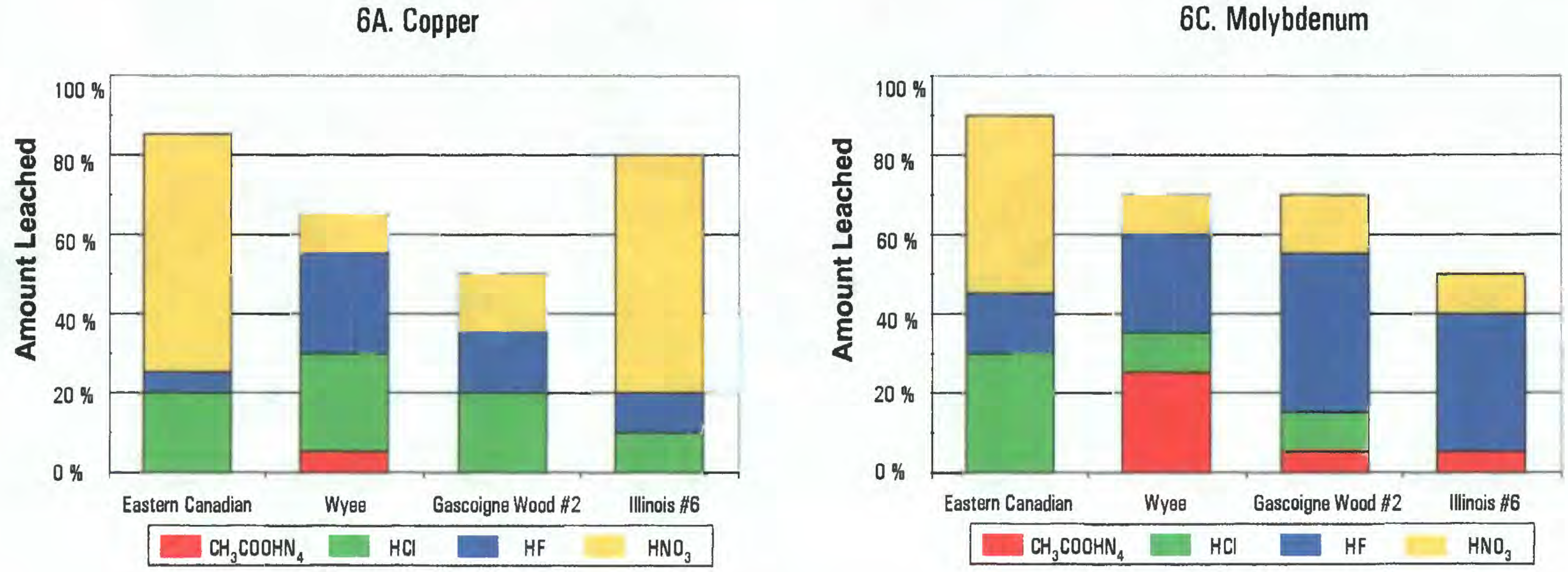
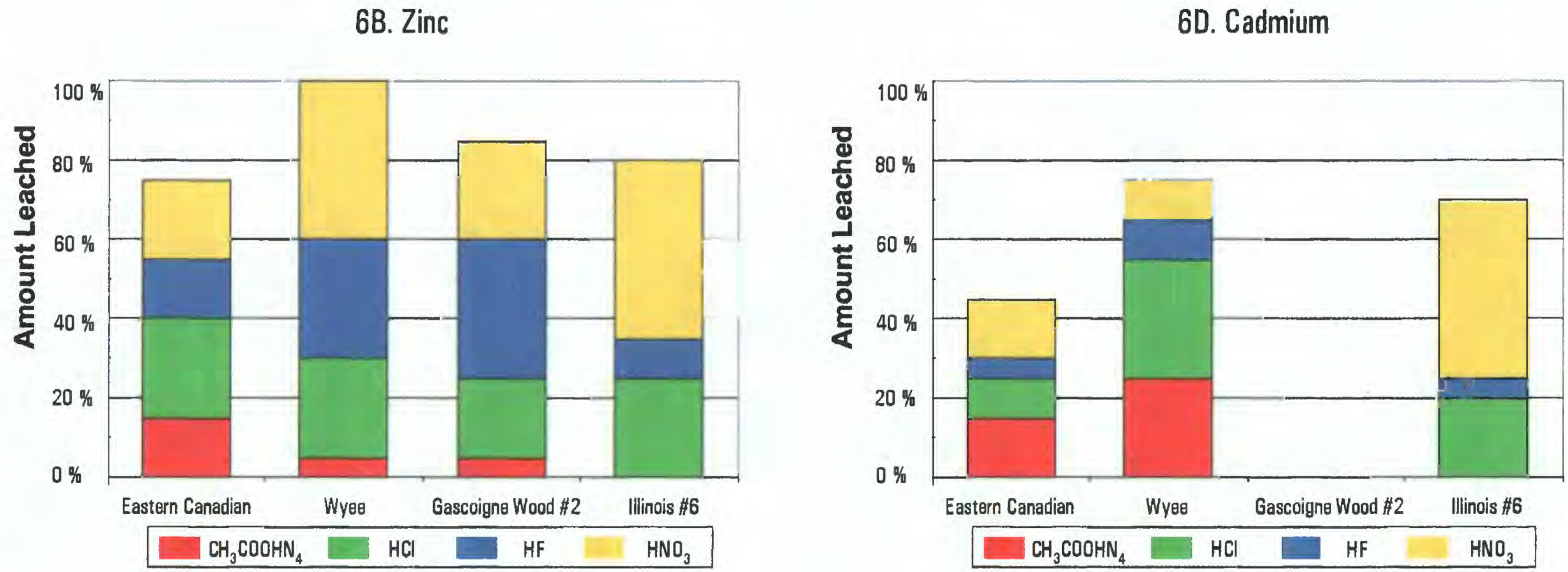


