THE NATIONAL COAL WASTEWATER SURVEY: 1982 - 1984

by

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This report was written by the Mining, Minerals and Metallurgical Processes Division of the Industrial Programs Branch of Environment Canada.

It was funded by the Office of Energy Research and Development (Energy, Mines and Resources Canada)/Panel on Energy Research and Development (PERD) under Task 24201 "Environmental Protection Criteria for Coal Mining and Processing".

December 1987

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6.3 Wastewater Treatment Practices at Coal Facilities Selected

In order to assess the efficacy of wastewater treatment practices at coal facilities in responding to and meeting production expansions in the coal mining industry (with expected increases in wastewaters produced) it is necessary to assess the efficiency of wastewater treatment practices presently employed by the coal facilities.

This section summarizes wastewater treatment information at the coal facilities investigated during the sampling program.

6.3.1 CBDC: Victoria Junction Coal Preparation Plant, Sydney, NS. The Victoria Junction preparation plant is designed to operate on a closed cycle basis whereby supernatant from the slurry pond is recycled to become plant process water rather than being discharged from the system. In practice, however, surface runoff and groundwater inflows to the pond and the accumulation of chlorides in the recycle water result in the need to discharge water from the slurry pond through the lime treatment plant and into Northwest brook which discharges to the Atlantic ocean.

Surface runoff from the property, coal stock piles and settling ponds is directed by ditches to settling ponds in the northeast side of the site (7). Overflow is directed through a lime treatment system for pH control. A second treatment pond allows sedimentation of suspended matter before discharge of effluents to Northwest brook. The volume discharged varies with rainfall, but is approximately 350 gal/min (22.1 L/s).

6.3.2 CBDC: Lingan Mine, Lingan, NS. Coal wastewaters originating from the site include mine water and surface runoff. Mine water is pumped from the bottom of the main shaft to an outfall located on the northeast side of the property which discharges directly to the Atlantic ocean. The average discharge is about 5.3 L/s. During wet weather surface runoff drains from the entire mine site and most of this water is directed by ditches to Gracie brook which also discharges to the ocean.

Due to the acid generating capabilities of Eastern Canadian coals and attendant heavy metal concentrations, the discharge of such wastewaters to the ocean (and not fresh water systems) is fortuitous in that the ocean possesses a high pH, high buffering capacity, and high ionic strength which assists in the assimilation of such wastewaters. Thus, the impact of such wastes on the ocean aquatic environment is usually limited to the immediate area around the point of discharge.

7.1.2 Cape Breton Development Corporation: Lingan Mine, Lingan, NS. The Lingan Mine is the largest of the underground (submarine) coal mines producing high volatile A bituminous coals from the Sydney coal field. Run of mine coal is either washed at Victoria Junction Preparation plant or sold directly to the Nova Scotia Power Corporation for use at the Lingan thermal power generating stations.

Production from this facility in 1983 was 1.745 million tonnes, 1.895 million tonnes in 1984 and 1.898 million tonnes in 1985.

Sampling Information:

The one sampling site selected at Lingan Colliery was at an ocean outfall discharging mine water pumped from the bottom of the main shaft. After discharge, the water cascades over a cliff to a beach approximately 15 metres below. Final receptor of the mine drainage water is the Atlantic Ocean. The average discharge at this sample location is 320 L/m. Lingan Collieries was sampled on two separate occasions: 15/09/1982 and 18/11/1983. Figure 10 presents a plan view of the Lingan Colliery including the sampling site, which is site No. 7 in the figure.

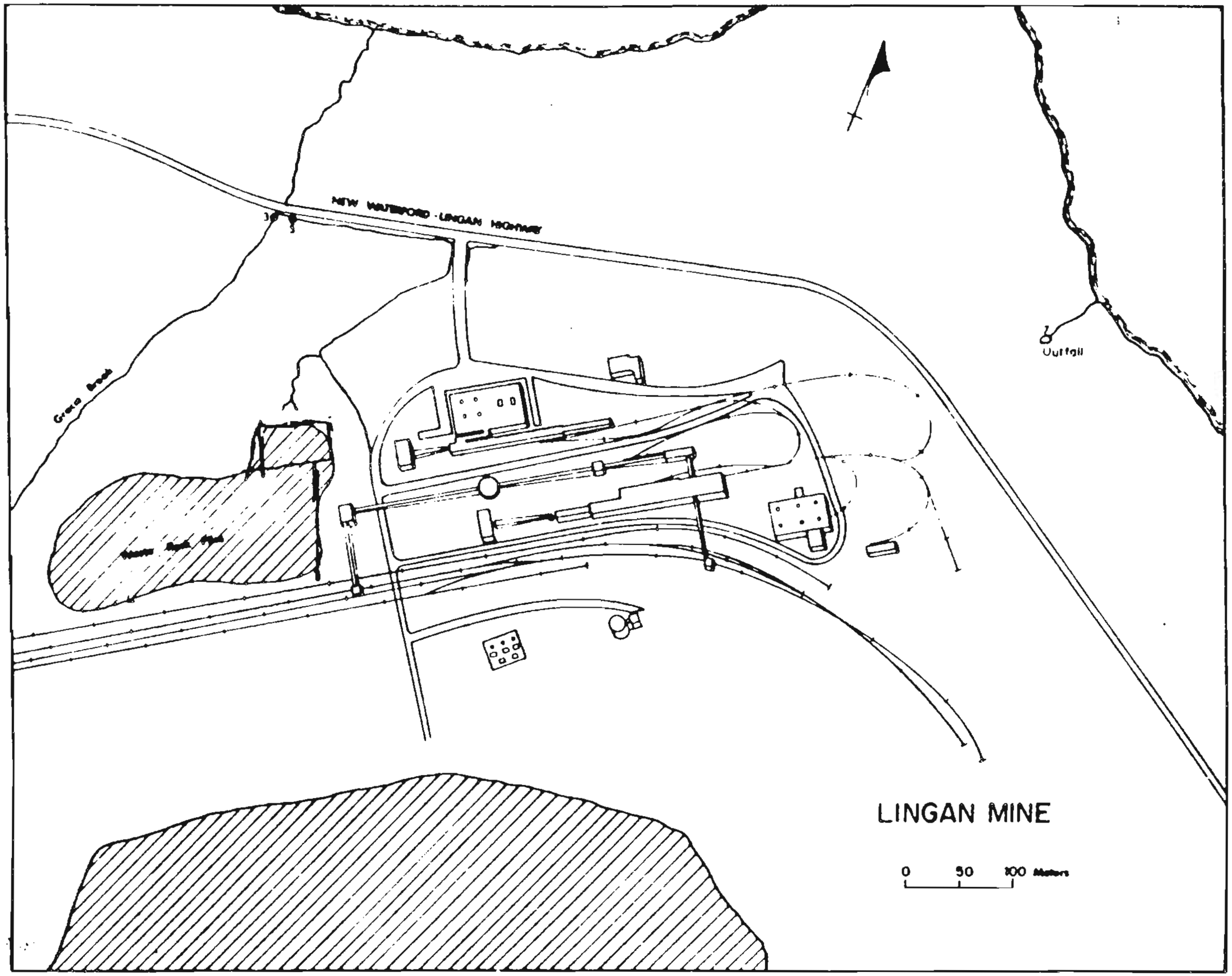

FIGURE 10 LINGAN MINE, LINGAN, NOVA SCOTIA (Site 7 Was Used For Sample Collection)

(i) TRACE ELEMENTS: LINGAN COLLIERY

		Coal Analyses*	Wastewater Analysis			
Trace Elements(Total)		(NAA) ppm	(PES) ppm	Outfall[1]	Outfall[2]	
				A	A	B
Aluminum	(Al)	1 940	2 640	0.025	L0.025	0.22
Antimony	(Sb)	0.75	-	-	L0.10	L0.001
Arsenic	(As)	10.4	-	0.05	L0.05	L0.03
Barium	(Ba)	L 70	13.6	1.01	1.03	0.08
Beryllium	(Be)	-	-	0.01	L0.01	L0.003
Boron	(B)	-	-	-	-	0.22
Cadmium	(Cd)	-	-	0.01	L0.01	L0.025
Chromium	(Cr)	5.09	20.3	0.11	L0.01	L0.03
Cobalt	(Co)	2.0	22.7	0.11	0.04	0.031
Copper	(Cu)	-	13.6	0.01	0.10	0.13
Lithium	(Li)	-	-	0.32	0.40	-
Iron	(Fe)	8 130	2 373	25.7	18.8	21.6
Lead	(Pb)	-	10.9	0.02	L0.02	L0.08
Manganese	(Mn)	96.9	102.5	8.23	7.38	7.69
Mercury	(Hg)	-	-	0.00005	-	-
Molybdenum	(Mo)	-	145.2	0.01	L0.01	L0.04
Nickel	(Ni)	-	8.2	0.23	0.07	0.084
Selenium	(Se)	L 3.0	-	ND	-	L0.001
Silver	(Ag)	-	2.3	-	L0.01	L0.03
Strontium	(Sr)	L 70.0	10.4	52.6	65.1	59.2
Thallium	(Tl)	-	-	Sample not received	-	L0.005
Thorium	(Th)	0.30	2.7	-	-	-
Titanium	(Ti)	L 400	127.0	-	-	L0.006
Uranium	(U)	0.20	-	Sample not received	-	L0.002
Vanadium	(V)	3.88	5.3	ND	L0.01	L0.10
Zinc	(Zn)	-	11.8	0.30	0.42	0.50
Zirconium	(Zr)	-	104.3	Sample not received	-	L0.025

EPS Cantest

* Coal analyses in ppm.
NAA = Neutron Activation Analysis.
PES = Plasma Emission Spectroscopy.
All wastewater results mg/L.
[1] Sampling Date: 15/09/1982.
[2] Sampling Date: 18/11/1983.

