BRITISH COLUMBIA HYDRO AND POWER AUTHORITY

HAT CREEK PROJECT

British Columbia Hydro and Power Authority - Hat Creek Project
Trace Elements in Coal and Effects of Redistribution in the Environment - December 1980

ENVIRONMENTAL IMPACT STATEMENT REFERENCE NUMBER: 15

BRITISH COLUMBIA HYDRO AND POWER AUTHORITY

TRACE ELEMENTS IN COAL AND EFFECTS OF REDISTRIBUTION IN THE ENVIRONMENT FOR THE PROPOSED HAT CREEK PROJECT

SYSTEM ENGINEERING DIVISION

Report No. SE 7933

December 1980

ACKNOWLEDGEMENT

B.C. Hydro wishes to acknowledge the contributions of Mr. Kirk D. Winges of Environmental Research and Technology, Inc., and Dr. Tom A. Watson, a specialist consultant to James F. MacLaren Ltd., in the preparation of this document.

TRACE ELEMENTS IN COAL AND EFFECTS OF REDISTRIBUTION IN THE ENVIRONMENT FOR THE PROPOSED HAT CREEK PROJECT

CONTENTS

Section	Subject	Page
	SUMMARY	vi
1.0	INTRODUCTION	1 - 1
2.0	TRACE ELEMENTS IN HAT CREEK COAL AND MINE WASTE PRODUCTS	
	2.1 Introduction	2 - 1
	2.2 Characteristics of the Hat Creek Coal Deposit that Affect Trace Element Sampling	2 - 1
	2.3 Sampling and Analytical Programs for Hat Creek Coal	2 - 4
	2.4 Sampling and Analytical Programs for Hat Creek Soils, Overburden and Waste Rock	2 - 7
	2.5 Sample Preparation for Coal, Waste Rock, Overburden and Soils	2 - 7
	2.6 Analytical Methods	2 - 8
	2.7 Trace Elements in Hat Creek Coal	2 - 18
	2.8 Trace Elements in Hat Creek Waste Rock and Overburden	2 - 23
	2.9 Enrichment of Trace Elements in Coals	2 - 27
	2.10 Hat Creek Coal Compared to Other Coals	2 - 33
	2.11 References	2 - 33
3.0	REDISTRIBUTION OF TRACE ELEMENTS BY ATMOSPHERIC PROCESSES	3 - 1
	3.1 Powerplant	3 - 2
	3.2 Mine	3 - 9
	3.3 References	3 - 14
4.0	ENVIRONMENTAL IMPACT OF TRACE ELEMENTS	
	4.1 Trace Elements of Concern	4 - 1
	4.2 Toxicity of Trace Elements	4 - 21
	4.3 Assessment of Background Trace Elements for Hat Creek Biota	4 - 29
	4.4 Trace Element Sources from the Project	4 - 39
	4.5 Assessment of Ambient Trace Element Concentrations from the Project on the Biota	4 - 49

CONTENTS - (Cont'd)

Section	Subject	Page
4.0	ENVIRONMENTAL IMPACT OF TRACE ELEMENTS - (Cont'd)	
	4.6 Receptor Accumulation of Trace Elements and Impacts from the Project on the Biota	4 - 56
	4.7 Selection of Trace Elements for Continuing Detailed Environmental Studies	4 - 91
	4.8 References	4 - 97

TABLES

Table No.		
2-1	Coal from Hat Creek Open-pit No. 1 Defined by Zone	2 - 3
2-2a	Summary of Analytical Methods for Total Trace Elements in Coal -	2 - 9
2-2b	Summary of Analytical Methods for Total Trace Elements in Waste Rock and Surficial Materials	2 - 11
2-3	Analyses of DDH 76-137:1-8 for Comparison of Dummy Versus Replicate Variability	2 - 17
2-4	Trace Element Concentrations in Coal by Zone	2 - 19
2-5	Coal Zones and Sampling Intervals for Trace Element Analyses	2 - 21
2-6	Trace Element Concentrations for Mine Mean Coal	2 - 22
2-7	Total Trace Elements in Waste Rocks	2 - 24
2-8	Ranges of Total Trace Elements and Some Major Elements in Sedimentary Rock and Soils	2 - 26
2-9	Organic Affinity of Trace Elements in Coal	2 - 28
2-10	Comparison of Hat Creek Coal with Crustal Rocks	2 - 30
2-11	Comparison of Trace Elements among Hat Creek Coal and Average Coals from Five Coal Provinces of the United States	2 - 31

CONTENTS - (Cont'd)

TABLES - (Cont'd)

Table No.		Page
3-1	A Comparison of the Fractions of Total Trace Elements Contained in the Coal which were Assumed to be Emitted in the Previous Work and the Fractions Currently Assumed	3 - 3
3-2	Trace Element Emission Rates from the Powerplant as Used in the Original ERT Work and as Currently Estimated	3 - 4
3-3	Change in Emission Rate for Various Contaminants during Fuel Switching	3 - 6
3-4	Maximum Trace Element Concentrations Resulting from Powerplant Emissions	3 - 7
3-5	Annual-average Trace Element Concentrations Corresponding to Coded Isopleths Resulting from Powerplant Emissions	3 - 8
3-6	Annual-average Trace Element Deposition Rates for Coded Isopleths Resulting from Powerplant Emissions	3 - 10
3-7	Ambient Trace Element Concentrations Resulting from Mine Dust Emissions	3 - 12
3-8	Annual-average Deposition Rates for Trace Elements Resulting from Mine Dust	3 - 13
4-1	Trace Elements Essential to Animals	4 - 6
4-2	Categorization and Essentiality of Elements Found in Coal to Biological Materials	4 - 7
4-3	Characteristics of Trace Elements Selected for Detailed Environmental Review by ERT	4 - 10
4-4	Rough Estimate of Airborne Trace Elements Released from Coal-fired Powerplants in 1970	4 - 13
4-5	Potential Toxicity of Trace Elements in Coal	4 - 15
4-6	Significance of Trace Element Emissions in Terrestrial Ecosystems	4 - 17

CONTENTS - (Cont'd)

TABLES - (Cont'd)

Table No.		Page
4-7	Hat Creek Receptors Analyzed for Trace Elements	4 - 31
4-8	Projected Waste Dump Leachate Characteristics for Trace Elements	4 - 41
4-9	Projected Quality of Intercepted Surface Water - Medicine Creek Area for Trace Elements	4 - 42
4-10	Projected Low Grade Coal and Coal Leachate Characteristics for Trace Elements	4 - 44
4-11	Projected Combined Ash Leachate Quality for Trace Elements	4 - 46
4-12	Chemical Characteristics of Cooling Water and Cooling Tower Drift	4 - 48
4-13	Ambient Air Quality Standards for Trace Elements	4 - 52
4-14	Trace Element Soil Accumulations, after 35 Years Operation	4 - 58
4-15	Projected Annual and 35-Year Increase of Selected Trace Elements in Soil due to Cooling Tower Drift	4 - 60
4-16	Trace Element Accumulation after 35 Years Operation from Stack Emissions and Cooling Tower Drift	4 - 61
4-17	Projected Trace Element Additions to the Bonaparte River from the Hat Creek Powerplant	4 - 71
4-18	Trace Element Concentrations Observed in the Bonaparte River and Hat Creek Relative to the Projected Water Concentrations during Operation of the Hat Creek Powerplant	4 - 72
4-19	Trace Element Water Quality Projections - Case 1	4 - 75
4-20	Trace Element Water Quality Projections - Case 2	4 - 76
4-21	Trace Element Water Quality Projections - Case 3	4 - 77
4-22	Water Quality Criteria for Agricultural Uses	4 - 78

CONTENTS - (Cont'd)

TABLES - (Cont'd)

Table No.		Page
4-23	Water Quality Criteria for Fish and Other Aquatic Life	4 - 84
4-24	Trace Element Safe Concentrations Derived from 96-hour LC50 Data and Guideline Application Factors	4 - 88
4-25	Calculation of Final Mercury Concentration (µg/L) in the Bonaparte River Resulting from Powerplant Emissions from the Hat Creek Project	4 - 90

APPENDICES

Appendix No.	
A	Analyses of Hat Creek Coals
B	Trace Element Concentrations in Hat Creek Receptors and Naturally Occurring Levels in Selected Ecosystem Components
C	Literature Review of the Environmental Consequences of Trace Element Redistribution
D	Mercury Content in Hat Creek and the Bonaparte River at Selected Stations

SUMMARY

The Environmental Research and Technology, Inc. (ERT) report on "The Influence of the (Hat Creek) Project on Trace Elements in the Ecosystem" (Appendix F) was completed in July 1978. Since that time there have been changes in the proposed mine and powerplant construction and operation, new data have been acquired and new questions have been raised. For these reasons, it was decided by B.C. Hydro and Power Authority that a revised Hat Creek Trace Element Report should be prepared.