Figure 6 - Copper (A); Zinc (B); Molybdenum (C); Cadmium (D)


6A. Copper

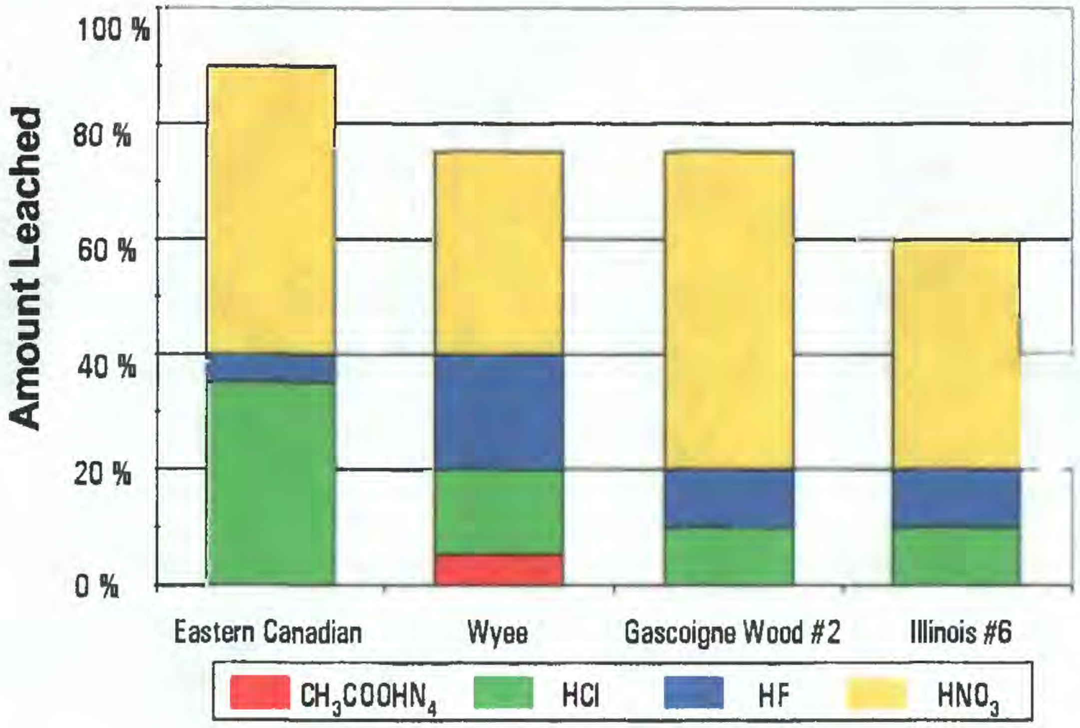
6C. Molybdenum


6B. Zinc

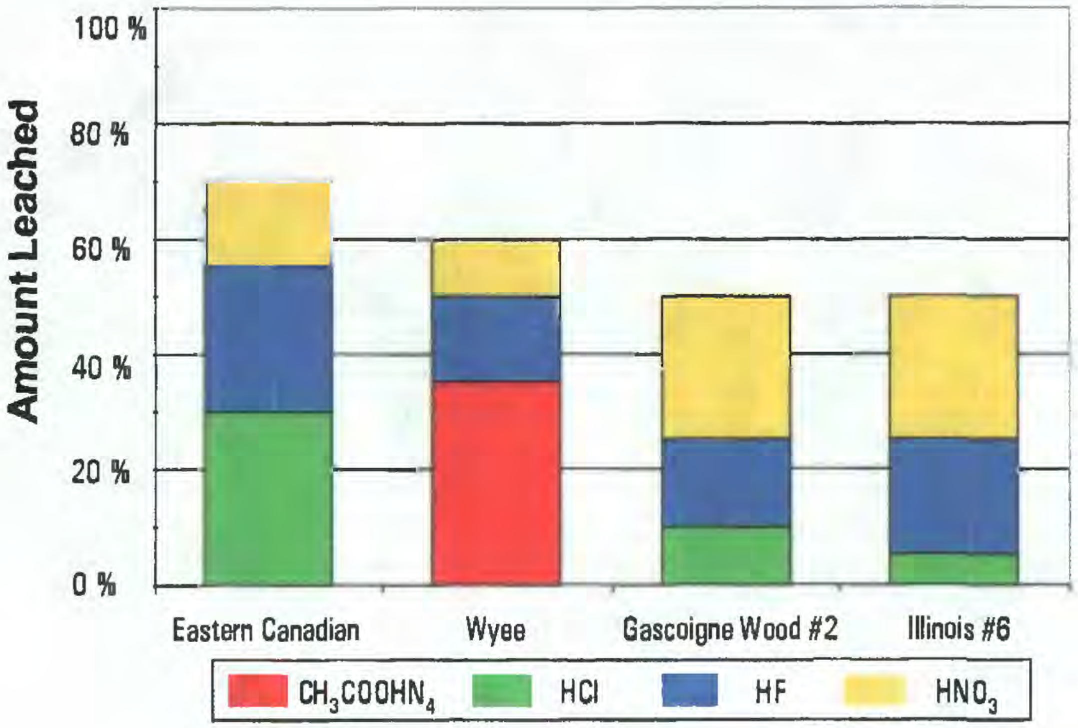
6D. Cadmium

Figure 7 - Arsenic (A); Selenium (B); Antimony (C); Mercury (D)