A: Analysis by EPS
B: Analysis by contest

Trace Elements: Results from the first survey (15/09/1982) show that the concentrations of iron (25.7 mg/L) and manganese (8.23 mg/L) are relatively high. Strontium (52.6 mg/L) is very high. The remaining trace element concentrations are in accordance with water quality guidelines. Results from the second survey (18/11/1983) show that iron (18.8 mg/L) and manganese (7.38 mg/L) are still high with an increase in strontium (65.1 mg/L).

Figures 11 and 12 present trace element concentrations in wastewaters at the Lingan mine.

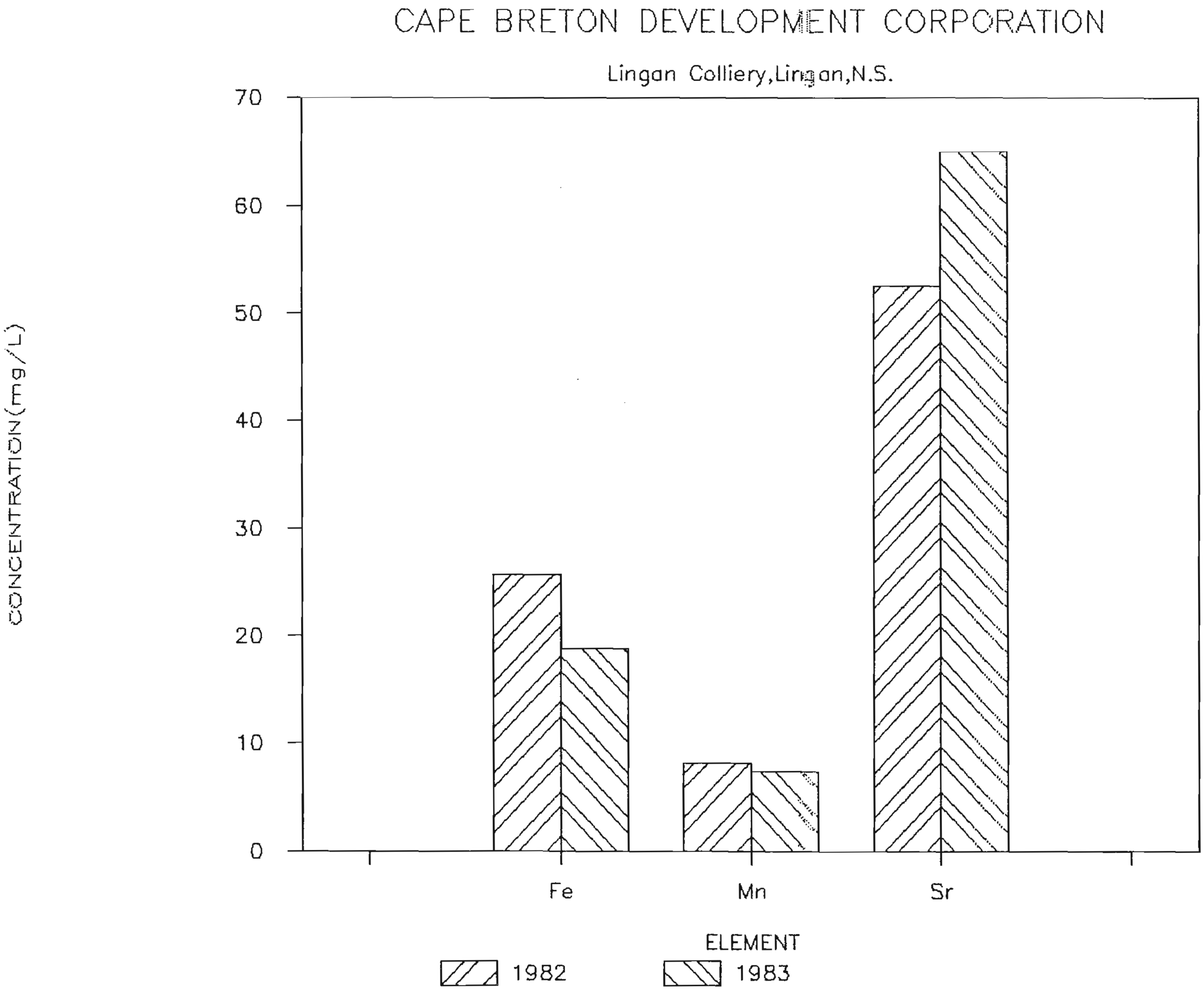

FIGURE 11 CBDC LINGAN MINE, LINGAN (Trace Elements: Fe, Mn, Sr)

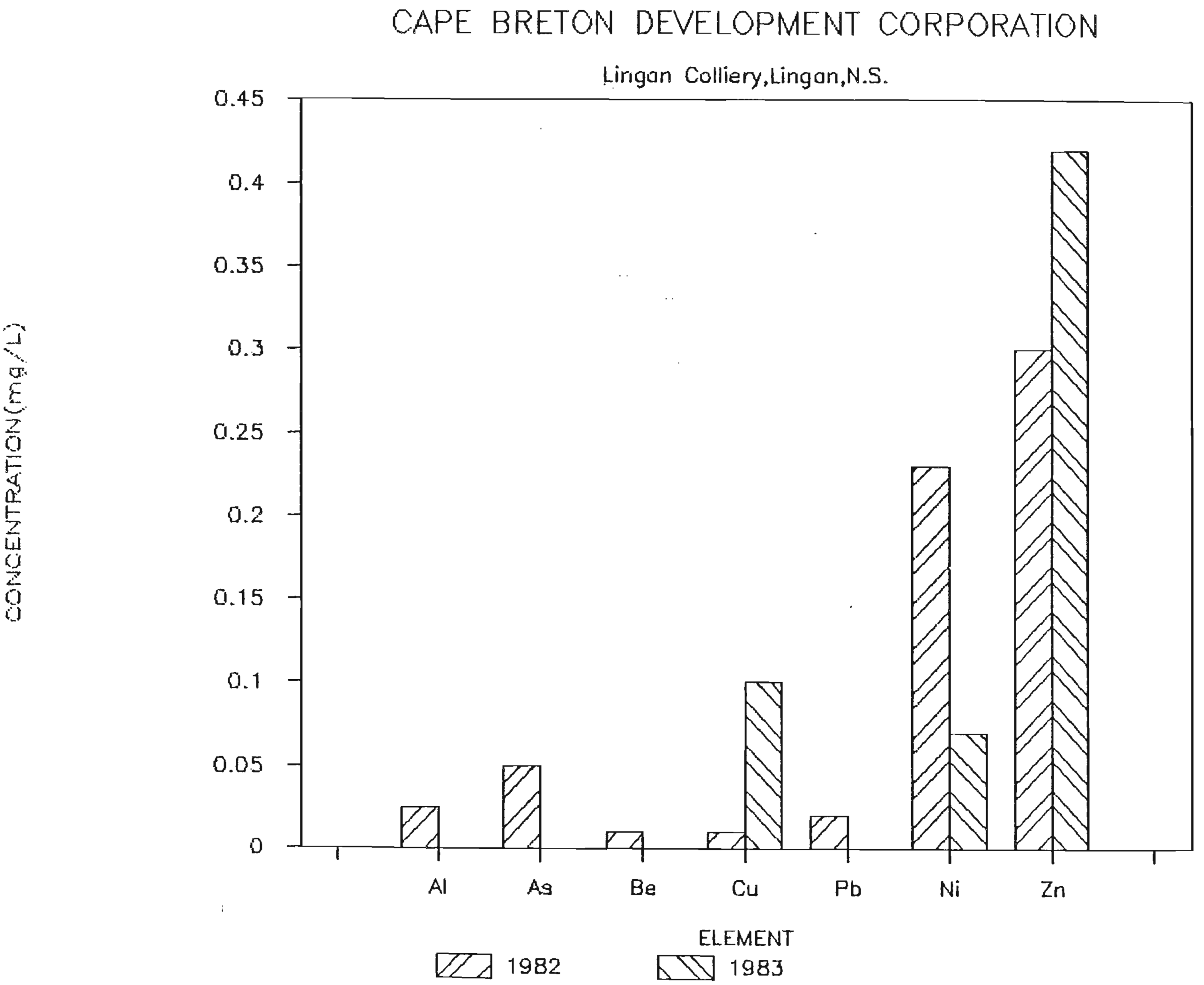

FIGURE 12 CBDC LINGAN MINE, LINGAN (Trace Elements: Al, As, Be, B, Cu, Pb, Hg, Ni, Se, Tl, Ti, U, Zn, Zr)

(ii) CONVENTIONAL PARAMETERS: LINGAN COLLIERY

Conventional Parameters	Wastewater Analysis Outfall[1]	Outfall[2]
TSS	22 900	370
TDS	35.0	23 100
TOC	7.0	10
pH	5.5	6.0
NH_3	5.3	5.88
NO_3	1.6	0.035
NO_2	0.005	0.008
Oil and Grease	4.30	6.0
CN	0.02	L 0.15
Phenols	0.007	0.005
SO_4	750.0	-

All wastewater results mg/L (except pH).
[1] Sampling date: 15/09/1982.
[2] Sampling date: 18/11/1983.

<u>Inorganic Compounds</u>: From the first survey, the level of total suspended solids (22 900 mg/L) is very high. Oil and grease (4.3 mg/L) is also high. Ammonia (5.3 mg/L) is high, whereas nitrite (0.005 mg/L) is very low and nitrate (1.5 mg/L) is relatively high but within water quality guidelines. The value of pH (5.5) is slightly acidic, which favours the ammonium ion (NH_4^+). From the second survey (18/11/83), TSS (370 mg/L) is significantly lower with TDS (23 100 mg/L) significantly higher than that of the first survey. In addition NH_3 (5.88 mg/L), TOC (10 mg/L) and oil and grease (6.0 mg/L) are also higher than that of the first survey.