The principal objective of this report is to identify the trace element content of the coal and the redistribution of the trace elements to the environment through coal combustion. Twenty-three trace elements have been selected on the basis of source contributions (coal, overburden, mine dust, stack emissions, cooling tower drift, as well as waste rock and ash disposal), and their potential toxicity to biotic receptors. An extensive literature review of the biological implications of trace elements contributed to this report. The 23 trace elements selected are antimony, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, thorium, tin, tungsten, uranium, vanadium and zinc.

The recent investigations have resulted in lower coal quality, but a more realistic operating regime for the powerplant; the overall effect is to lower trace element emissions. The revised mine mean coal is increased in As, Be, B, Mn, Sr, Sn and Zn above that of the ERT mine mean coal and lower in Cr, Cu, F, Hg, Mo, Ni and V. The mean values of trace elements in Hat Creek coal fall within the range of regional averages for United States coals;* however, Hat Creek coal

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* U.S. coals were selected for comparison since data were available. Only limited data are available for Canadian and western Canadian coals (see Swanson, V.E. et al. 1976).

tends to be slightly higher in Cr, Cu, F and V than most U.S. coals, and lower or average in the remainder of the 23 elements listed.

An evaluation of the analytical techniques used to characterize trace element quantities in biological receptors has also been performed. Of the 23 elements selected for discussion, adequate background data for biotic receptors are available for the following 14 elements: antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, fluorine, lead, manganese, mercury, nickel, vanadium and zinc. Factors contributing to the comparatively small data base of trace element measurements for the remaining elements include small sample size and the use of inappropriate or semi-quantitative analytical methods.

Emission rates for trace elements released to the atmosphere have been revised on the basis of new information on the combustion properties of some elements as well as the deposition properties of others. The number of trace elements in this revision has increased to 23 from the previous nine which were extensively analyzed by ERT. Based on these new data, the emission rates for Hg have decreased while those for Sb, Be, B, Cu, F, Pb, Mn, Mo, Ni, Se and U have increased and the remainder (As, Cd, Cr, Co, Ag, Tl, Th, Sn, W, V and Zn) are unchanged from the original ERT assessment.

Trace element concentrations have been calculated using SO_2 model predictions and the ratio of emission rates between each trace element and SO_2. Projected ambient concentrations of trace elements for the local area are below those of the PCB* regulatory guideline values for 24-hour and annual averages. Most trace elements with the exception of fluorine are more than an order of magnitude below any guideline level. The 24-hour average for fluorine of 1.9 $\mu g/m^3$ is close to the guideline level of 2.0 $\mu g/m^3$ for the same averaging period.

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* Pollution Control Board, Ministry of Environment, B.C. Government.

Deposition patterns of trace elements have been revised from the original ERT work. The most significant areas of deposition for the major trace element contaminants are outside the local scale. These revised deposition patterns are based on the publication of the report on the long range transport and the implications of acid precipitation (ERT, Appendix I, 1979). The deposition of trace elements was previously calculated for only the local scale. In this assessment the isopleths of regional annual SO_2 deposition include the plant site. This revised approach provides a much more conservative (worst case) estimate of soil accumulations in the local area as trace element depositions, regionally, were typically greater than in the local area.

The potential impacts of the 23 trace elements were assessed for biotic receptors on the basis of the information obtained from the literature survey and revised emission/deposition characteristics for the elements. Projections of ground level concentrations of trace elements from powerplant stack-emissions suggest that plants or animals respiring airborne trace elements will not be adversely affected. Although the maximum 24-hour average concentration for fluorine of 1.9 $\mu g/m^3$ approaches the guideline value of 2.0 $\mu g/m^3$, it is unlikely that any long-lasting or deleterious effects to the biota will occur. Fugitive dust emissions and cooling tower drift will be highly localized and will not be important sources of trace elements to receptors in the Hat Creek area.

Projections of trace element accumulations in soils have been estimated assuming the following: that the powerplant will operate for 35 years at 65 percent capacity; soils in the deposition zones have a bulk density of 1.75 g/cm^3; all deposited trace elements will remain in residence in the top 3 cm of soil; and neither trace element uptake by vegetation nor erosion of soil to watershed drainages will occur. Trace element deposition rates have been calculated for cooling tower drift and have been added to the depositions from stack emissions. Generally, trace element enrichment in local and regional soils represents less than 1 percent of background trace element concentrations

after the lifetime of the powerplant. The ultimate enrichment of soils resulting from the project does not alter the soil contents beyond those reported as natural. The impacts of trace elements in soils to plants or animals is expected to be negligible. The alkaline nature of the soils will render most deposited trace elements relatively unavailable. This characteristic will result in the soils acting as a sink for most trace elements.

Trace elements would enter the aquatic environment by leaching from coal, overburden and waste rock piles in addition to the principal contribution of elements emitted through the stack. The impacts of contributions from sources other than stack emissions have been assessed on the basis of the zero discharge approach for contaminated waters and for seasonal fluctuations.

The Bonaparte River watershed would receive the largest concentration of trace elements compared with other systems as a large portion of it lies within the zone of greatest deposition. A worst case example for this watershed was examined which included the following conservative assumptions:

1. All of the trace elements that fall on the Bonaparte River watershed make their way into the aquatic system.

2. All trace elements that enter the water dissolve completely.

This approach was used to determine which elements showed inconsequential concentration increases in water and which elements would appear to be of concern and were therefore deserving of further analysis. A similar assessment was not possible with trace elements depositing from stack emissions. Increases in the trace element content of waters within the Bonaparte River watershed are anticipated with the project. These projected increases, however, for all elements except Hg, meet a number of regulatory agency guideline criteria for crop irrigation and livestock watering, the protection of fish and other aquatic life, and ingestion by wildlife.

With the assumptions used in the assessment, the Hg concentration resulting from stack emissions meet all of the above criteria except for those recommended for the protection of fish and aquatic life. It is expected that the contributions of Hg to background levels in the Bonaparte River watershed will be negligible.

From the original list of 23 trace elements addressed in this report, a rationale has been developed to select those that should be monitored during detailed continuing studies throughout the operation of the plant. The basis of the selection process included: trace element volatility, ambient concentration, mobility, methylation potential, toxicity and bioaccumulation. The following 13 trace elements are suggested for monitoring during plant operation: arsenic, boron, cadmium, chromium, copper, fluorine, lead, mercury, nickel, tin, uranium, vanadium and zinc.

No significant impact on local or regional ecosystems is expected from the release of trace elements by the Hat Creek project, provided that the data from the air quality model (ERT, Appendix C, 1978) and the acid rain report (ERT, Appendix I, 1979) are representative.

SECTION 1.0 - INTRODUCTION

The upper Hat Creek valley contains two major coal deposits, one of which has been selected as the source of fuel for a 2000 MW thermal generating station with a planned life of 35 years. At the end of 35 years appreciable reserves would still remain in the No. 1 deposit and in the remainder of the upper Hat Creek valley. These resources could be used to extend the life of the proposed plant, to enlarge thermal generating capacity or for a variety of alternative uses.

The upper Hat Creek valley lies midway between Ashcroft and Lillooet, 200 km northeast of Vancouver, British Columbia. The proposed plant site is in the Trachyte Hills, 4.8 km east of the No. 1 deposit and at an elevation of 1410 m.

The purpose of this report is to review the trace element data collected as part of the detailed environmental studies. It has been necessary to re-examine data and conclusions in view of a number of changes to the project description, new data acquired since completion of the ERT Report on trace elements in July 1978, and the addition of some new trace element information based on a recent literature review.

This report is divided into three principal sections which address:

1. Trace element concentrations in coal and mine waste (Section 2.0).

2. The atmospheric redistribution of trace elements (Section 3.0).

3. The environmental impact of trace elements entering the biota (Section 4.0).

Section 2.0 describes the trace element concentrations in Hat Creek coal and mine waste products and the sampling and analytical procedures necessary to determine them. In order to place the concentrations of trace elements in Hat Creek coal into perspective, the organic affinity of trace elements and the composition of trace elements in U.S. coals have been compared to those at Hat Creek.

Section 3.0 addresses the redistribution of trace elements by atmospheric processes. Projections of increases in atmospheric concentration and surface deposition rates have been evaluated on the basis of the revised content of trace elements in Hat Creek coal. Improvements in the estimation of atmospheric movements and deposition of trace elements have become available with the publication of the ERT (1979) report, "Long Range Transport and Implications of Acid Precipitation". The average annual SO_2 patterns described in this report were used to calculate deposition patterns and ambient concentrations for trace elements arising from powerplant emissions.