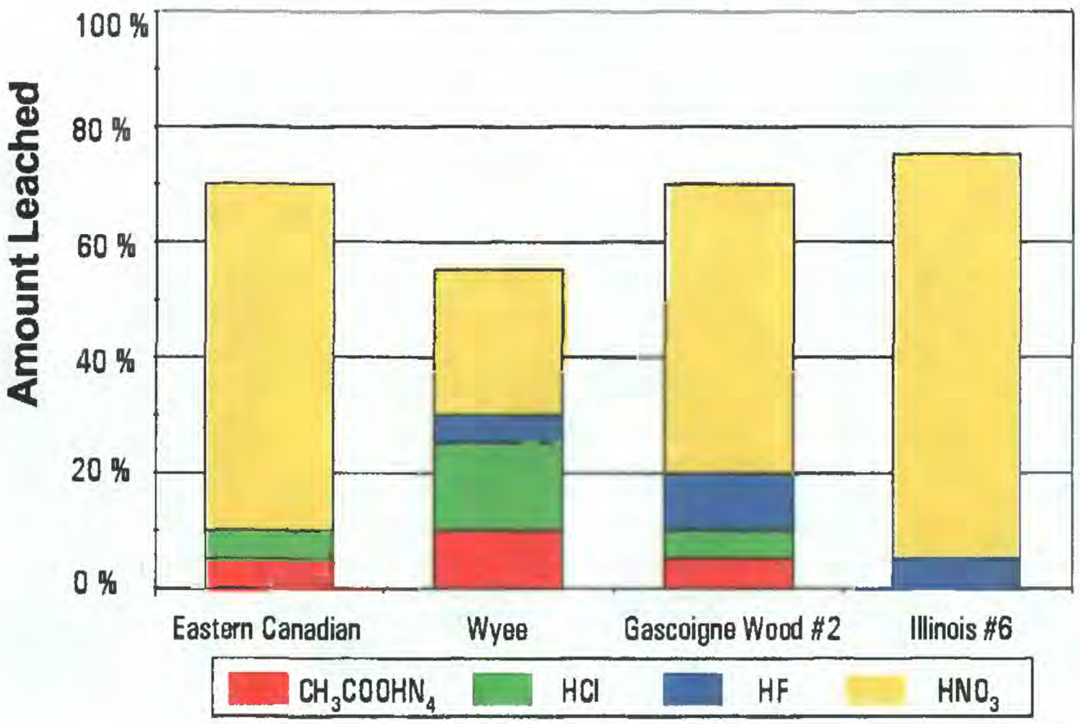
7A. Arsenic



7C. Antimony



7B. Selenium



7D. Mercury