(iii) ORGANIC COMPOUNDS: LINGAN COLLIERY

Purgeables	Lingan Mine Water
Trichlorofluoromethane	ND
Dichloromethane	112.0
Trichloromethane	12.0
Benzene	ND
Toluene	ND
Tetrachlorethylene	ND
Ethylbenzene	ND

Semi-Volatiles	Lingan Mine Water
1,2-dichlorobenzene	ND
Naphalene	ND
Diethylphthalate	ND
Phenanthrene	ND
Anthracene	ND
Di-n-butylphthalate	16.11
Bis (2 ethyl hexyl) phthalate	17.89
Benzo (k) fluoranthene	ND
Indeno (1,2,3,c,d) pyrene	ND
Dibenzo (a,k) anthracene	ND
Benzo (g,h,i) perylene	ND

All wastewater results in ppb (or mg/kg).
Trace = Less than 5 ppb.
ND = Not detected.
[1] Sampling date: 15/09/1982.

Organic Compounds: Dichloromethane at a relatively high concentration of 112 mg/L and trichloromethane (12 mg/L) were the only purgeable organic compounds detected. Of the semi-volatile organic compounds, only di-n-butyl phthalate (16.11 mg/L) and bis(2 ethyl hexyl)phthalate (17.89 mg/L) were detected.

7.2 Concentration of Trace Elements in Coal and Coal Wastewaters

Due to various biochemical and geological processes, such as the bioaccumulation of elements and minerals by vegetation and the transport of minerals and sediments involved in the deposition and accumulation of vegetation from which, ultimately, coal evolved, the coal itself is the major source of trace elements that are present in coal wastewaters.

Although certain trace elements may be contained in overburden or adjacent wasterock piles or may be introduced to the coal from other agents such as groundwater, these are minor sources when compared to the parent coal which represents the accumulation, compression and thermal alteration of several feet of precursor vegetal material.

The varieties and concentration of trace elements in a coal are commonly related to its rank with certain elements exhibiting a propensity for higher concentrations in coals of specific rank. Table 40 summarizes specific trace element contents for selected Canadian lignite, sub-bituminous and bituminous coals, and Figures 45 to 49, derived from Table 40, depict the variation of specific trace element content with coal rank.

In the course of surface and underground mining operations, coal seams are shattered or fractured and exposed to the weathering agents air and water. Coal preparation processes, moreover, expose additional surface area to contacting fluids (usually water) which, to a certain degree, remove from the coal trace elements and inorganic compounds. Greater dissolution and mobility tend to occur at neutral to slightly acidic pH values. In addition, the oxidation of coal generates humic acids which may accelerate the leaching of certain elements and inorganic compounds from the coal structure. There are, however, differences of opinion as to the degree, nature and extent of this mechanism (9).

As a result of the combined effects of coal fracture, weathering, precipitation, dissolution, elution and the solvent action of water, trace element concentrations in coal wastewaters may be several orders of magnitude greater than those in indigenous surface waters. Consequently, untreated coal wastewaters containing elevated levels of trace elements have the potential to significantly degrade the quality of receiving waters into which they may be discharged.

TABLE 40 TRACE ELEMENT CONTENT[1] FOR CANADIAN COALS OF DIFFERENT RANK (5)

COAL RANK

Element		Lignite (Saskatchewan)	Sub-Bituminous (Alberta)	Bituminous (Alberta)	Bituminous (BC)	Bituminous (Nova Scotia)
Al	AVG[2]	14 034	14 513	13 414	16 376	19 004
	MAX	16 440	20 930	18 660	25 430	42 760
	MIN	10 150	7 078	11 160	8 460	1 590
As	AVG	1.57	1.16	1.67	1.73	28.99
	MAX	5.89	2.36	6.07	8.6	86.3
	MIN	0.20	0.62	0.3	0.2	4.33
Be	AVG	1.65	0.5	-	-	0.96
	MAX	1.8	0.6	-	-	1.1
	MIN	0.5	0.4	-	-	0.9
B	AVG	1 134.2	1 029.6	640.4	818.5	1 010.6
	MAX	1 540	1 413	1 004	1 152	1 872
	MIN	741.0	833.6	427.3	544.7	149.1
Cd	AVG	-	7.5	-	8.4	-
	MAX	-	7.9	-	8.6	-
	MIN	-	7.0	-	8.2	-
Cu	AVG	-	6.03	-	13.77	-
	MAX	-	9.5	-	29.9	-
	MIN	-	3.6	-	8.8	-
Fe	AVG	3 537	3 921.7	1 772.6	2 766	18 682
	MAX	4 442	5 250	2 530	4 568	37 900
	MIN	1 005	2 438	283	803.6	5 180
Pb	AVG	9.21	6.76	8.06	5.21	25.88
	MAX	12.8	19.4	13.0	7.6	52.7
	MIN	5.6	1.9	3.7	2.7	1.8
Mn	AVG	47.87	85.5	15.7	19.85	111.54
	MAX	106.0	154.2	21.7	32.7	219
	MIN	24.3	25.1	10.0	10.7	51.3
Hg	AVG	0.074	0.12	0.10	0.06	-
	MAX	0.1	0.44	0.13	0.07	-
	MIN	0.06	0.02	0.07	0.06	-
Ni	AVG	10.1	7.95	5.63	76.42	18.54
	MAX	21.7	9.7	7.5	341.6	28.1
	MIN	4.8	6.2	4.7	6.4	4.5
Se	AVG	3.5	2.88	3.6	3.35	3.89
	MAX	4.0	3.0	4.0	4.0	5.0
	MIN	3.0	2.0	3.0	2.49	3.46
Sr	AVG	401.8	331.6	331.8	405.1	162.8
	MAX	456.6	500	500.0	600	500
	MIN	201.1	100	88.9	65.5	70
Th	AVG	3.74	3.73	2.61	1.57	3.85
	MAX	6.6	6.7	4.82	1.97	6.1
	MIN	1.0	1.8	1.51	1.26	1.9
U	AVG	1.88	1.17	1.68	1.15	0.86
	MAX	2.91	1.73	2.02	1.57	1.78
	MIN	0.78	0.49	1.15	0.62	0.1
Zn	AVG	51.04	25.67	35.58	27.7	32.0
	MAX	138.3	110.6	53.2	88.1	49.8
	MIN	6.7	4.9	14.9	10.1	5.4
Zr	AVG	124.4	75.2	44.42	36.8	46.54
	MAX	334.2	256.1	66.6	59.1	104.3
	MIN	23.9	24.7	33.0	21.2	2.6

[1] Trace element content determined by Neutron Activation Analysis (NAA) or Plasma Emission Spectrometry (PES).

[2] All values in ppm.

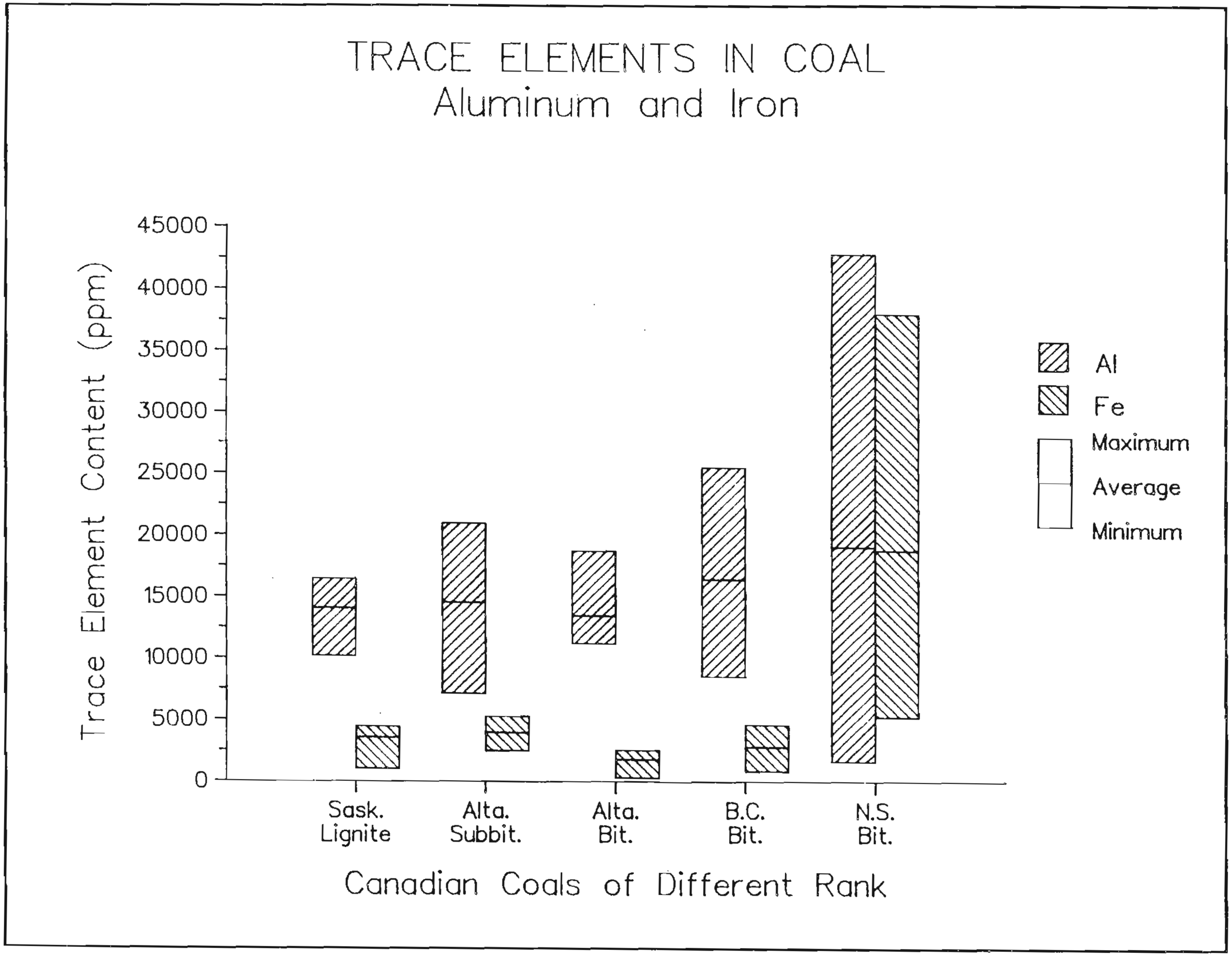

FIGURE 45 TRACE ELEMENTS IN COAL (Aluminum and Iron)