The third principal portion, Section 4.0, describes the potential impacts of trace element redistribution on the aquatic and terrestrial biota. The number of trace elements considered has been progressively reduced throughout the study from most of the elements in the periodic table to only those that proved to be of importance in the environmental assessment of the proposed project. The factors considered in the selection of these trace elements included their mobility, volatility, essentiality to biological materials, methylation potential and toxicity, as well as their tendencies for bioaccumulation and biomagnification.

The impacts of trace elements entering the environment from stack emissions, overburden and waste rock piles, coal and low grade waste stockpiles, ash disposal sites, mine dust and cooling tower drift have been assessed. This assessment included the movements of the trace elements through abiotic (soils, sediments and water) and biotic (wildlife, vegetation, as well as fish and other aquatic life) systems.

Particular attention was focused on the potential of trace elements for toxicity, bioaccumulation and biomagnification in receptors for both the local and regional areas.

A computerized literature search of recent pertinent reference-material was undertaken to provide an accurate and reliable basis for the selection of trace elements of concern as well as projections of their movement and toxicity. The methods used in this particular study have been developed in order to address the redistribution of significant trace elements in coal through the powerplant and into the numerous receptors of the natural environment.

SECTION 2.0 - TRACE ELEMENTS IN HAT CREEK COAL AND MINE WASTE PRODUCTS

2.1 INTRODUCTION

All naturally occurring materials contain trace elements. Coals tend to contain high concentrations of certain trace elements while being deficient in others in relation to averages for crustal rocks (clarke values). Therefore trace elements comprise an important study area in relation to the development of coal-fired power plants.

Although investigations into trace elements in coal were conducted as early as 1887 on European coals,[1] it was not until recently that interest was expressed in trace elements from Western Canadian coals.[2] Trace element studies began on Hat Creek coal in 1975 with the advent of the current series of environmental programs and these studies are continuing.[3]

This chapter describes the distribution of trace elements in the Hat Creek coal deposit and the altered mining scheme that has resulted in changes in trace elements concentrations in proposed run-of-mine coal. It provides additional information on sampling and on the relationship of trace elements in Hat Creek coal to those of other coals. Additional analyses of mine waste that were not available in earlier studies are also included.

2.2 CHARACTERISTICS OF THE HAT CREEK COAL DEPOSIT THAT AFFECT TRACE ELEMENT SAMPLING

The Hat Creek No. 1 coal deposit has been drilled on approximately 150 m centres. On this basis the deposit was divided into four zones (labelled A through D) and subsequently into several subzones. The deposit is folded into a syncline flanked on the east by a faulted anticline and another syncline. These structures plunge to the south

at 15° to 20°. Therefore each coal zone forms part of the subcrop over the area of the No. 1 deposit.

A number of characteristics of the deposit specifically affect sampling procedures for trace elements:

1. The No. 1 deposit is approximately 420 m in true thickness[4] and contains 717 Mt of coal,[5] although only 331 Mt would be mined[6] in the first 35 year phase of operations.

2. The deposit varies laterally from northeast, where the coal is of high grade (>20 000 kJ/kg, db*) to southwest, where the coal is of low grade (<14 000 kJ/kg, db) and where waste partings are more numerous.[4]

3. Vertical variations in coal quality through the deposit are more pronounced than horizontal variations within a single stratigraphic horizon. There is evidence that this relationship can be extended to some trace elements.

Coal quality has a pronounced influence on emissions of trace elements because it affects the amount of coal that would be required to generate a specified amount of electricity. Coal quantities and qualities are summarized in Table 2-1.[6]

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* db indicates the value is on a dry basis.

2.2 CHARACTERISTICS OF THE HAT CREEK COAL DEPOSIT THAT AFFECT TRACE ELEMENT SAMPLING - (Cont'd)

TABLE 2-1

COAL FROM HAT CREEK OPENPIT NO. 1
DEFINED BY ZONE

Zone	Coal (Mt @ >7100 kJ/kg, Moist)		Heating Value (kJ/kg, Moist)
A	86 246		11 860
B	69 996		13 770
C	48 683		10 580
D	126 025		16 170
TOTAL	330 950	MEAN	13 720

Mine planning is a dynamic process. As planning continues, concepts change and result in changes of trace element emissions. In the document "Air Quality and Climatic Effects of the Proposed Hat Creek Project - Appendix F - The Influence of the Project on Trace Elements in the Ecosystem"[7] the following assumptions were made:

1. The coal quality would be approximately 14 700 kJ/kg (6300 Btu/lb) with 26.0 percent ash and 0.45 percent sulphur at 20 percent moisture.

2. The powerplant would operate at a 100 percent capacity factor.

3. The quantity required was estimated at 42 600 t/d.

More recent assumptions that have been adopted based on additional drilling, additional coal quality information, an alternate mine plan and the proposed powerplant operating regime, are as follows:

1. The coal quality would be approximately 13 720 kJ/kg (5900 Btu/lb) with 25.6 percent ash and 0.39 percent sulphur at 23.6 percent moisture.[8]

2.2 CHARACTERISTICS OF THE HAT CREEK COAL DEPOSIT THAT AFFECT TRACE ELEMENT SAMPLING - (Cont'd)

2. The powerplant would operate at a 65 percent capacity factor over 35 years.

3. The quantity required from the mine averages approximately 26 000 t/d based on 9.5 Mt for an average year and 365 operating days per year. Peak consumption for a 24 hour period would be approximately 40 000 t.

2.3 SAMPLING AND ANALYTICAL PROGRAMS FOR HAT CREEK COAL

Several suites of samples have been analysed for trace elements at Hat Creek. The methods of analysis are explained in Section 2.6 and in the Environmental Research and Technology (ERT) report "Air Quality and Climatic Effects of the Proposed Hat Creek Project - Appendix F - The Influence of the Project on Trace Elements in the Ecosystem".[7]

During 1975, between four and 21 elements were analysed from nine samples of diamond drill core. The results are included in the "Preliminary Environmental Impact Study for the Proposed Hat Creek Development".[3] These samples were analysed by emission spectroscopy and were used as a guide to potential trace element impacts from combustion of Hat Creek coal.

In 1976 Dr. K. Fletcher of the University of British Columbia analysed 24 samples of diamond drill core from one hole.[9] The samples form a continuous section through the Hat Creek coal deposit and they were analysed for 11 elements by atomic absorption spectrophotometry. The results and a description of the methods of analysis are included in Appendix A of this report.

Because of an apparent anomaly in Cu and Mo all available composite samples were analysed for these elements by Dr. H.V. Warren

of the University of British Columbia who also used atomic absorption spectrophotometry.[10] These composites had been prepared for ultimate analysis of the coal. Subsequently the anomalous interval was resampled and analysed for Cu and Mo by atomic absorption spectrophotometry at Acme Analytical Laboratories Ltd.[11]

The Canada Centre for Mineral and Energy Technology (CANMET) analysed two sets of samples, one in 1976 and the other one in 1978. The analyses were conducted on samples collected from bucket auger drill holes at three sites. The samples were prepared by taking grab samples from each drum of homogenized coal collected for the test burn at the Canadian Combustion Research Laboratory (CCRL-Ottawa). The samples were made homogeneous at Birtley Engineering Ltd. (Calgary) where part of each sample underwent beneficiation tests.[12] Nine samples comprising one suite, were analysed for mercury by using flameless atomic absorption as part of a preliminary report on mercury in Canadian coals.[13] The second suite consisted of three samples which were analysed for 12 elements; one of these samples was done in duplicate.[14,15] Mercury was analysed by flameless atomic absorption; the remaining elements were analysed by conventional atomic absorption.