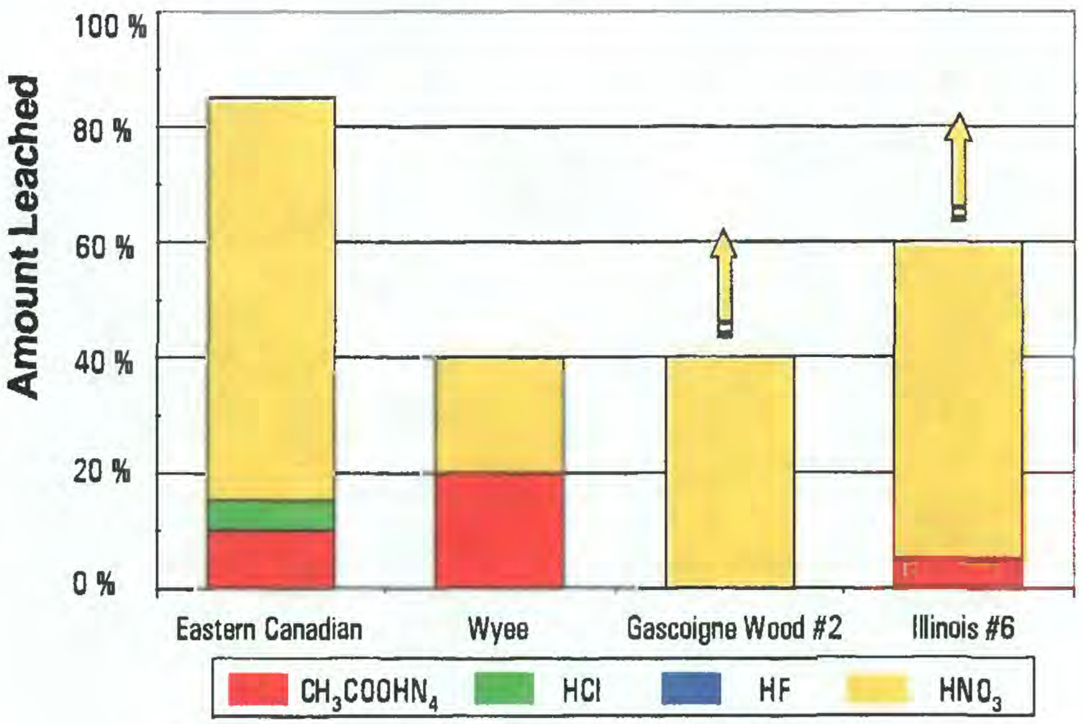
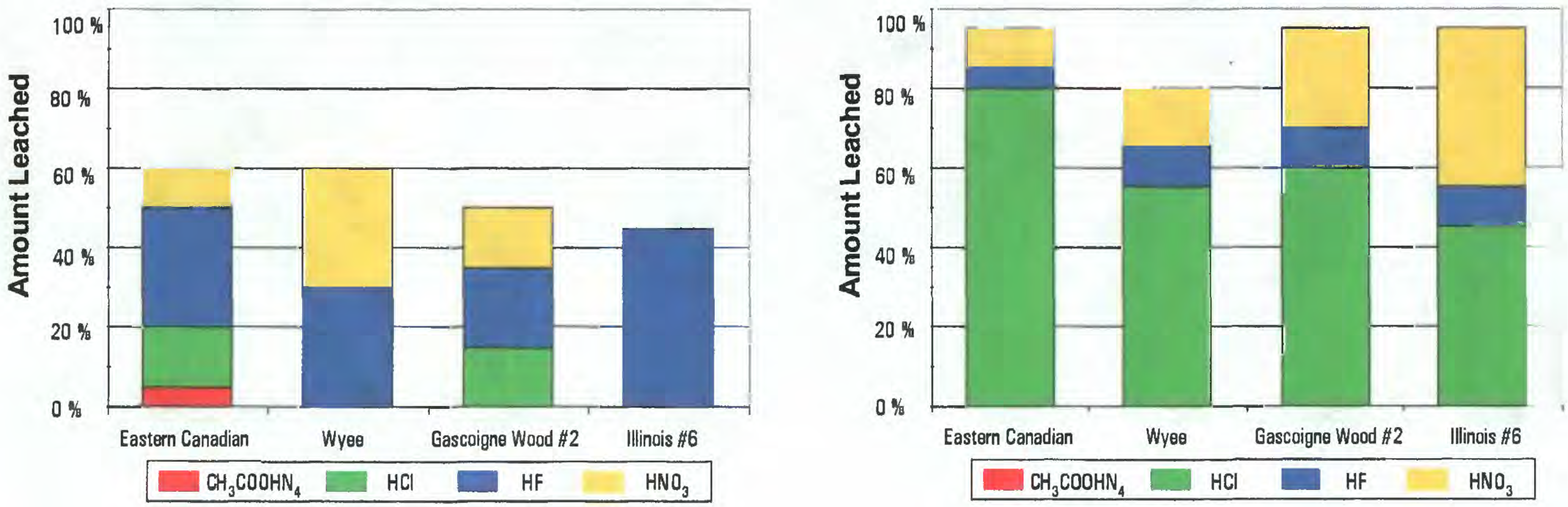
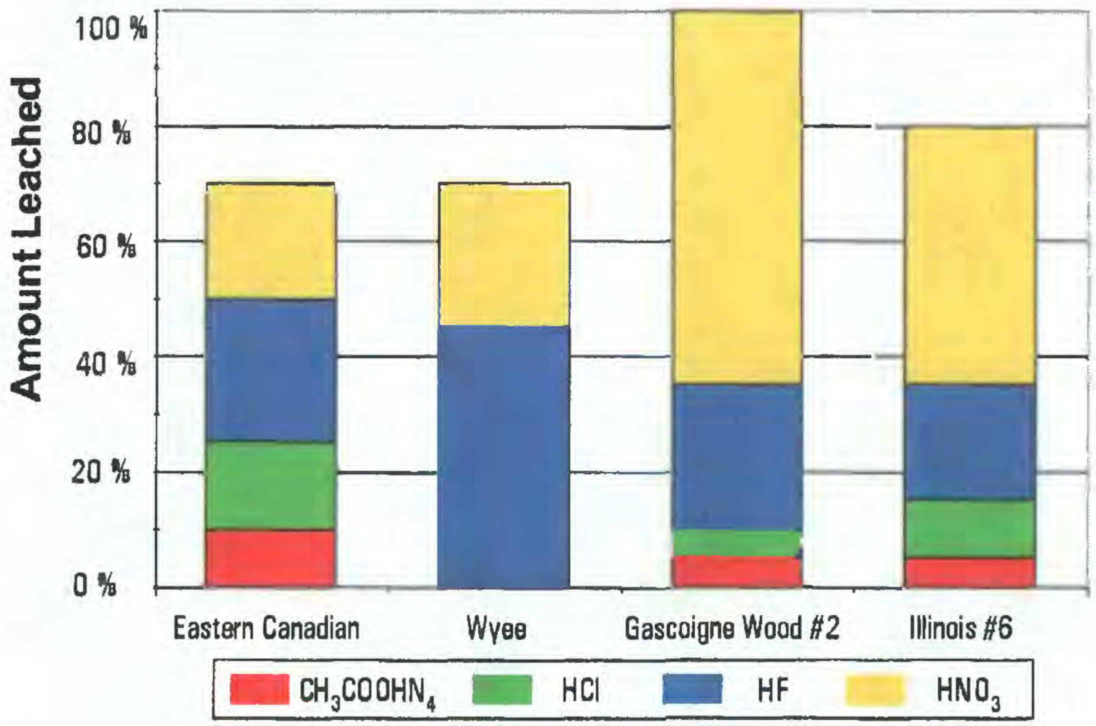