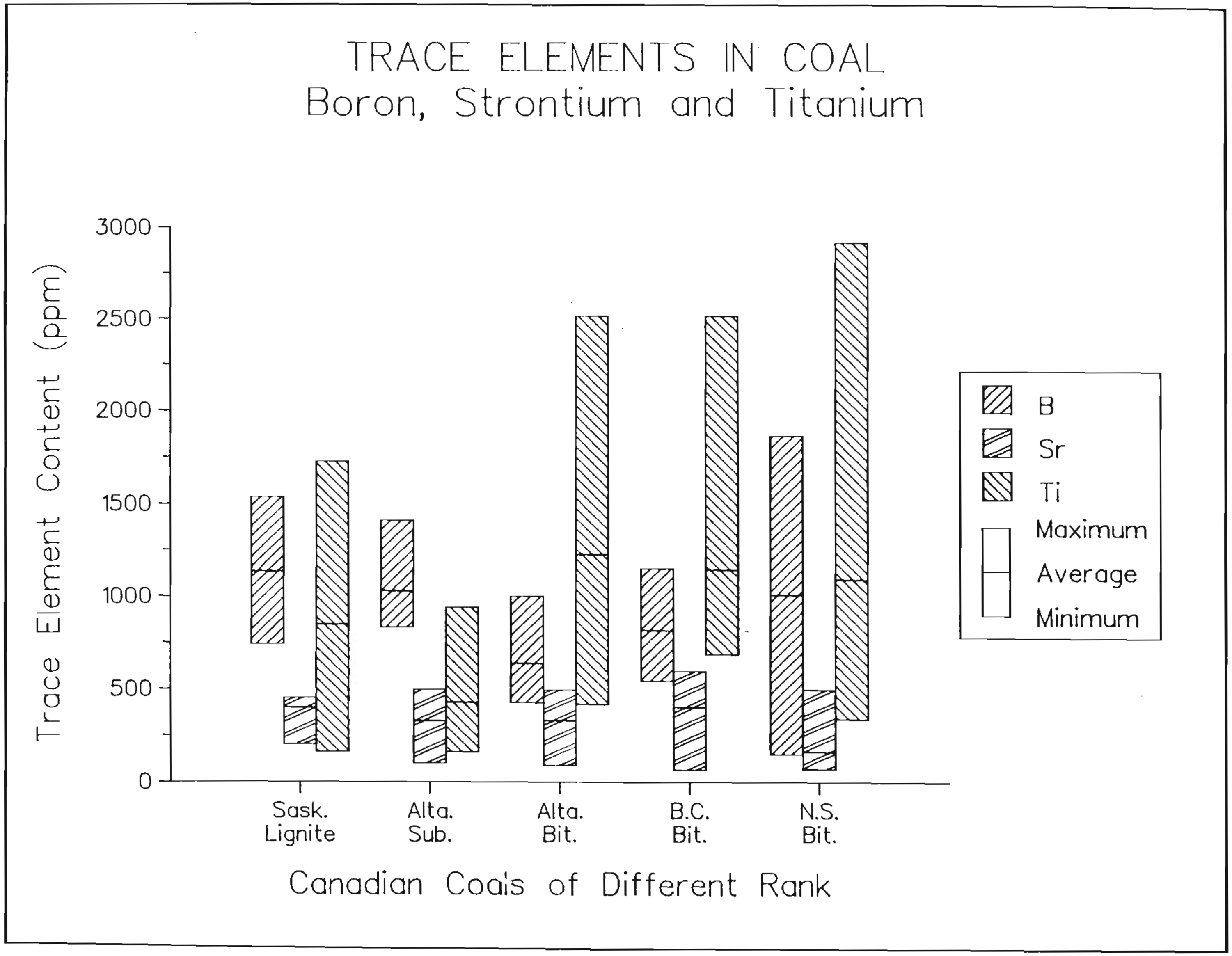

FIGURE 46 TRACE ELEMENTS IN COAL (Boron, Strontium and Titanium)

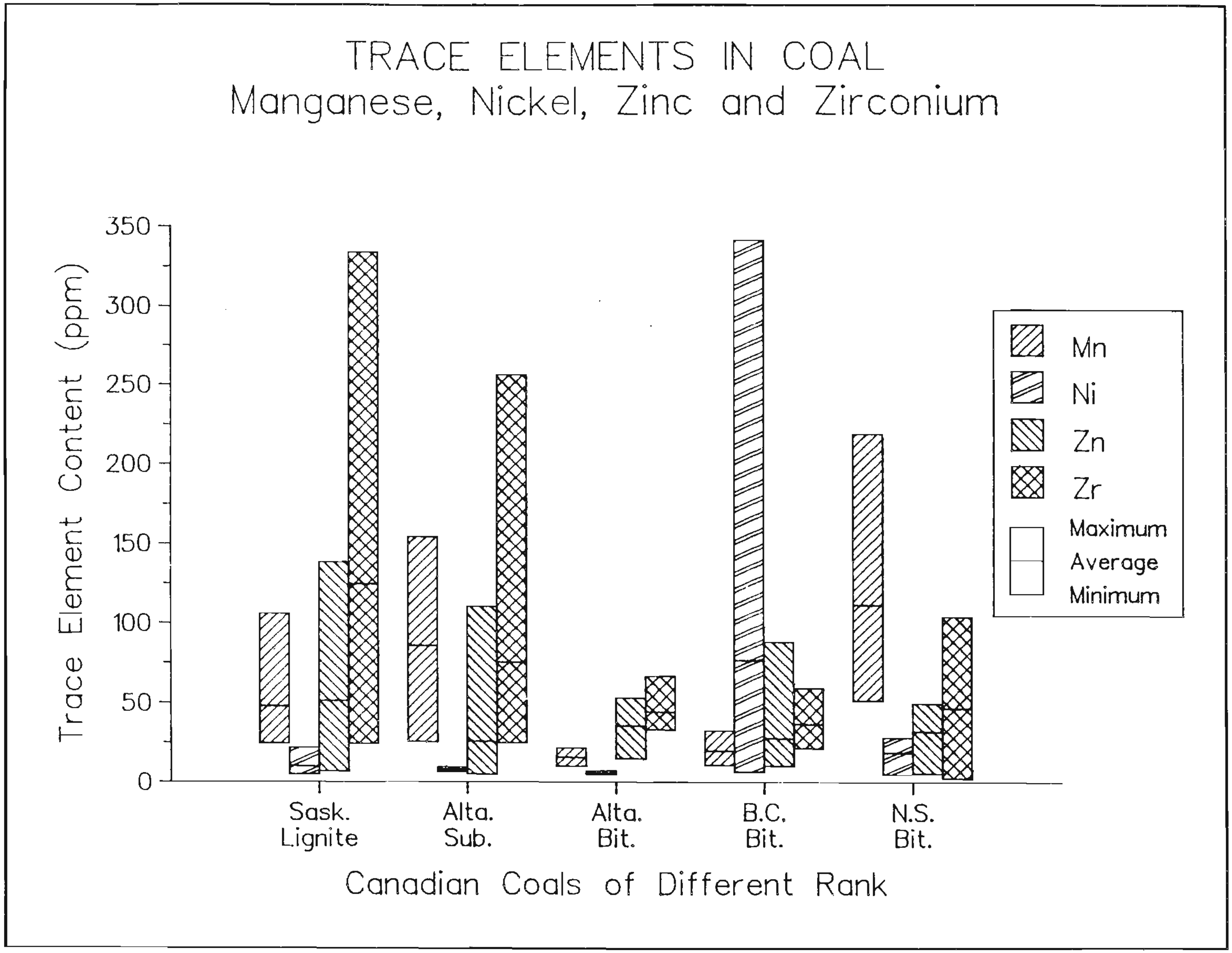

FIGURE 47 TRACE ELEMENTS IN COAL (Manganese, Nickel, Zinc and Zirconium)