ERT employed Commercial Testing and Engineering Co. (CTE) to analyse 3 samples from the bucket auger program in 1976; one sample was from A zone and two samples were from B zone.[7] The samples were collected from composites in the same manner as the samples collected for CANMET. It was recognized that these samples, from only a few tens of metres of the coal section, would not be representative; therefore CTE was given 11 additional composite samples for analysis. These samples were collected from drill cores with a wide spatial distribution over the deposit (Fig. 2-1). Composites were prepared by sampling each interval on a volume basis; this method avoided the problem resulting from wide fluctuations in specific gravity among intervals

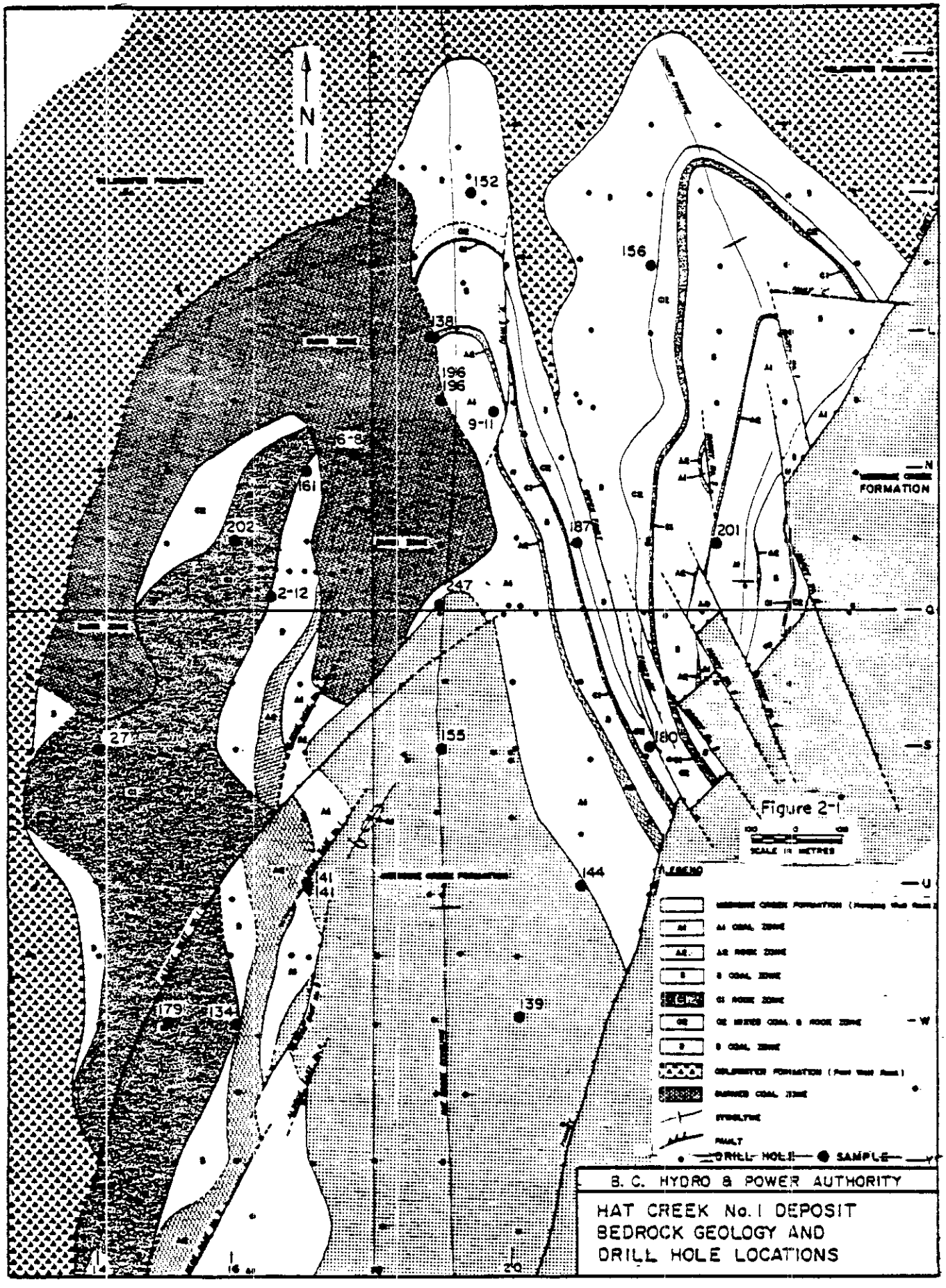
N
152
156
138
196
196
9-11
86-88
161
202
2-12
247
187
201
27
155
180
144
141
141
179
134
139
FORMATION
SCALE IN METRES
B. C. HYDRO & POWER AUTHORITY
HAT CREEK No. 1 DEPOSIT
BEDROCK GEOLOGY AND
DRILL HOLE LOCATIONS

Figure 2-1

and should produce a suite of samples that are representative* of the deposit. Each of these sets of samples was analysed in duplicate or in triplicate. The analyses were conducted by spark source mass spectroscopy for 61 trace elements; in addition mercury was analysed by flameless atomic absorption, lead by conventional atomic absorption and fluorine by specific ion electrode. These results are summarized as mine mean coal in the ERT report.[7]

In order to determine laboratory precision and accuracy, three coal samples were selected in 1978 and analysed for 16 trace elements at three laboratories: CTE,[16] Chemex Ltd.,[17] and CAN TEST Ltd.[18] CTE used primarily the same methods as in previous analyses, however mercury was analysed by double-gold-amalgamation. Chemex and CAN TEST analysed Be, Cd, Cr, Cu, Mo, Pb, Sr, V and Zn by conventional atomic absorption, Th by colorimetry, Hg by flameless atomic absorption and F by specific ion electrode. Chemex used flameless atomic absorption for As and CAN TEST used graphite furnace atomic absorption.[19] The selection of these 16 elements from the original list of 64 was based on the 15 elements specifically recommended by ERT for further analysis[20] plus Th which was added to the list by British Columbia Hydro and Power Authority (B.C. Hydro). This list comprises the elements believed to be of concern because of their toxicity, volatility or concentrations in coals.

Literature research of trace element information was conducted in 1979. Based on this search, eight additional elements have been added to the earlier list because of specific association with coal-fired thermal plants, toxicity to specific plants and animals or volatility. On the revised list of trace elements Sb, Co, Mn, Ni, Ag, Sn, Tl and W have been added. The total list of 24 elements will be abbreviated for monitoring as described in Section 4.0.

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* Standard deviations among samples are large. This problem is described in Section 2.7.

2.3 SAMPLING AND ANALYTICAL PROGRAMS FOR HAT CREEK COAL - (Cont'd)

Subsequent to analysing the three samples, Chemex analysed eight additional samples plus one dummy sample from the previous suite for the 16 elements.[21] All samples were done in duplicate and standards were also analysed as a guide to accuracy. The samples were selected to improve the sampling distribution over the deposit (Fig. 2-1) and were obtained from the pulverized rejects generated for coal analysis.

2.4 SAMPLING AND ANALYTICAL PROGRAMS FOR HAT CREEK SOILS, OVERBURDEN AND WASTE ROCK

The sampling for the 1976 and 1977 programs conducted by ERT are described in their report.[7] These sites were resampled in 1978 and the procedures and results are described in Section 4.0.

Samples were collected in April and October of 1978 from the eight test plots at Aleece Lake and from the sloped test plots at Houth Meadows and Medicine Creek.[21] The samples were collected by first loosening the soil surface to a depth of approximately 20 cm with a shovel blade and sampling was conducted along the untouched surface with a heavy plastic scoop. Four individual samples were collected from each plot. These were placed in dry, white sheets of paper, thoroughly mixed and subsampled. Thirteen wet and 13 air-dried samples were collected. The wet samples were analysed as received for Hg only and the dried samples were analysed for 23 elements. The analyses were conducted by Chemex Labs Ltd. and the methods are described in Section 2.6.

2.5 SAMPLE PREPARATION FOR COAL, WASTE ROCK, OVERBURDEN AND SOILS

Samples collected in 1976 and 1977 were analysed by CTE. The methods and results are described in detail in the ERT report "Air Quality and Climatic Effects of the Proposed Hat Creek Project - Appendix F - The Influence of the Project on Trace Elements in the Ecosystem".[7] To prepare the samples CTE dried them at 40°C and they

2.5 SAMPLE PREPARATION FOR COAL, WASTE ROCK, OVERBURDEN AND SOILS - (Cont'd)

were pulverized and screened to minus 75 µm; the fine grain size was necessary due to the small sample size (0.1 g) used in Spark Source Mass Spectroscopy (SSMS) analysis. The samples were made homogeneous during pulverizing in a homogenizer.

In 1978 samples of coal, waste rock, soil and overburden were sent in two batches (April, May and October) to Chemex Laboratories Ltd.[21] The April samples of waste rock, overburden and soil were oven dried overnight at 55° to 60°C, pulverized and screened to minus 150 µm. In October samples were dried at 45°C and screened to minus 850 µm to more closely compare with the CTE drying procedure. The October soil samples were collected for direct comparison with those from 1976 and 1977. For each analysis 1.0 g of sample was used. Waste rock and overburden samples were not re-analysed.

2.6 ANALYTICAL METHODS

Three laboratories have conducted the analyses used in this document for assessment of total trace elements in Hat Creek coal and waste. These laboratories and their methods are summarized in Tables 2-2a and 2-2b.