Figure 8 - Tungsten (A); Thallium (B); Lead (C)



8A. Tungsten

8C. Lead

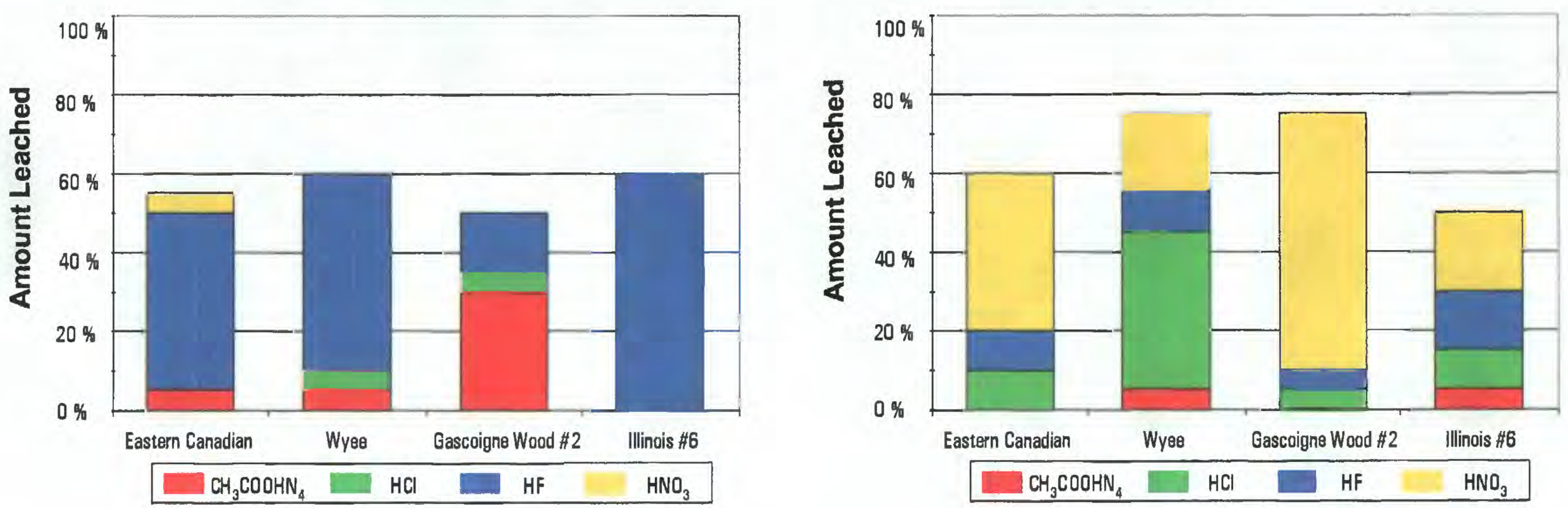


8B. Thallium

Figure 9 - Hafnium (A); Tantalum (B); Thorium (C); Uranium (D)