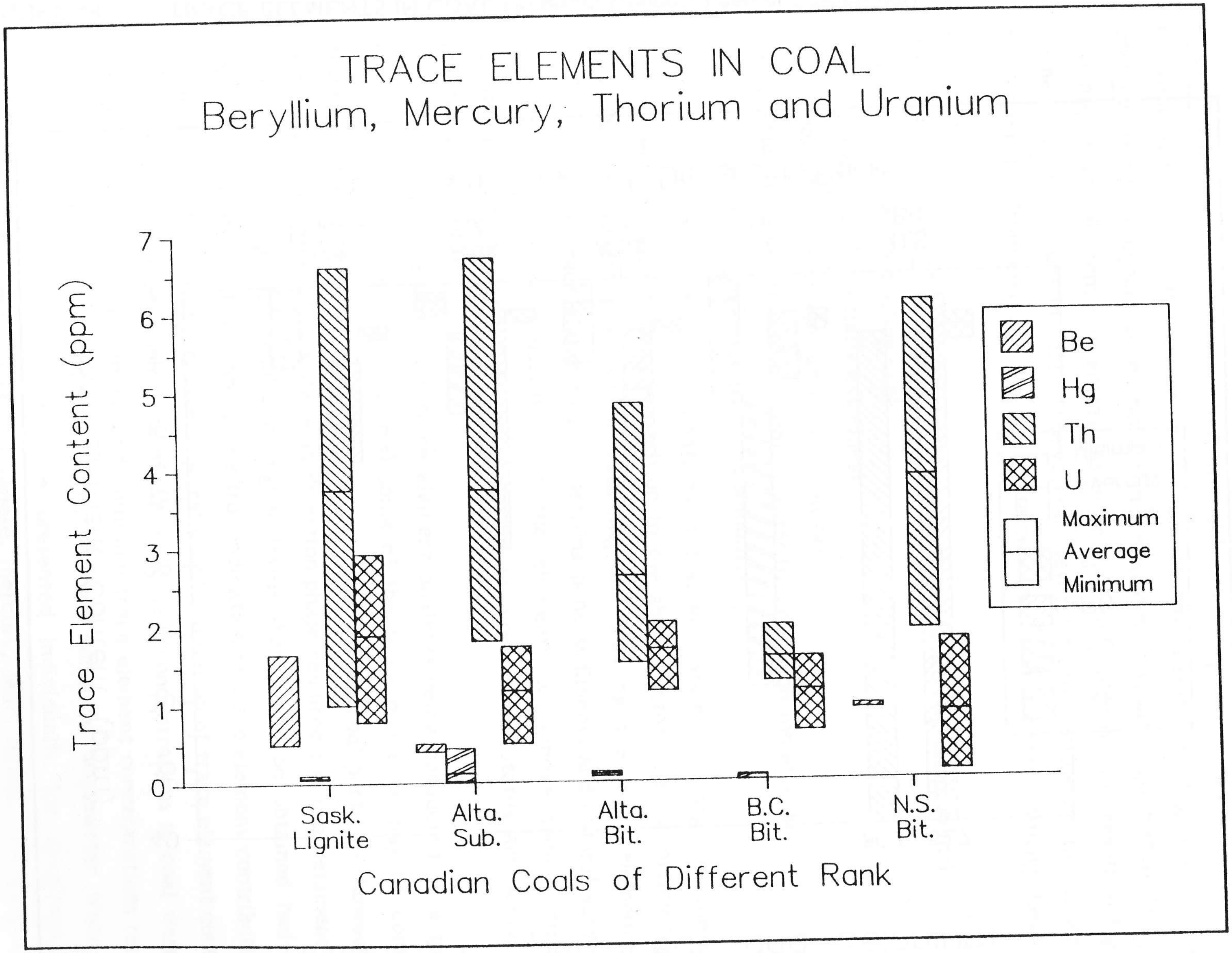

FIGURE 48 TRACE ELEMENTS IN COAL (Beryllium, Mercury, Thorium and Uranium)

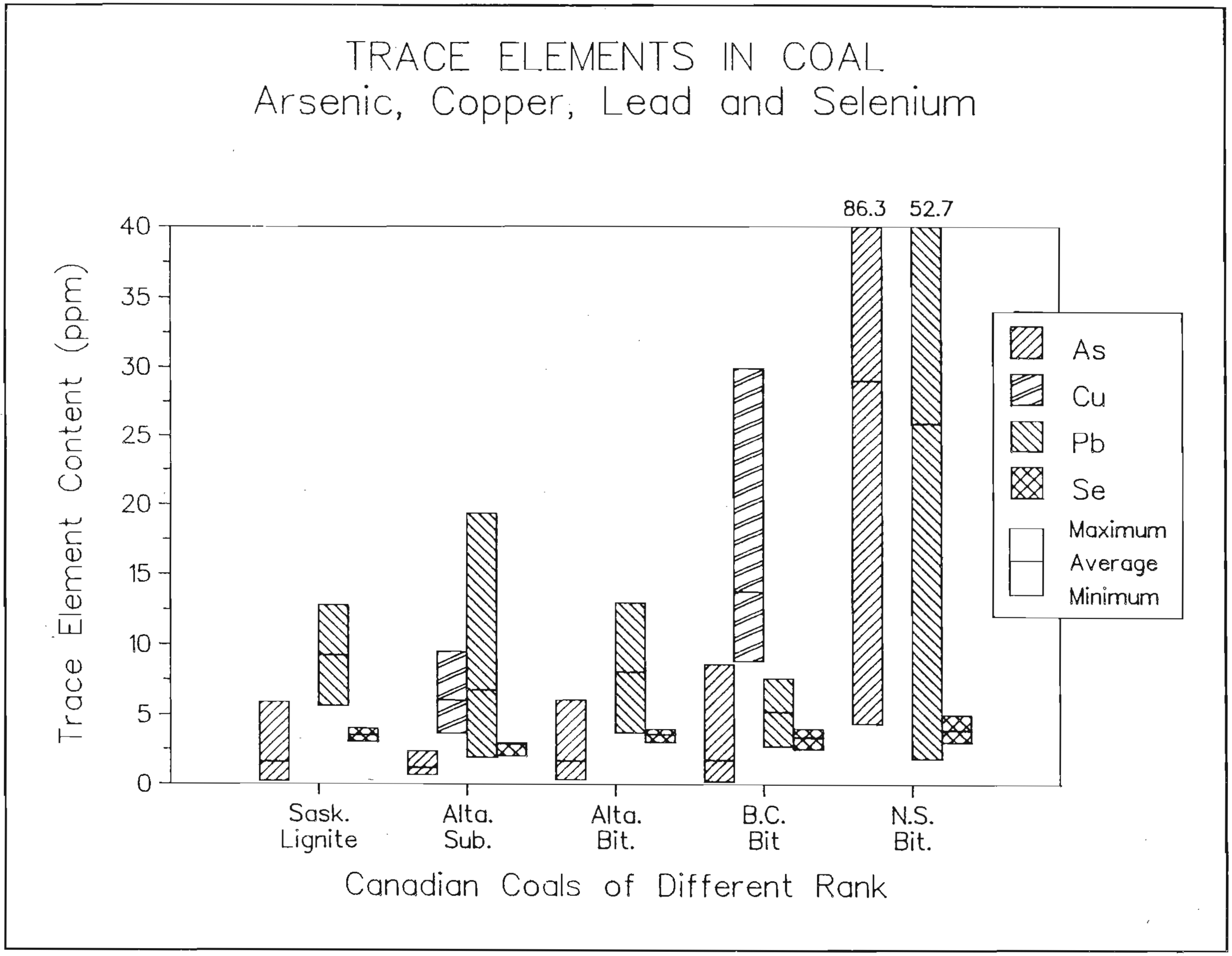

FIGURE 49 TRACE ELEMENTS IN COAL (Arsenic, Copper, Lead and Selenium)

When coal wastewater trace element concentrations are compared with the average trace element concentrations in coal (neglecting, maximum and minimum values) the general trend is that elements which are present at relatively high concentrations in coal may result in higher concentrations in the wastewater, although it should be stressed that high trace element concentrations in coal do not automatically result in high trace element concentrations in coal wastewaters. Several factors influence the dissolution of trace elements from coal and their ultimate concentration in water. Among these are:

(i) Rank of coal
(ii) Degree or extent of oxidation of coal (with production of humic acids)
(iii) pH of water contacting coal
(iv) Temperature (especially extremes)
(v) Chemistry of element (general solubility)
(vi) Initial concentration of element in water (i.e. common-ion effect)
(vii) Concentration gradients affecting solubility.

Trace element concentrations in coal wastewater discharges to the receiving environment will also depend, in addition to the above factors, on the efficiency of any associated treatment practices in retaining and treating the trace elements, uptake and/or release of trace elements from settling pond sediments and natural scavenging or degradative mechanisms operating on the elements to remove them from solution (chelation, complex formation and oxidation to more stable states are some of these mechanisms).

Due to wastewater trace element analyses being conducted on a total basis (i.e. suspended plus dissolved forms) some of the trace elements may be contained in suspended material, which includes coal particles. These coal particles, however, would normally be dissolved during the acid digestion phase required for total element analysis. Consequently, digestion results in higher levels than would be obtained had dissolved analyses been used and does not give a true indication of trace element contribution solely from coal. It does, however, give a "worst case" estimation of trace element content.

As an overall summary of trace element concentrations in coal wastewaters, Table 41 presents the maximum and minimum trace element concentrations recorded at each coal facility. In addition, maximum and minimum wastewater trace element concentrations at each facility are presented individually for aluminum, arsenic, beryllium, boron, copper, iron, manganese, mercury, lead, nickel, selenium, strontium, thallium, titanium, uranium, zinc and zirconium in Figures 50 to 66.