Commercial Testing and Engineering Company (CTE) used spark source mass spectroscopy (SSMS), conventional flame atomic absorption spectroscopy (AA), plasma emission spectroscopy (PES) and specific ion electrode (SI) in the 1976 analyses. These methods are described in the report, "Air Quality and Climatic Effects of the Hat Creek Project - Appendix F - The Influence of the Project on Trace Elements in the Ecosystem".[7]

The methods used in the 1978 program are described in this chapter; detection limits and coefficients of variation are also listed. Chemex Labs Ltd. performed most of these analyses and they were instructed to use their most accurate and precise methods, to

TABLE 2-2a

SUMMARY OF ANALYTICAL METHODS
FOR TOTAL TRACE ELEMENTS IN COAL

	No. of Samples	Lab	Method	Date	Detection Limit (mg/kg)	C.V.[1] (%)
Sb	9	CTE	SSMS[2]	1976		100
As	14	CTE	SSMS	1976		50-100
	11[3]	Chemex	FAA[4]	1978	1	20
Be	14	CTE	SSMS	1976		100
	11	Chemex	AA[5]	1978	1	100
B	14	CTE	SSMS	1976		50-100
	11	Chemex	ES[6]	1977	20	35[7]
Cd	14	CTE	SSMS	1976		100
	11	Chemex	AA	1977	0.2	100
Cr	14	CTE	SSMS	1976		50-75
	11	Chemex	AA	1977	5	20
Co	14	CTE	SSMS	1976		25
Cu	14	CTE	SSMS	1976		25-75
	11	Chemex	AA	1977	1	20
F	13	CTE	SI[8]	1976		
	11	Chemex	SI	1977	20	-
Pb	14	CTE	AA	1976		
	11	Chemex	AA	1977	1	20-100
Mn	14	CTE	SSMS	1976		50
Hg	14	CTE	FAA	1976		
	11	Chemex	FAA	1977	.005	-
Mo	14	CTE	SSMS	1976		75-100
	11	Chemex	AA	1977	1	100
Ni	14	CTE	SSMS	1976		50
Se	14	CTE	SSMS	1976		100
	11	Chemex	AA	1977	1	100
Ag	9	CTE	SSMS	1976		100

TABLE 2-2a - (Cont'd)

	No. of Samples	Lab	Method	Date	Detection Limit (mg/kg)	C.V.[1] (%)
Sr	14	CTE	SSMS	1976		50
	11	Chemex	AA	1977	5	20
Tl	4	CTE	SSMS	1976		100
Th	14	CTE	SSMS	1976		100
	11	Chemex	C[9]	1977	4	100
Sn	12	CTE	SSMS	1976		100
W	4	CTE	SSMS	1976		100
U	14	CTE	SSMS	1976		100
	1	Chemex	NA[10]	1977	0.2	100
V	14	CTE	SSMS	1976		50-100
	11	Chemex	AA	1977	5	20
Zn	14	CTE	SSMS	1976		75-100
	11	Chemex	AA	1977	1	20

---

1 C.V. is the abbreviation for coefficient of variation. The values are based mainly on Le Geyt (1979) Ref. 19 and apply to a single sample.

2 SSMS is the abbreviation for spark source mass spectroscopy. Detection limits range from 0.1 mg/kg to 1.0 mg/kg.

3 Although 11 different samples were analysed, three of these were spread appreciably over two zones in the revised zone designations and were not included in the revised calculation of mine mean coal.

4 FAA is the abbreviation for flameless atomic absorption.

5 AA is the abbreviation for atomic absorption.

6 ES is the abbreviation for emission spectroscopy.

7 The coefficient of variation was estimated by Le Geyt (1979) Ref. 17.

8 SI is the abbreviation for specific ion electrode.

9 C is the abbreviation for colorimetry.

10 NA is the abbreviation for neutron activation.

TABLE 2-2b

SUMMARY OF ANALYTICAL METHODS
FOR TOTAL TRACE ELEMENTS IN WASTE ROCK AND SURFICIAL MATERIALS

	No. of Samples	Lab	Method	Date[1]	Detection[2] Limit (mg/kg)	C.V. (%)
Sb	-	-	-	-	-	-
As	10[3]	Chemex	FAA	1978	1	20-100
Be	10	Chemex	AA	1978	1	100
B	10	Can Test	PES[4]	1978	10	-
Cd	10	Chemex	AA	1978	0.2	100
Cr	10	Chemex	AA	1978	5	10-20
Co	10	Chemex	AA	1978	1	10-20
Cu	10	Chemex	AA	1978	1	10-20
F	10	Chemex	SI	1978	20	-
Pb	10	Chemex	AA	1978	1	20-100
Mn	10	Chemex	AA	1978	5	5-20
Hg	10	Chemex	FAA	1978	.005	-
Mo	10	Chemex	AA	1978	1	100
Ni	10	Chemex	AA	1978	1	10-20
Se	10	Chemex	FAA	1978	1	100
Ag	-	-	-	-	-	-
Sr	10	Chemex	AA	1978	5	5-20
Tl	-	-	-	-	-	-
Th	10	Chemex	AA	-	4	20-100
U	10	Chemex	F[5]	1978	0.5	100

TABLE 2-2b - (Cont'd)

	No. of Samples	Lab	Method	Date[1]	Detection[2] Limit (mg/kg)	C.V. (%)
V	10	Chemex	AA	1978	5	10-20
Zn	10	Chemex	AA	1978	1	10-20

---

1 Analyses were conducted only for leachable trace elements prior to 1978.

2 Detection limits for SSMS range from 0.1 to 1.0 mg/kg.

3 The suite of 10 samples is composed of the rock materials collected from the Aleece Lake test plots.

4 PES is an abbreviation for plasma emission spectroscopy.

5 F is an abbreviation for fluorimetry.

2.6 ANALYTICAL METHODS - (Cont'd)

apply all recommended correction procedures and to analyse samples in duplicate.[22]

(a) Atomic Absorption

In the 1978 program Chemex Labs Ltd. analysed coal, waste rock and surficial materials for the following elements by atomic absorption after a nitric-perchloric acid digestion:[25]

1. Co, Cu, Mo, Ni, Pb and Zn which have a detection limit of 1 mg/kg.[23,24]

2. Cd which has a detection limit of 0.2 mg/kg.[24]

3. Cr, Mn and V which have a detection limit of 5 mg/kg.[23,24]

Lead and cadmium were corrected for background effects. For Be and Sr a hydrofluoric-nitric-perchloric acid digestion was used and the detection limits are 1 mg/kg and 5 mg/kg respectively.[24] Samples for Se analysis were subjected to a nitric-sulphuric acid digestion and chelation extraction; the detection limit is 1 mg/kg.

For atomic absorption it is felt that the coefficients of variation of 100 percent near the detection limit, 20 percent at 10 times the detection limit and 5 to 10 percent at levels of one hundred times the detection limit, can realistically be applied to routine analyses performed by commercial laboratories[19] (Tables 2-2a and 2-2b).

(b) Flameless Atomic Absorption

Flameless atomic absorption was used for mercury analysis of coal and for mercury, arsenic and selenium analysis of overburden and waste rock in 1978.[22,25] The method differs from

conventional atomic absorption in that the element of interest is first converted to a volatile form by reduction then swept into an absorption cell for thermal decomposition and atomization of the metal.

For mercury analysis the samples were digested in nitric and sulphuric acids, potassium permanganate and potassium persulphate. Mercury is easily volatilized, so a high temperature is not required. The detection limit is 5 µg/kg.[24]

Arsenic and selenium from overburden and waste rock were analysed as their hydrides by hot vapour flameless atomic absorption. The matarials were wet ashed with a combination of nitric and perchloric acids prior to analysis. The detection limit for As and Se using this method is 1.0 mg/kg.[24]

(c) Double-Gold Amalgamation

In the method of double-gold amalgamation for mercury determination used by CTE in 1978, a sample is thermally decomposed and the evolved mercury vapour is swept through a packing of gold where it is amalgamated.[19] Subsequently a purification step is used in which the amalgam is rapidly heated and the mercury redistilled onto a second gold packing. The second amalgam is then rapidly heated and the purified mercury is swept into an absorption cell where the mercury is measured by its absorption.

An early paper describing this technique appeared in 1964.[26] In this paper, a single amalgamation was used and the authors, in discussing interferences, note: "The principal interference encountered in this technique is from smoke from organic matter in the samples." Samples containing less than 10 percent organic matter can be analysed reliably.

The CTE procedure of double amalgamation includes a second purification step which is a definite improvement and should provide reasonably good data. One weakness of the method is that to avoid problems with organic material, extremely small sample aliquots are required, in the range of 5-80 mg. With very small samples such as this, the danger increases that the aliquot selected may not be representative unless the sample is very well homogenized. In the data reviewed to date there is reasonable to good agreement between the gold amalgamation method and the wet digestion methods favoured by other laboratories. The method was used in only three samples to determine variability among laboratories and the analyses were not used in determining mean mercury content.