9A. Hafnium

9C. Thorium



9B. Tantalum

9D. Uranium

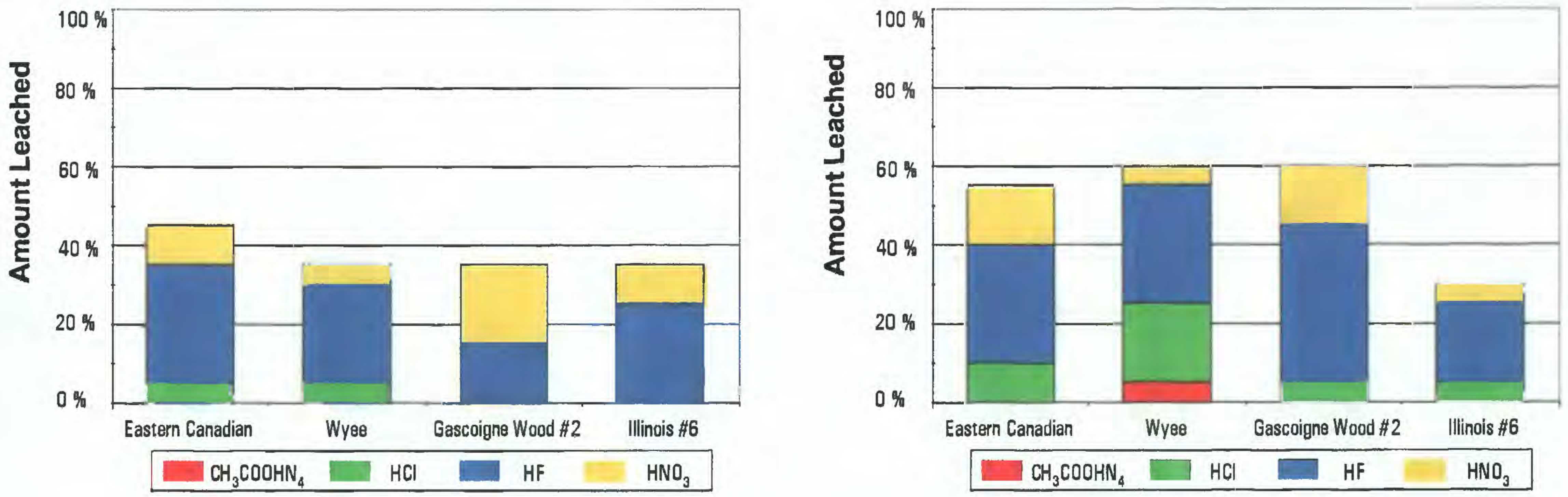