TABLE 41 TRACE ELEMENT CONCENTRATIONS IN COAL WASTEWATERS - MAXIMUM AND MINIMUM VALUES AT EACH FACILITY

Element	CBDC VJ (1)* (1984)	CBDC VJ (1) (1983)	CBDC Lingan (1) (1982)	CBDC Lingan (1) (1983)	Thunder Bay Terminals (2)		Thunder Bay Terminals (2)		Bienfait (4)		Sask. Power Corporation (4)		Cardinal River (4)	
Aluminum	0.025	29.9	0.025	0.22	L 0.01	L 0.01	L 0.15	L 0.15	10.6	L 0.15	L 0.15	L 0.15	0.97	0.31
Antimony	-	L 0.10	-	L 0.001	-	-	0.002	0.010	0.001	L 0.001	L 0.001	L 0.001	0.022	L 0.001
Arsenic	0.05	0.19	0.05	L 0.03	0.001	0.001	L 0.30	L 0.30	0.12	0.005	L 0.005	L 0.005	0.005	L 0.005
Barium	0.19	0.09	1.01	0.08	-	-	0.11	0.099	L 0.40	L 0.40	L 0.40	L 0.40	0.50	L 0.40
Beryllium	0.01	L 0.01	0.01	L 0.003	-	-	L 0.003	L 0.003	L 0.003	L 0.003	L 0.003	L 0.003	L 0.003	L 0.003
Boron	-	-	-	0.22	-	-	0.23	0.21	1.57	0.35	1.75	1.08	0.14	0.091
Cadmium	0.01	0.01	0.01	L 0.025	L 0.005	L 0.005	L 0.025	L 0.025	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02
Chromium	0.01	0.03	0.11	L 0.03	L 0.02	L 0.02	L 0.03	L 0.03	L 0.05	L 0.05	L 0.05	L 0.05	L 0.05	L 0.05
Cobalt	0.02	0.49	0.11	0.031	L 0.02	L 0.02	L 0.02	L 0.02	L 0.05	L 0.05	L 0.05	L 0.05	L 0.05	L 0.05
Copper	0.01	0.36	0.01	0.13	0.01	0.01	L 0.015	L 0.015	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02
Iron	0.21	49.7	25.7	21.6	4.7	0.43	0.027	0.025	18.0	0.6	2.3	0.23	0.93	0.45
Lead	0.02	L 0.02	0.02	L 0.08	L 0.03	L 0.03	L 0.08	L 0.08	0.0	L 0.10	L 0.10	L 0.10	L 0.10	L 0.10
Lithium	0.09	0.20	0.32	-	-	-	2.82	1.26	-	-	-	-	-	-
Manganese	5.42	21.3	8.23	7.69	0.41	0.06	0.96	0.47	0.47	L 0.02	0.3	L 0.02	0.07	0.03
Mercury	0.00005	0.0001	0.00005	-	L 0.05	L 0.05	-	-	L 0.0002	L 0.0002	L 0.0002	L 0.0002	L 0.0002	L 0.0002
Molybdenum	0.01	L 0.01	0.01	L 0.04	L 0.05	L 0.05	L 0.04	L 0.04	L 0.10	L 0.10	L 0.10	L 0.10	0.05	L 0.04
Nickel	0.05	1.0	0.23	0.084	L 0.02	L 0.02	L 0.025	L 0.025	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03
Selenium	-	-	-	L 0.001	-	-	L 0.001	L 0.001	L 0.001	L 0.001	L 0.001	L 0.001	0.003	L 0.001
Silver	-	L 0.01	-	L 0.03	-	-	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03
Strontium*	8.63	1.0	52.6	59.2	-	-	0.48	0.42	6.04	0.21	0.97	0.80	3.10	0.97
Thallium*	-	-	-	L 0.005	-	-	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005
Thorium	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Titanium	-	-	-	L 0.006	-	-	L 0.006	L 0.006	0.41	L 0.006	L 0.006	L 0.006	0.011	L 0.006
Uranium*	-	-	-	L 0.002	-	-	0.0012	L 0.0002	0.012	L 0.0002	0.01	L 0.0002	0.019	0.004
Vanadium	-	L 0.01	-	L 0.10	-	-	L 0.01	L 0.01	0.031	L 0.01	L 0.01	L 0.01	L 0.01	L 0.01
Zinc	0.01	2.19	0.30	0.50	0.03	0.01	0.021	L 0.015	0.07	L 0.01	0.04	L 0.01	0.04	L 0.01
Zirconium*	-	-	-	L 0.025	-	-	L 0.025	L 0.025	0.017	L 0.015	L 0.015	L 0.015	L 0.015	L 0.015

*Number in parenthesis denotes the number of sites per facility.
All results (mg/L).
L = Less than.

TransAlta (4) Utilities		Smoky River (5) Coal		Fording Coal (9) (10/08/1982)		Fording Coal (10) (13/10/1982)		Fording Coal (10) (27/10/1983)		Pacific Coast (3) Terminals		Westshore (3) Terminals	
52.1	0.40	0.81	L 0.15	94.3	L 0.06	1.72	L 0.06	161.0	L 0.05	6.85	0.64	9.84	7.78
0.21	L 0.001	0.005	L 0.001	-	-	L 0.06	L 0.06	L 5.0	L 0.05	L 0.06	L 0.06	L 0.05	L 0.05
0.24	L 0.005	L 0.30	L 0.30	L 0.30	L 0.06	L 0.06	L 0.06	L 5.0	L 0.05	L 0.06	L 0.06	L 0.05	L 0.05
1.7	L 0.40	0.31	0.13	3.88	0.019	0.426	0.033	4.4	0.066	0.527	0.036	0.332	0.202
0.003	L 0.003	L 0.003	L 0.003	L 0.006	L 0.001	L 0.001	L 0.001	L 0.1	L 0.001	L 0.001	L 0.001	L 0.001	L 0.001
0.35	0.064	0.16	L 0.01	0.18	L 0.001	0.027	0.004	4.1	L 0.001	0.046	0.039	0.084	0.071
L 0.02	L 0.02	L 0.025	L 0.025	L 0.01	L 0.002	L 0.002	L 0.002	L 0.2	L 0.002	L 0.002	L 0.002	0.003	L 0.002
0.14	L 0.05	L 0.030	L 0.030	0.14	L 0.006	0.007	L 0.006	L 0.5	L 0.005	0.009	L 0.006	0.065	0.015
L 0.05	L 0.05	L 0.02	L 0.02	L 0.03	L 0.006	L 0.006	L 0.006	L 0.5	L 0.005	L 0.006	L 0.006	0.009	L 0.005
0.07	L 0.02	L 0.015	L 0.015	0.42	L 0.006	0.026	L 0.006	L 0.5	L 0.005	L 0.006	L 0.006	0. 044	0.036
76.0	1.9	0.73	L 0.03	86.4	0.16	15.9	0.011	138.0	L 0.02	4.42	0.315	9.02	5.52
L 0.10	L 0.10	L 0.08	L 0.08	0.20	L 0.02	L 0.02	L 0.02	-	-	0.02	L 0.02	0.07	0.02
-	-	0.18	0.021	0.082	0.002	0.059	0.002	L 2.0	L 0.02	0.004	0.003	-	-
0.33	0.02	0.023	0.004	0.37	L 0.001	0.362	L 0.001	0.7	0.003	0.055	0.021	0.132	0.069
L 0.0002	L 0.0002	-	-	L 0.0002	L 0.0002	L 0.0002	L 0.0002	L 0.002	L 0.002	L 0.0002	L 0.0002	L 0.00005	L 0.00005
L 0.04	L 0.04	L 0.04	L 0.04	0.11	L 0.006	0.021	L 0.006	L 0.05	L 0.005	L 0.006	L 0.006	0.009	L 0.005
0.05	L 0.03	L 0.025	L 0.025	0.10	L 0.02	0.06	L 0.02	2.0	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02
0.002	L 0.001	0.015	L 0.001	-	-	L 0.06	L 0.06	L 5.0	L 0.05	L 0.06	L 0.06	L 0.05	L 0.05
L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03	L 0.001	L 0.001	-	-
0.62	0.30	1.21	0.37	0.831	0.085	0.544	0.107	0.9	0.119	0.11	0.034	0.106	0.052
L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005	L 0.005
-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.28	0.01	0.014	L 0.006	0.21	L 0.002	0.044	L 0.002	3.3	L 0.002	0.036	0.019	0.195	0.111
0.017	0.004	0.0015	L 0.0002	0.01	0.002	0.008	L 0.0002	0.0085	L 0.0002	L 0.002	L 0.002	L 0.0002	L 0.0002
0.056	L 0.01	L 0.01	L 0.01	0.49	L 0.01	0.01	L 0.01	L 1.0	L 0.01	0.04	0.02	0.04	0.03
0.19	L 0.01	0.09	L 0.015	0.65	L 0.002	0.089	L 0.002	0.6	L 0.002	0.04	0.03	0.121	0.092
0.084	L 0.015	L 0.025	L 0.025	L 0.015	L 0.015	L 0.015	L 0.015	L 0.025	L 0.025	L 0.015	L 0.015	L 0.025	L 0.025

7.3 Concentrations of Organic Compounds in Coal Wastewaters

The major source of organic compounds in coal wastewaters is the coal itself which may be considered as being metamorphosed organic rock. Because coal acts as a synthetic copolymer there is little potential for organic compounds to be leached from its matrix at ambient temperatures if water is the leaching fluid. Mining, preparation and transportation activities may also release hydrocarbons that are transported as site runoff to the settling ponds and hence to the receiving environment. Organic compounds may also be added to coal through contact with surface and groundwater contaminated with hydrocarbons such as oils, solvents or industrial chemicals. Organic compounds in industrial air emissions may also be an additional source of potential contamination to coal in open storage.

Coal wastewater samples collected at each of the selected facilities were analysed for a total of eighteen organic compounds (seven volatile and eleven semi-volatile). Results* of these analyses have been presented in section 7.1. Overall, results show that several of the organic compounds were not detected and that others were detected only at trace concentrations (i.e. <5 µg/L). The remaining compounds were at detectable levels (i.e. >10 µg/L).

Table 43 presents a summary of the frequency of occurrence of the organic compounds at any detectable level and Table 44 presents the same data after subtracting field blanks. From these tables it can be seen that only a few organic compounds occur with any frequency at concentrations greater than 10 µg/L. Correcting for background contamination as measured by field blanks slightly reduces the number of compounds detected at levels greater than 10 µg/L as well as slightly reducing the frequency at which each is found.

The organic compounds most commonly found above 10 µg/L were the three phthalates compounds, diethyl, di-n-butyl and bis (2-ethylhexyl) with levels ranging from detectable to a high of 170 µg/L. Dichloromethane was also found in many samples, however in no case was it found in the samples but not in the field blanks. Its presence in wastewater samples cannot be discounted because it was at far greater concentrations than in the field blanks. However, the fact that these high concentrations were eliminated with rigorous bottle preparation for the wastewater sampling conducted during

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* From: "Determination of Trace Organic Compounds in Canadian Goal Wastewaters and Wastewater Sludges", J.W. Atwater and D.S. Mavinic, Department of Civil Engineering, University of British Columbia, August 1985.

TABLE 42 SUMMARY OF THE FREQUENCY OF OCCURRENCE OF ORGANIC COMPOUNDS

	1	2	3	4	5
Compound	No. of Samples Analyzed[1]	No. of Samples in Which Compound Found[2]	No. of Samples Where Conc. is at Detection	No. of Samples Where Conc. is Trace (5 µg/L - 10 µg/L)	No. of Samples Where Conc. >10 µg/L
dichloromethane (Phase I,II)	50	21,4	7,4	3,0	11,0
trichloromethane	50	4	2	1	1
trichlorofluoromethane	50	0	0	0	0
tetrachloroethylene	50	0	0	0	0
benzene	50	0	0	0	0
toluene	50	7	6	0	1
ethylbenzene	50	0	0	0	0
1,-2 dichlorobenzene	59	2	0	1	1
naphthalene	59	8	4	0	4
anthracene	59	6	5	1	0
phenanthrene	59	10	6	1	3
benzo(k)fluoranthene	59	3	3	0	0
dibenz(a,h)anthracene	59	1	1	0	0
benzo(g,h,i)perylene	59	0	0	0	0
indeno(1,2,3,-c,d) pyrene	59	0	0	0	0
diethyl phthalate	59	31	16	8	7
di-n-butyl phthalate	59	31	18	5	8
bis(2-ethylhexyl) phthalate	57	34	13	9	12

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[1] Does not include field or lab duplicates, spiked samples or sediments.
[2] Sum of columns 3, 4 and 5.