(d) Fluorimetry

Chemex used fluorimetry for analysis of uranium. At the time of the analyses they used a weak acid attack, that is digestion with 4M HNO_3, followed by direct fluorimetry. The resulting analyses are low for two reasons, not all of the uranium is dissolved and the fluorescent effects can be lowered by such common elements as iron and manganese.[19] The Chemex procedure has since been modified, however all of the Chemex fluorimetry results for uranium were rejected because they are too low.[19]

(e) Inductively Coupled Plasma Torch (PES)

In 1978 Can Test Ltd. analysed some soil and waste rock samples for boron using an inductively coupled plasma torch.[22] In preparing the samples they were ashed overnight at 550°C and the ash was dissolved in hydrochloric and nitric acids. The detection limit is 10 mg/kg.[27] The instrumentation is described in the ERT report.[6]

2.6 ANALYTICAL METHODS - (Cont'd)

(f) Emission Spectrography

Chemex Labs Ltd. analysed the coal samples from 1978 for boron using an emission spectrograph with a detection limit of 20 mg/kg.[24] Sample preparation consisted only of pulverizing the samples to minus 150 μm.

(g) Colorimetry

Thorium in coals was analysed colorimetrically.[24] A nitric-hydrofluoric-hydrochloric acid digestion was used and thorium was determined using Arsenazo-3 reagent. The detection limit is 4 ppm.[24]

(h) Neutron Activation

A single analysis has been incorporated in this paper which was determined by neutron activation analysis - delayed neutron counting at the Novatrack Facility. The sensitivity level is 0.2 mg/kg.[28]

(i) Accuracy and Precision

A study of accuracy and precision among trace element analyses was conducted.[19] Analyses were obtained in duplicate or in triplicate throughout the trace element studies; in addition the trace elements were compared to standards.[7,17,23] In general replicates have been very close to the initial value obtained. Dummy samples (previously analyzed samples sent again under different numbers) have a wider separation than replicates analyzed in the same suite (Table 2-3). Of these samples Cr and Zn are significantly different between the two sets of samples. These differences may be due to sample inhomogeneity or digestion techniques. Expected variations between duplicates for the various analytical methods used in this study are summarized in Tables 2-2a and 2-2b as a percentage of the value obtained.

TABLE 2-3

ANALYSES OF DDH 76-137:1-8

FOR COMPARISON OF DUMMY VERSUS
REPLICATE VARIABILITY
(mg/kg)

Replicates	Original Sample			Dummy Sample		Detection Limit
	1	2	3	1	2	
As	6	6.5	6.5	4	4	1
Be	1	1	1	1.5	1.5	1
B	<20	<20	<20	<20	-	20
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	0.2
Cr	50	48	49	75	80	5
Cu	42	41	41	44	44	1
F	95	95	105	110	115	20
Pb	4	5	4	4	4	1
Hg	0.20	0.21	0.21	0.17	0.18	.005
Mo	1	1	1	2	2	1
Se	<1	<1	<1	<1	1	1
Sr	175	170	180	140	140	5
Th	<4	<4	<4	<10	<10	4
U	-	2.0	-	-	-	0.2
V	100	100	95	110	110	5
Zn	29	29	30	46	48	1

2.6 ANALYTICAL METHODS - (Cont'd)

Expected variations are appreciably larger among samples analysed by spark source mass spectroscopy, a semi-quantitative method, than among samples analysed by quantitative methods. In general, among quantitative methods, expected variations become very large near the detection limit and this is evident from the coefficients of variation in Tables 2-2a and 2-2b. As a result of collecting several samples in each zone and analyzing each sample in duplicate or triplicate the values are expected to be close approximations to the actual value.

2.7 TRACE ELEMENTS IN HAT CREEK COAL

There is considerable variability in most trace elements throughout the Hat Creek No. 1 coal deposit (Table 2-4). Standard deviations are commonly in excess of 50 percent of the mean value. The samples generally represent between 50 and 100 m of the coal interval with the thicker waste sections removed. Samples were selected for an adequate distribution both areally and vertically over the No. 1 deposit (Table 2-5 and Fig. 2-1). Three of the 25 samples that were selected were not used in determining mine mean coal because of the redistribution of coal zones. The three samples are from B and C zones. If these samples were included the mine mean coal would contain lower concentrations of each trace element.

The mine mean coal established by ERT[6] is based on a numerical average of samples from different drill holes. The revised mine mean coal is compared to the previously described mine mean coal in Table 2-6. The revised mine mean coal is calculated by incorporating new analyses and by weighting the samples based on their zonal relationship and the quantity that is expected to come from each zone.

TABLE 2-4

TRACE ELEMENT CONCENTRATIONS IN COAL BY ZONE
(mg/kg)

Zone	A[1]		B		C		D	
Element[2]	M	S	M	S	M	S	M	S
Sb	N.D.[3]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
As	11	7	15	7	8	5	5	3
Be	0.7	0.7	0.5	0.5	0.5	0.2	0.7	0.4
B	<11	N.D.	<7	N.D.	<8	N.D.	<30	N.D.
Cd	<0.3	N.D.	<0.4	N.D.	<0.2	N.D.	<0.3	N.D.
Cr	125	96	43	15	72	15	56	36
Co	7	3	6	1	7	N.D.	4	2
Cu	46	31	42	19	44	21	29	17
F	114	53	134	34	205	7	86	23
Pb	6	2	5	2	10	4	5	3
Mn	180	120	376	432	128	103	178	93
Hg	0.15	0.04	0.13	0.03	0.15	0.06	0.12	0.05
Mo	3	1	2	1	2	0	2	1
Ni	40	39	22	6	35	8	11	6
Se	<0.9	N.D.	<1.2	N.D.	<0.5	N.D.	<0.6	N.D.
Ag	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sr	103	36	110	9	90	30	68	45
Tl	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Th	<6	N.D.	<4	N.D.	<3	N.D.	<7	N.D.
Sn	0.9	0.2	0.9	0.1	0.6	N.D.	0.8	0.5

Table 2-4 - (Cont'd)

Zone / Element[2]	A[1] M	A[1] S	B M	B S	C M	C S	D M	D S
W	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
U	2.2	0.4	2.4	0.7	2.5	0.7	2.4	0.8
V	167	103	93	37	110	0	81	33
Zn	35	15	46	19	38	13	29	22

---

1 M is the mean and S the standard deviation.

2 Numbers of samples are as follows:

	A	B	C	D
As, Be, B, Cd, Cr, Cu,) F, Pb, Hg, Mo, Se, Sr,) Th, V and Zn)	8	4	2	8
Mn, Ni	5	4	2	3
Co	5	3	2	4
Sn	5	3	1	3
U	5	4	2	4

3 N.D. is an abbreviation for not determined due to the small number of samples.

TABLE 2-5

COAL ZONES AND SAMPLING INTERVALS FOR
TRACE ELEMENT ANALYSES

Drill Hole No.	Zone	Depth (m)
BAH 9-11	A	4.6-19.5
DDH-76-155	A	123.2-216.1
DDH-76-196	A	9.1-78.6
DDH-76-141	A	62.1-160.3
DDH-76-144	A	185.6-312.2
DDH-76-134	A	167.9-229.5
DDH-76-139	A	278.5-389.5
DDH-76-247	A	58.5-155.0
BAH 6-8	B	14.9-29.0
BAH 2,3,5,12	B	10.7-25.3
DDH-76-196	B	78.6-140.5
DDH-76-141	B	283.7-344.7
DDH-76-202	C	30.3-83.3
DDH-76-138	C	68.8-129.8
DDH-76-127	D	96.6-153.0
DDH-76-152	D	7.6-88.6
DDH-76-156	D	65.8-147.2
DDH-76-187	D	29.2-84.1
DDH-76-180	D	129.5-202.6
DDH-76-161	D	123.1-215.4
DDH-76-179	D	243.5-272.6
DDH-76-201	D	160.6-252.0

TABLE 2-6

TRACE ELEMENT CONCENTRATIONS FOR MINE MEAN COAL
(mg/kg)

Element	ERT Mine Mean Coal (1978)	Revised Mine Mean Coal (1979)
Sb	0.47	0.5
As	7.8	9
Be	0.38	0.7
B	15	<17
Cd	<0.48	<0.3
Cr	100	74
Co	5.8	5.8
Cu	43	38
F	137	121
Pb	<6.6	6
Mn	200	213
Hg	0.14	0.13
Mo	4.9	2.3
Ni	33	24
Se	<1.0	<0.8
Ag	<0.5	<0.4
Sr	76	89
Tl	<0.1	<0.5
Th	<3.0	<5.3
Sn	0.76	0.83
W	<0.1	<1.0
U	<2.3	<2.4
V	140	110
Zn	25	35

2.7 TRACE ELEMENTS IN HAT CREEK COAL - (Cont'd)

The apparent anomaly in Cu and Mo determined by Fletcher (1976),[9] was examined by Warren[10] and Acme.[11] The Warren study determined that values of Cu and Mo for composite samples ranged from 16 to 143 mg/kg and averaged 46 mg/kg for Cu. They ranged from 1.2 to 4.6 mg/kg and averaged 3 mg/kg for Mo. The sample analyzed by Fletcher was resampled and reanalyzed by Acme Analytical Laboratories; the values obtained were 43 mg/kg for Cu and 1 mg/kg for Mo as compared with 4150 mg/kg Cu and 21.2 mg/kg Mo in the Fletcher study. These results indicate that the sample from the Fletcher study was contaminated and the results from that sample should be disregarded.