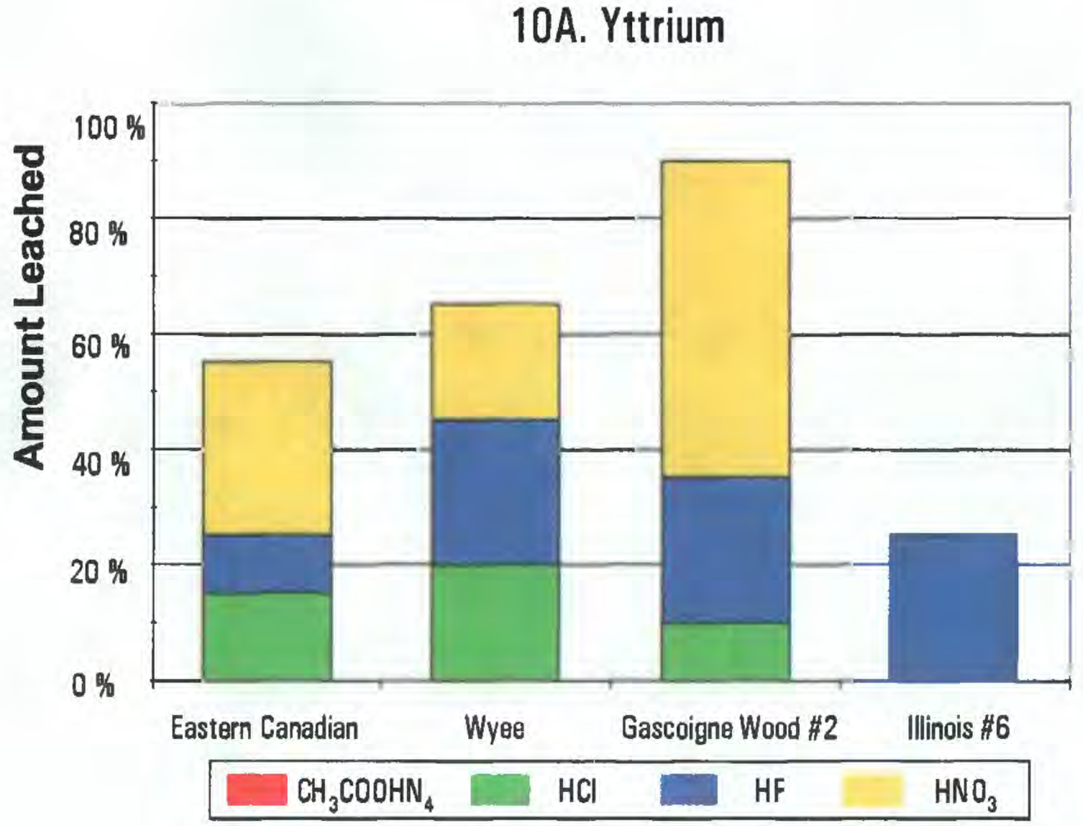
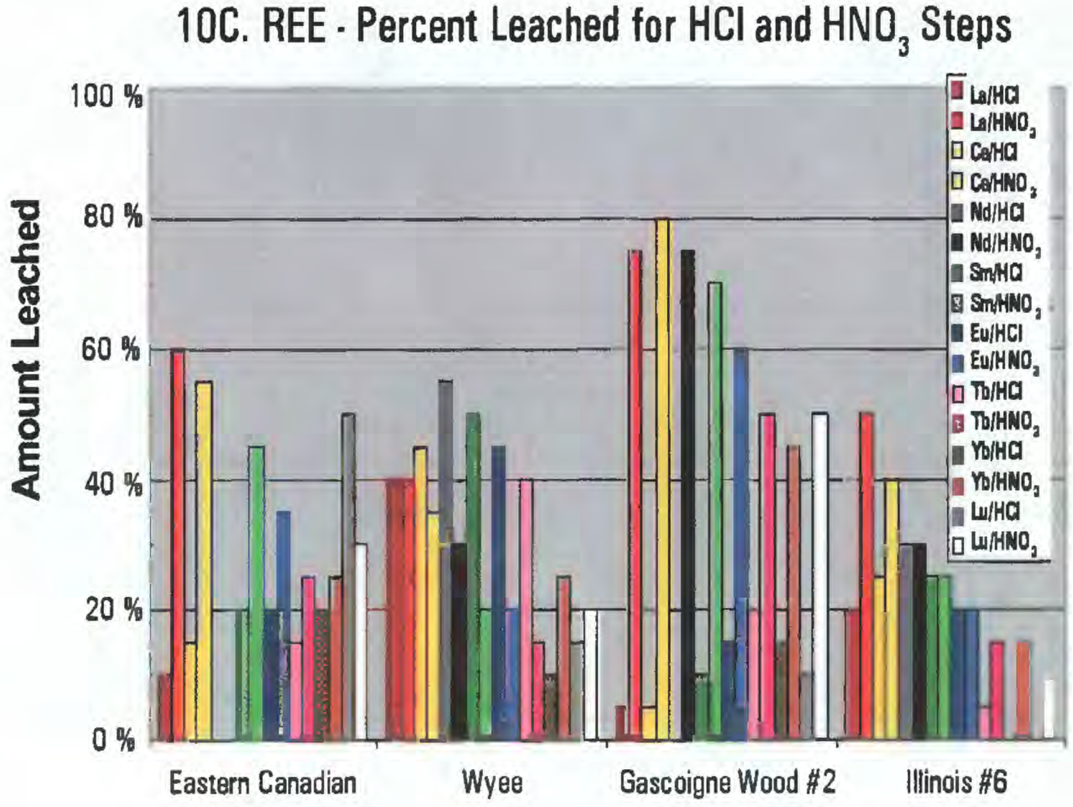
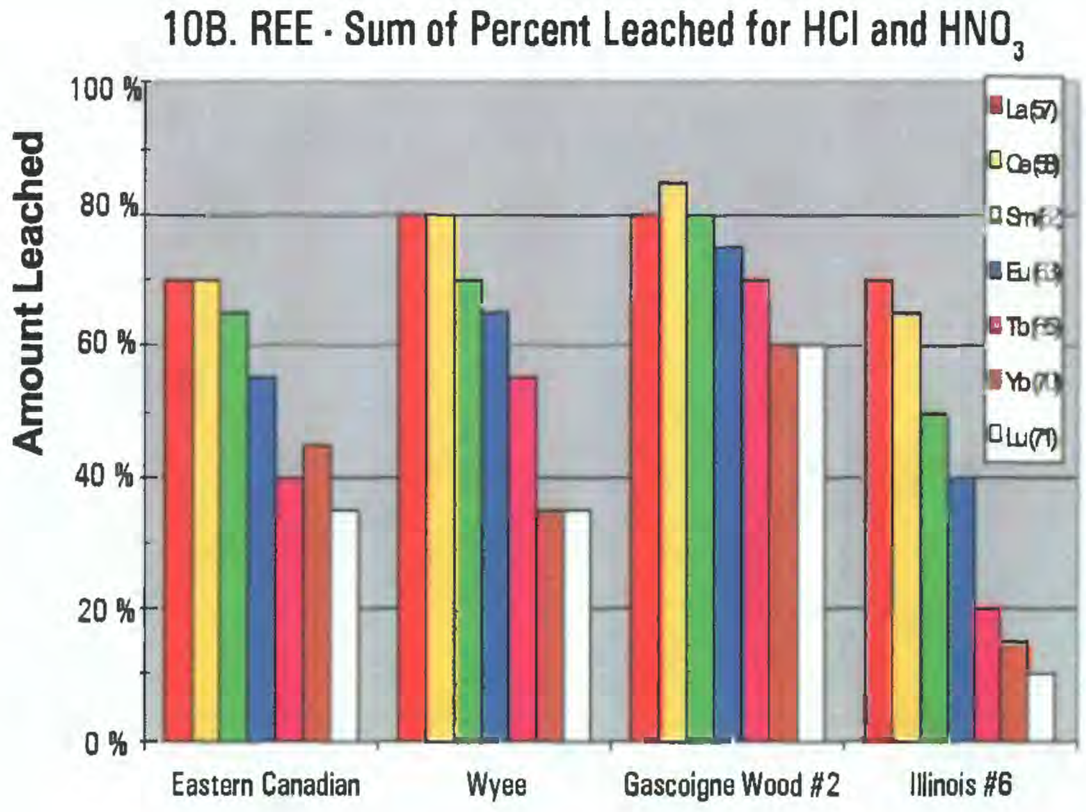