TABLE 43 SUMMARY OF ORGANIC COMPOUNDS FOUND AFTER SUBTRACTING CONCENTRATIONS FOUND IN FIELD BLANKS

Compound	1 No. of Samples Analyzed[1]	2 No. of Samples in Which Compound Found[2]	3 No. of Samples Where Conc. is at Detection	4 No. of Samples Where Conc. is Trace (5 µg/L - 10 µg/L)	5 No. of Samples Where Conc. >10 µg/L
dichloromethane	38	13	7	1	5
trichloromethane	38	2	2	0	0
trichlorofluoromethane	38	0	0	0	0
tetrachloroethylene	38	0	0	0	0
benzene	38	0	0	0	0
toluene	38	2	1	0	1
ethylbenzene	38	0	0	0	0
1,-2 dichlorobenzene	56	2	0	1	1
naphthalene	56	6	2	0	4
anthracene	56	5	4	1	0
phenanthrene	56	7	4	0	3
benzo(k)fluoranthene	56	3	3	0	0
dibenz(a,h)anthracene	56	1	1	0	0
benzo(g,h,i)perylene	56	0	0	0	0
indeno(1,2,3,-c,d)pyrene	56	0	0	0	0
diethyl phthalate	54	27	15	7	5
di-n-butyl phthalate	54	26	16	3	7
bis(2-ethylhexyl) phthalate	56	11	2	2	7

[1] Does not include field or lab duplicates, spiked samples or sediments.
[2] Sum of columns 3, 4 and 5.

Note: Only samples which had appropriate field blanks were used.

1983 and 1984 suggests that the presence of dichloromethane is an artifact. Other organic compounds found at levels above 10 µg/L were trichloromethane, toluene, 1,2-dichloromethane and naphthalene. Benzo(k)fluoroanthene and dibenz(a,h)anthracene were also detected at levels below 5 µg/L. Table 44 summarizes the organic compounds occurring at concentrations greater than 10 µg/L, together with their alternate names, formula, molecular weight and CAS number.

7.3.1 Potential Sources of Organic Compounds. The potential sources of these organic compounds detected at concentrations greater than 10 µg/L are tentatively identified below:

(i) Dichloromethane: This compound is used as a solvent during the extraction of other organic compounds from solution and also in the preparation of glassware required for priority pollutant sampling. The relatively high concentrations found in the Lingan Mine Wastewater sample (112 µg/L) and the observations that it was found in both wastewater samples and field blanks may indicate that sample contamination occurred either during sample extraction or glassware preparation. With improved glassware preparation procedures, dichloromethane levels in field blanks were reduced in the 1983 and 1984 surveys. Thus it is reasonable to conclude that the presence of dichloromethane was due to improper preparation procedures. In a study of US coal wastewaters, the US EPA present similar results for dichloromethane and conclude that the presence of this compound was due to its use during analysis.

(ii) Toluene: Toluene is a volatile organic compound that is relatively insoluble in water. The low detected concentration (13 µg/L, maximum) in wastewater may indicate contamination within the laboratory.

(iii) 1,2-Dichlorobenzene: The chemical structure of this compound consists of two chlorine atoms attached to a benzene ring, which makes it unlikely to exist in nature. Consequently, it is most likely an anthropogenic contaminant.

(iv) Napthalene: Napthalene is a polyaromatic hydrocarbon consisting of two fused benzene rings. It is an organic compound thought to be present in the structure of coal and consequently may be derived from coal.

(v) Phthalate Compounds: (Bis(2-ethylhexyl) phthalate, diethylphthalate, di-n-butyl phthalate). These three organic compounds were the most commonly found contaminants above 10 µg/L, ranging from detectable (<5 µg/L) to a maximum of 170 µg/L. The US EPA (8) report maximum concentrations of bis(2-ethylhexyl)

TABLE 44 ORGANIC COMPOUNDS OCCURRING AT CONCENTRATIONS GREATER THAN 10 mg/L IN COAL WASTEWATER SAMPLES

Compound	Formula	Molecular Weight	CAS Number	Alternate Names
Dichloromethane	CH_2Cl_2	84.93	75-09-2	Methylene Chloride Methylene Dichloride
Toluene	$C_6H_5CH_3$	92.15	108-88-3	Methylbenzene Phenylmethane
1,2-Dichlorobenzene	$C_6H_4Cl_2$	147.0	95-50-1	Orthodichlorobenzene
Naphthalene	$C_{10}H_8$	128.18	91-20-3	Tar Camphor
Bis (2-ethylhexyl) phthalate		390.62	117-81-7	Bis (2-ethylhexyl) Ester
Diethylphthalate	$C_6H_4(CO_2C_2H_5)_2$	222.26	84-66-2	Ethyl phthalate; DEP
Di-n-butyl phthalate	$C_6H_4(COOC_4H_9)_2$	278.38	84-74-2	Benzene-o-dicarboxylic acid

phthalate, diethylphthalate and di-n-butylphthalate of 11 000 µg/L, 790 µg/L and 960 µg/L, respectively.

Phthalate compounds are not generally recognized as being present in the structure of coal, consequently their presence in coal wastewaters may be due to the widespread use of plastic and plastic compounds. Phthalates are used in plasticizers and are added to a polymer to facilitate processing and to increase the flexibility and toughness of the final product. Possible sources of phthalates are:

- Plastic containers and tubing (PVC) used to hold distilled water (laboratory contamination).
- Older laboratory distillation units exhibiting increasing phthalate release rates (laboratory contamination).
- Widespread use of plastic at coal facilities (mine, preparation plant or storage /transfer terminal). This source of phthalates may be regarded as a consequence of coal production.

In summary, of the eighteen organic compounds analysed for in wastewaters from Canadian coal facilities, nine were present at levels above 10 µg/L. An additional three compounds were detected at levels below 10 µg/L. The remaining six compounds were not detected. Although sample contamination, improper glassware cleaning and preparation and the widespread use of plastics may be sufficient to explain the presence of dichloromethane and the three phthalate compounds, which collectively were the most frequently occurring compounds during the 1982 survey, their presence during the 1983 and 1984 surveys with overall improved glassware and distilled water preparation procedures, cannot be solely attributed to contamination (18).

7.4 Concentration of Inorganic Compounds in Coal Wastewaters

The concentration of inorganic compounds in coal wastewater samples was determined to provide a gross or overall indication of potential water contamination which may be caused by coal wastewater discharges to the aquatic environment. These analyses also provide a basis for comparing current or existing coal wastewater quality with that collected before the advent of more sophisticated analytical techniques and equipment.

Before the introduction and use of Atomic Absorption (AA) and Gas Chromatography/Mass Spectrometry (GC/MS) in wastewater analysis, these conventional parameters were often the only criteria for water pollution or contamination problems. Table 46 summarizes those conventional parameters for which analysis was conducted, the information provided by the analyses and the associated limitations.

As knowledge of the chemical nature of coal increased, it was found that the "conventional" parameters did not provide sufficient indication of the presence of trace elements, such as the toxic "heavy" metals (As, Cd, Hg, Pb), or organic compounds. The most common parameters conventionally used to qualitatively assess coal wastewaters were pH, Total Suspended Solids, Turbidity, Iron and Manganese - parameters with limitations on their ability to indicate the degree of hazard associated with coal wastewater discharges. The limitations on these parameters are summarized below.

(i) pH: This parameter determines the hydrogen ion concentration of the wastewater. Because aquatic life is sensitive to both acidic and alkaline extremes, there is an acceptable range of pH in wastewater discharges to allow for dilution in the receiving environment. pH does not give an indication of the total acidity of the wastewater, which is an important consideration, when discharges are to aquatic environments.

(ii) Total Suspended Solids: This parameter is a measure of the suspended matter in a given wastewater. Aquatic life and vegetation depend on adequate light penetration, thus high TSS levels in wastewaters discharged to aquatic environments can blanket or smother benthic activity. The limitation of this parameter is that it is a gravimetric measurement that does not identify or quantify potentially toxic trace elements or compounds that may be associated with the suspended matter.

(iii) Turbidity: Turbidity is a measure of the light scattering in a sample due to colloidal particulate matter. Wastewater discharges with high turbidity levels can limit light penetration in streams resulting in diminished aquatic photosynthetic activity. Although Turbidity and TSS may be correlated there are many constraints in such a correlation. Turbidity gives no direct indication of the degree of toxicity of a waste other than the implicit assumption that some (toxic) trace elements may be adsorbed to the colloids.

(iv) Iron and Manganese: Iron and manganese are elements abundant in both coal and adjacent rocks and were conventionally selected parameters on the basis of exhibiting similar chemistry on exposure to aerobic oxidizing conditions in an aquatic environment. On such exposure, both iron and manganese are oxidized from the Fe^{2+} and Mn^{3+} states to the Fe^{3+} and Mn^{5+} states with resultant formation of an unaesthetic colloidal hydroxide precipitate in the water. This precipitate interferes with light penetration to aquatic organisms.

The tolerance of aquatic life to iron and manganese depends on the associated anions (i.e. Cl^-, SO_4^{-2}, NO_3^-), and the degree of dissociation of the iron or manganese compound. Fe and Mn combine with hydroxide ions to form precipitates and may also lower pH to acidic levels thereby further endangering aquatic life.

Results of the inorganic compound analyses for all facilities are summarized in Table 47, which shows the range of each parameter at all coal facilities investigated.