2.8 TRACE ELEMENTS IN HAT CREEK WASTE ROCK AND OVERBURDEN

An experimental program at Aleece Lake was designed to evaluate, on a large scale, the revegetation potential of various waste materials from the proposed coal mine.[21] Many of these waste materials contain concentrations of trace elements different from those found in surface soils. As part of the experimental revegetation program, therefore, total and leachable trace element levels in the various waste materials were determined.

Twenty-three elements were studied including some macronutrient elements as well as trace elements. Their selection was based upon many factors including: potential environmental effects, levels known to be present in similar wastes, ability of plants to concentrate certain elements, mobility in the environment and toxicity to plants and animals.

The results of the analyses for total trace elements are presented in Table 2-7. Leachable trace elements are described in Section 4.0. Each value in Table 2-7 is the average of duplicate analyses. Only about 10 percent of the more than 300 pairs of analyses for rock and soil differed by more than 10 percent. The results for a

TABLE 2-7

TOTAL TRACE ELEMENTS IN WASTE ROCKS[1]
(mg/kg)

Element	Sand-stone	Coal Waste	Carbonaceous Shale (Carbonaceous Claystone)	Baked Clay	Colluvium	Bentonitic Clay	Glacio-fluvial Gravels	Till	Recent Fluvial Gravels from Trench B	Mouth Meadows Parent Material
Sb	N.D.[2]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
As	6	5	8	9	10	9	6	6	4	5
Be	2.0	1.5	2.0	2.5	2.0	2.0	2.0	1.5	1.5	1.0
B	8.8	17	12	13	11	24	15	<20	<20	<20
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2
Cr	133	105	110	135	125	123	140	155	157	120
Co	18	11	16	14	15	16	14	14	12	7
Cu	46	55	69	61	39	40	44	41	29	23
F	200	133	198	123	203	265	160	218	173	260
Pb	6	6	6	3	4	7	3	1.5	1.5	1.3
Mn	330	140	200	453	533	313	668	675	643	393
Hg(dried)	.095	.080	.012	.045	.090	.017	.065	.050	.040	.058
Hg(wet)	.094	.013	.016	.052	.011	.025	.081	.065	.047	.049
Mo	2	4	3	3	2	2	2	2.5	1.5	3
Ni	51	45	55	60	45	52	59	61	50	24
Se	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ag	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sr	205	80	110	300	275	255	205	220	290	390
Tl	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Th	20	10	20	10	20	30	10	10	10	10
Sn	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
W	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
U	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
V	145	150	190	245	135	130	160	130	135	90
Zn	82	57	57	51	75	68	75	71	59	53

[1] Analyses by Chemex Labs Ltd., samples collected April 1978.

[2] N.D. is an abbreviation for not determined.

divided sample, which was analysed as two unrelated samples, show an average difference of 9.2 percent for the 23 elements analysed. Six results differed by more than 20 percent, mainly when the results were close to the detection limits of the tests. No analyses of total trace elements in mine waste products were conducted for the ERT study. All trace element data are within the range of values normally found in natural soils[29] as is evident by comparing colluvium, glaciofluvial gravels, till, Recent fluvial gravels and Houth Meadows parent material from Table 2-7 with soils from Table 2-8.

Mercury levels for the Hat Creek project were determined on both air/oven-dried samples and on undried, as-collected samples. The mercury concentration measured in the undried samples averaged 26 percent higher than the concentration measured in those samples dried overnight at 60°C.[21]

Ranges of total trace elements and some major elements in sedimentary rocks are summarized in Table 2-8. It is evident in comparing these ranges with analyses of similar waste rocks associated with Hat Creek coal from Table 2-7 that most Hat Creek waste rock trace element concentrations are comparable to those of similar rock types. Hat Creek sandstone is however much lower in boron, slightly lower in iron and lead and slightly higher in chromium, cobalt, copper, molybdenum, nickel, vanadium and zinc. Hat Creek bentonitic clay resembles typical shale in a geologic sense therefore these rock types are comparable. The bentonitic clay is higher in arsenic, lower in fluorine, iron and lead and much lower in boron and mercury. These rocks contain similar concentrations of the other elements. Carbonaceous shale and claystone have been compared. These Hat Creek waste materials are in the range of concentration of similar rocks for all but lead, molybdenum and zinc. For each of these elements Hat Creek carbonaceous sedimentary rocks are lower than the ranges for typical carbonaceous shales.

TABLE 2-8

RANGES OF TOTAL TRACE ELEMENTS AND SOME MAJOR ELEMENTS IN SEDIMENTARY ROCKS AND SOILS[1]
(mg/kg)

Element	Sandstone	Shale	Carbonaceous Shale	Soil
Sb	1	3	N.D.[2]	N.D.
As	N.D.	4	75-225	1-50
Be	<1	1-6	1	6
B	155[31]	130[31]	N.D.	10
Cd	N.D.	0.3	N.D.	0.5
Cr	10-100	100-400	10-500	5-1000
Co	1-10	10-50	5-50	1-40
Cu	10-40	30-150	20-300	2-100
F	290[30]	690[30]	N.D.	200
Pb	10-40	20	20-400	2-200
Mn	385[30]	N.D.	N.D.	200-3000
Hg (dried)	0.03	0.40	N.D.	0.03-0.30
Mo	0.1-1.0	1.0	10-300	0.2-5.0
Ni	2-10	20-100	20-300	5-500
Se	1	0.5-1	N.D.	0.1-2.0
Ag	0.4	N.D.	5-50	0.1
Sr	N.D.	N.D.	N.D.	N.D.
Tl	N.D.	N.D.	N.D.	N.D.
Th	N.D.	N.D.	N.D.	N.D.
Sn	N.D.	40	N.D.	10
W	1.6	N.D.	N.D.	N.D.
U	0.45	4.1[31]	2-300[32]	1
V	10-60	50-300	50-2000	20-500
Zn	5-20	50-300	100-1000	10-300

1 Data from Krauskopf[30] in Geochemistry of Mineral Exploration by Hawkes and Webb[33] except where noted.

2 No values were found in the references used.

2.9 ENRICHMENT OF TRACE ELEMENTS IN COALS

Some trace elements are enriched in coals during three stages of coal formation and during subsequent groundwater movement:

1. During their life some plants extract elements preferentially.

2. During partial decay of the vegetal material and leaching of the peat there is differentiation of trace elements.

3. During coalification as oxygen, nitrogen, hydrogen and water are reduced other elements are concentrated.

4. During movement of groundwater through the coal and the resultant filtration of these waters, trace elements are concentrated in the coal.

Recently interest has been directed toward identification of organically versus inorganically bound trace elements in coals. A paper by Smith et al (1979)[34] summarized the work of five groups of researchers on the relative organic affinity of a number of trace elements from various coals. The results for the 24 elements of interest are summarized in Table 2-9 in addition to results determined by Schultz et al (1973)[35] Gluskoter et al (1977)[37] and those determined for Hat Creek coal.