Figure 10 - Yttrium (A) and Rare Earth Elements (B-D)


10A. Yttrium


10C. REE - Percent Leached for HCl and HNO$_3$ Steps


10B. REE - Sum of Percent Leached for HCl and HNO$_3$

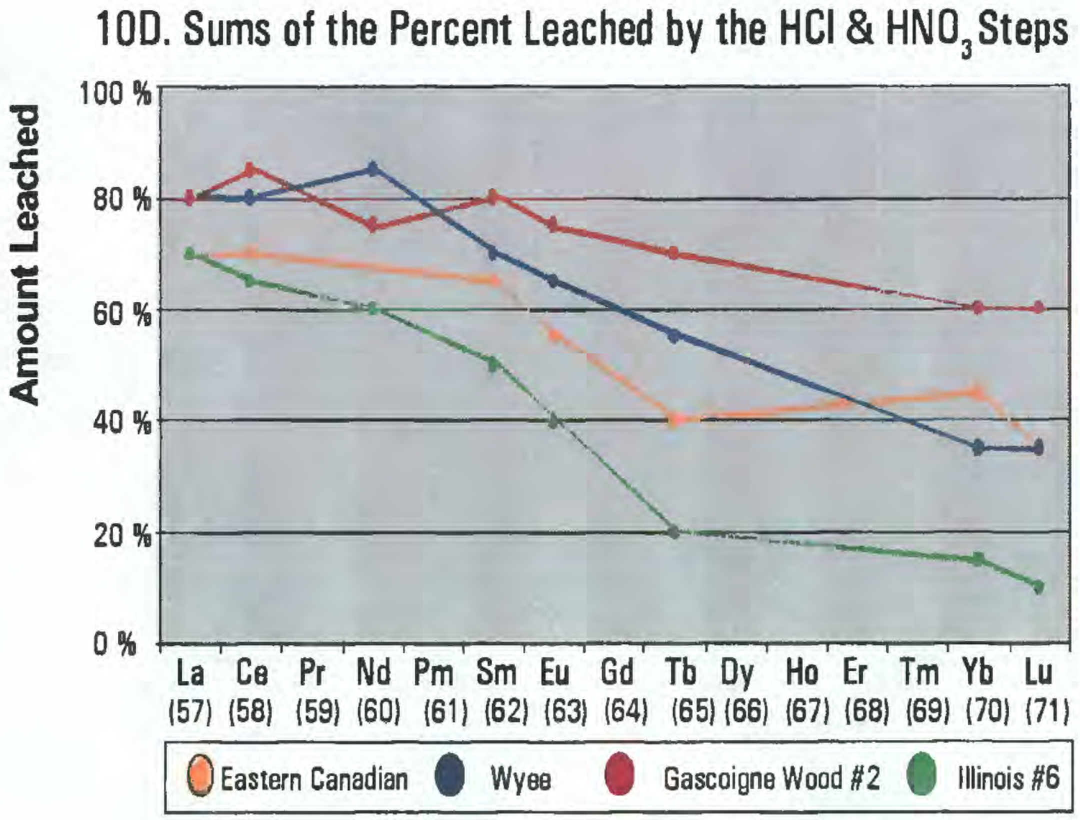

10D. Sums of the Percent Leached by the HCl & HNO$_3$ Steps

Figure 11. SEM photomicrograph showing circular areas of gorceixite ($BaAl_3(PO_4)_2(OH)_5{\bullet}H_2O$) At the margin of a large sphalerite grain (at the center of field of view) in the Wyee sample. Scale bar is 10 micrometers.