7.4.1 Possible Sources of Inorganic Compounds.

The presence of inorganic compounds in coal wastewaters may indicate contamination from several possible sources within the coal facility. Each source, moreover, can contribute a characteristic contaminant.

The most probable sources of contamination are:

- The coal itself
- Blasting agents
- Coal preparation and handling activities
- External anthropogenic activities.

(i) Coal: Several inorganic species can be leached from the coal matrix. The variety and quantitites of the leached materials depend upon the rank of coal, degree of exposure and weathering of in-situ coal, chemical nature of the inorganic species, pH of leaching fluid, and the type, nature and concentration of reagents used in the flotation phase of coal preparation.

The major inorganic constituents in coal are clay minerals (the aluminosilicates), carbonate minerals, sulphides and silica. These inorganic constituents are also sources of trace elements.

TABLE 45 CONVENTIONAL PARAMETERS USED TO ASSESS COAL WASTEWATERS

Conventional Parameters	Species Determined	Information Provided	Information Limitations
Total Suspended Solids (TSS)	Suspended Solids (SS)	- SS from mining activities - potential for blanketing sensitive aquatic life	- none
Total Dissolved Solids (TDS)	Dissolved Solids (DS)	- dissolved inorganic substances in ionized form, providing information on dissolved mineral content of wastewater	- no provision of individual mineral and non-mineral species present
Total Organic Carbon (TOC)	Organic Carbon	- all forms of organic carbon in wastewater	- does not provide any information on individual organic compounds that may be toxic - no indication of overall toxicity of waste
pH	Hydrogen ion concentration	- degree of acidity (or alkalinity) of wastewater and potential impact on environment	- fundamental parameter in wastewater analysis - does not provide an indication of the total acidity of wastewater
NH_3, NO_2, NO_3	Organic and inorganic forms of Nitrogen	- eutrophication potential of wastewater from organic and inorganic nitrogen fractions - concentration of NH_3, NO_2, NO_3 provides indication of how recent contamination is (high NH_3 indicates recent contamination, high NO_3 indicates that contamination is not recent)	- none
Oil and Grease	Solvent (which is usually hexane (C_6H_{14})) extractable hydrocarbons	- degree of miscibility of waste and amount present in the wastewater sample	- applies to a wide variety of materials (hydrocarbons, oils, esters, fats, waxes) dissolved by hexane
Total Cyanide (CN_T)	All forms of cyanide	- degree of toxicity of waste, as cyanide is highly toxic	- different forms of cyanide present are not determined in total cyanide analysis
Phenols	Phenolic compounds, (hydroxy derivatives of benzene)	- concentration of phenols	- none
Sulphate	Sulphate ion (total)	- concentration of sulphate which is a relatively non toxic anion but can exert carthartic effects at high concentration; tendency to scale formation.	- no information on associated metallic cations, which may be toxic, e.g. strontianite ($SrSO_4$) occurs in coal seams.

TABLE 46 SUMMARY OF RANGES OF CONVENTIONAL PARAMETERS (INORGANIC COMPOUNDS) AT COAL FACILITIES SAMPLED

	COAL FACILITY							
Parameters	CBDC* VJ[1] (1)	CBDC VJ[2] (1)	CBDC Lingan[1] (1)	CBDC Lingan[2] (1)	Thunder Bay[1] Terminals (2)	Thunder Bay[2] Terminals (2)	M and S Coal Bienfait (4)	SPC Poplar River (4)
TSS	3 900	320	22 900	370	4 - 10	ND	L 1.0 - 812	4 - 6
TDS	8.0	1 700	35.0	23 100	1 566 - 1 740	1 510 - 1 890	2 100 - 9 460	850 - 1 100
TOC	8.0	45	7.0	10	ND	7.0 - 39.0	8 - 67	10 - 39
pH	7.8	3.0	5.5	6.0	7.5 - 8.3	ND	8.0 - 8.8	6.9 - 8.1
NH_3	1.0	0.34	5.3	5.88	L 0.01 - 0.18	ND	L 0.0 - 10.16	0.05 - 0.97
NO_3	0.3	0.046	1.6	0.035	0.02 - 0.05	ND	0.02 - 0.86	0.02 - 0.41
NO_2	0.07	L 0.005	0.005	0.008	0.001 - 0.004	ND	L 0.01 - 0.05	L 0.01 - 0.04
Oil and Grease	2.0	7.0	4.3	6.0	ND	L 2.0	L 5.0	L 5.0
CN	0.02	L 0.15	0.02	L 0.15	ND	L 0.01 - 0.6	L 0.01	L 0.01
Phenols	0.002	0.003	0.007	0.005	0.4 mg/L - 0.6 mg/L	ND	L 0.01	L 0.01 - 0.08
SO_4	460.0	-	750.0	-	300 - 347	ND	794 - 2 706	209 - 270

All results mg/L except pH and where indicated.
L = Less than.
ND = Not determined.
*Number in parenthesis refer to number of sample sites at facility.
[1] Sampling during 1982.
[2] Sampling during 1983.

Cardinal River Mine (4)	TransAlta Utilities (4)	Smoky River Coal (7)	Fording^1 Coal (9)	Fording^1 Coal (10)	Fording^2 Coal (10)	Pacific Coast Terminals (3)	Westshore Terminals (4)
10 - 69	25 - 1700	240 - 770	5 - 5 850	L 5.0 - 4 290	219 - 2 550	49 - 374	380 - 740
343 - 890	360 - 1 100	L 1.0 - 70.0	153 - 571	193 - 573	L 5.0 - 398	48 - 107	159 - 525
L 1.0 - 24.0	18 - 116	3 - 43	2.0 - 1 760	1.0 - 880	1.0 - 6 000	19 - 164	270 - 530
8.2 - 8.4	8.2 - 8.5	8.0 - 8.4	7.5 - 8.4	7.7 - 8.4	7.8 - 8.3	ND	6.4 - 6.9
0.08 - 0.84	L 0.01 - 0.18	L 0.01 - 0.06	0.007 - 7.25	L 0.005 - 1.8	0.013 - 0.887	0.082 - 0.096	L 0.005 - 0.118
0.31 - 13.8	0.08 - 0.57	L 0.01 - 8.8	L 0.01 - 26.3	0.04 - 19.8	0.07 - 73.5	0.10 - 0.11	0.15 - 0.24
0.08 - 1.20	0.01 - 0.10	L 0.01 - 0.05	L 0.005 - 0.406	L 0.005 - 0.8	L 0.005 - 0.592	0.016 - 0.058	0.006 - 0.94
L 5.0	L 5.0	L 5.0	L 2.0 - 4.5 mg/g	L 2.0 - 20.0	L 2.0	3.0 - 6.0	L 2.0
L 0.01	L 0.01 - 0.01	L 0.01	L 0.03	L .03 - 0.078	L 0.03	L 0.03	L 0.03
L 0.01	L 0.01	L 0.01	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02 - 0.04
37 - 320	30 - 95	50 - 370	23 - 206	38.5 - 140	53 - 150.5	62.0 - 82.0	6.0 - 8.0

Wastewater parameters related to the major inorganic constituents of coal are summarized below.

Inorganic Constituent	Parameters Related to the Presence of Inorganic Constituents
Clay Minerals	TSS, TDS, turbidity
Carbonate Minerals	Carbonate anion (CO_3^{2-}), TDS, alkalinity, pH
Sulphides	Sulphide anion (S^{2-}), SO_4, TDS, pH
Silica	TSS, TDS, turbidity

(ii) Blasting Agents: When used in either surface or underground coal mining operations, blasting agents are a potential source of ammonium nitrate (from ammonium nitrate/fuel oil - ANFO).

Due to the method of its deployment, placed as a slurry in holes into the seam and then detonated, any unexploded or excess ANFO may remain to be incorporated in the mine water, percolating through the mine. Ammonia on contact with water reacts to form the ammonium anion (NH_4^+) which can be biologically oxidized under the appropriate conditions to nitrite (NO_2^-) by the nitrosomonas sp. and nitrate (NO_3^-) by the nitrobacter sp. During this conversion (called nitrification) pH is depressed due to the formation of acid, with an additional potential for solubilization of minerals contributing to TDS and possible dissolution of metals.

(iii) Coal Preparation and Handling: Coal preparation or coal washing operations are designed to reduce the ash and the inorganic sulphur content of coal by removal of pyritic sulphur (Fe Sx) and ash forming minerals. Although most coal preparation plants are designed to operate on a closed-loop/water recycle basis, unanticipated wastewater discharges by overloading or accident have occurred. Depending on the location of the facility, such events may contribute high TSS, TOC and sulphide loadings to the aquatic environment. In addition to high TSS and TDS levels, which are common to untreated wastewater discharges from coal preparation plants, low pH values due to sulphide dissolution may be common to wastewaters from plants cleaning coals with sulphur content greater than one percent. The use of organic flotation reagents may also contribute to total organic carbon (TOC) and oil and grease levels. Kerosene and No. 2 fuel oil have been used as flotation reagents at the DEVCO-Victoria Junction preparation plant (11).

(iv) External Anthropogenic Activities: Anthropogenic inputs of inorganic compounds to coal wastewaters may arise from several sources within and adjacent to the mine/preparation plant/transfer terminal site.

Among these inputs are:

- Improperly designed and operated sewage treatment facilities which may contribute organic nitrogen, phosphorus and suspended solids. The organic nitrogen may also be sequentially converted to NH_4^+, NO_2^- and NO_3^-.
- Oil and grease and TOC from the operation and maintenance of vehicles and machinery used at the facility.
- Soil erosion (due to the operation of vehicles and machinery) which contributes TSS and turbidity.
- Contributions of surface runoff from adjacent farming or agricultural operations and mined land reclamation activities. These runoff waters may contain nitrates from chemical fertilizers. Such operations may also contribute other organic chemicals which are collectively manifested in TOC analyses.

In certain areas, acidic precipitation may further solubilize inorganic minerals from coal, contributing to TDS levels.