The method of assessing organic affinity relies on comparing trace element concentrations between raw and washed coals. The method is not very accurate because it does not examine whether or not the trace element is actually bound to an organic molecule. There is considerable variation among laboratories which is possibly due to the variations in the washability of the coals and analytical technique. Despite these inadequacies a number of trends are evident.* Schultz et

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* The Hat Creek analysis is for a single sample and is based on the ERT report.[7]

TABLE 2-9

ORGANIC AFFINITY OF TRACE ELEMENTS IN COAL[1]

Smith et al[34]	Zubovic et al[39]	Filby et al[38]	Horton et al[40]	Ruch et al[36]	Schultz et al[35]	Gluskoter et al[37]	Hat Creek
Ni(40)[2]	Be(82)	Hg(53)	V(100)	B	Cd(56)	Be	Sr(100)[3]
Pb(35)	B(77)	As(48)	Be(75-100)	Be	F(25-47)	Co	Cu(98)
Mn(33)	V(76)	Sr(29)	B(75-100)	Sb	Ni(24)	U	Th(82)
Sn(29)	Ni(59)	Sb(21)	Mo(50-75)	V	Hg(10-32)	Sr	Hg(72)
Mo(26)	Cr(55)	Co(17)	Cr(0-100)	Co	Cr(14-20)	W	Tl(65)
Sr(22)	Co(53)	Th(3)	Zn(50)	Se	Cu(13-20)	Ni	Be(50)
V(21)	Mo(40)	Cr(0)	Ni(0-75)	Ni	Pb(14)	Sb	B(50)
Se(14)	Cu(34)	Ni(0)	Cu(25-50)	Cu	Mn(5-11)	V	Cd(50)
Cu(10)	Sn(27)		Co(25-50)	Cr		B	Cr(50)
As(9)	Zn(0)		Sn(0)	Mn		Cu	Co(50)
Zn(7)				Mo		Se	Pb(50)
				Pb		Cr	Mo(50)
				Cd		Th	Se(50)
				Zn		Pb	Ag(50)
				Hg		Sn	Sn(50)
				As		Hg	W(50)
						Mn	U(50)
						Mo	Ni(40)
						Zn	V(39)
						As	Zn(34)
						Cd	Sb(22)
							Mn(17)
							As(16)
							F(5)

1 Numbers represent the percentage of the trace element associated with the organic component. Where no numbers are given only a ranking was listed in the reference.

2 These numbers are approximate values of organic affinity as determined from Fig. XI of Smith et al. (Ref. 34).

3 The value for organically-bound Sr exceeds 100 percent of the total Sr due to the semi-quantitative nature of the analyses.

2.9 ENRICHMENT OF TRACE ELEMENTS IN COALS - (Cont'd)

al. determined that fluorine is generally associated with the mineral matter in coal; fluorine had the lowest organic affinity of the Hat Creek analyses. Smith et al,[34] Ruch et al[36] and Gluskoter et al[37] found that As had a low organic affinity which compares favorably with results from Hat Creek; Filby et al[38] determined that As was approximately evenly divided between organic and inorganic constituents. Zinc has a low organic affinity in most coals that have been examined. Vanadium, boron and beryllium commonly have pronounced organic affinity.[36,37,39,40] Other elements have variable affinity. Additional analyses would be required to verify the trends in organic affinity of Hat Creek coals.

Any method of upgrading coal quality i.e. selective mining or beneficiation would improve the emissions of volatile trace elements. Elements with an inorganic affinity (i.e. <50 percent organic affinity) would be preferentially removed. All trace element emissions are improved by improving the quality of coal going to the powerplant. Upgrading the heating value of the coal also has the effect of decreasing trace element emissions by decreasing the quantity of coal consumed.

The mineral matter in Hat Creek run-of-mine coal is largely contained in partings of claystone and siltstone, the precursor of shale. The concentrations of trace elements in typical shale, in the earth's crust and in Hat Creek coal are listed in Table 2-10 for comparison. It is evident from the high concentrations of As, Be, B, Co, F, Pb, Mn, Hg, Sr, Th, U and Zn in shales that these elements are more concentrated in shales than in Hat Creek or U.S. coals. This relationship further illustrates the inorganic affinity of many elements.

TABLE 2-10

COMPARISON OF HAT CREEK COAL WITH CRUSTAL ROCKS
(mg/kg)

	Hat Creek Coal[7]	Crustal Average[41]	Typical Shale[42]
Sb	0.5	0.2	1.5
As	9	1.8	13.0
Be	0.7	2.8	3.0
B	<17	10	100
Cd	<0.3	0.2	0.3
Cr	74	100	90
Co	5.8	25	19
Cu	38	55	45
F	121	625	740
Pb	6	12.5	20
Mn	213	950	850
Hg	0.13	0.08	0.40
Mo	2.3	1.5	2.6
Ni	24	75	68
Se	<0.8	0.05	0.60
Ag	<0.4	.07	.07
Sr	89	375	300
Tl	<0.5	-	-
Th	<5.3	9.6	12.0
Sn	0.83	-	-
W	<1.0	-	-
U	2.4	2.7	3.7
V	110	135	130
Zn	35	70	95

TABLE 2-11

COMPARISON OF TRACE ELEMENTS AMONG HAT CREEK COAL
AND AVERAGE COALS FROM FIVE COAL PROVINCES OF THE UNITED STATES
(mg/kg)

	1	2	3	4	5	6	Average of Samples of U.S. Coals Analysed
Sb	0.5	1.7	0.9	0.6	0.4	1.2	1.1
As	9	21	6	3	2	27	15
Be	0.7	3.0	2.0	0.5	0.7	2.0	2
B	<17	100	100	70	70	30	50
Cd	<0.3	7.1	1.3	0.2	0.5	0.7	1.3
Cr	74	15	20	5	5	20	15
Co	5.8	7	7	2	2	7	7
Cu	38	20.2	28.0	8.3	9.1	24.0	19
F	121	71	124	45	70	80	74
Pb	6	55	20	5.3	5.5	15.3	16
Mn	213	138	240	51	36	620	100
Hg	0.13	0.14	0.18	0.09	0.06	0.24	0.18
Mo	2.3	5.0	3.0	2.0	1.5	3.0	3
Ni	24	30	20	3	3	15	15
Se	<0.8	4.6	7.0	1.0	1.6	4.7	4.1
Ag	<0.4	-	-	-	-	-	-
Sr	89	50	200	150	100	100	100
Tl	<0.5	-	-	-	-	-	-
Th	<5.3	5.2	8.3	2.7	3.6	4.9	4.7
Sn	0.83	-	-	-	-	-	-
W	<1.0	-	-	-	-	-	-
U	2.4	3.3	3.2	0.9	1.6	1.4	1.8
V	110	20	50	10	15	20	20
Zn	35	373[1]	40	25.6	9.9	20.0	39

Columr 1 Weighted mean of 22 samples of coal from the Hat Creek No. 1 deposit that were analysed at Commercial Testing and Engineering Laboratories, Golden, Colorado and Chemex Labs Ltd., North Vancouver, B.C. The analyses represent a revised mine mean coal.

Columr 2 Mean of coal samples from the Interior Coal Province, U.S.A.[43]

Columr 3 Mean of coal samples from the Gulf Province, U.S.A.[43]

Columr 4 Mean of coal samples from the Northern Great Plains Coal Province, U.S.A.[43]

Table 2-11 - (Cont'd)

Column 5 Mean of coal samples from the Rock Mountain Coal Province, U.S.A.[43]

Column 6 Mean of samples of nonanthracitic coal from the Eastern Province Appalachian Coal Region, U.S.A.[43]

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1 The geometric mean is 58 mg/kg.

2.10 HAT CREEK COAL COMPARED TO OTHER COALS

Hat Creek coal has not been burned over extended periods. To assess the implications of trace elements from Hat Creek coal it is useful to compare it with average values of 799 samples from five coal provinces of the United States (Table 2-11). Most of the samples are from some 150 mines producing coals that have been utilized over extended periods of time.

The mean values for most trace elements in Hat Creek coals fall within the range of regional averages for these United States coals. Hat Creek coal tends to be high in Cr, Cu, F and V and low or average in the remainder of the 24 elements listed. The significance of these elements is described in Section 4.0 of this report. Additional trace elements have been identified from Hat Creek coal and their significance is described in the report on "Air Quality and Climatic Effects of the Proposed Hat Creek Project".[7]

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SECTION 3.0 - REDISTRIBUTION OF TRACE ELEMENTS BY ATMOSPHERIC PROCESSES

In the previous sections an analysis has been made of trace element content in Hat Creek coal. The purpose of this chapter is to relate those mass fractions to increases which are anticipated to occur in atmospheric concentrations and surface deposition rates.

Both the mining of coal and the burning of coal to generate electricity will result in some release of trace elements to the atmosphere. An assessment of such effects has been previously conducted by ERT. It is necessary, however, to revise this assessment for several reasons:

1. The trace element contents in the coal have been revised since the ERT work.

2. Only nine elements were extensively analysed in the ERT work. To further define potential impacts, it is now deemed necessary to evaluate 24 elements.

3. New information is available on the combustion properties of some trace elements.

4. New information is available on deposition properties of emissions from the Hat Creek project.

5. In the original work only powerplant emissions were considered. It is now considered important to include mine dust redistribution.

3.1 POWERPLANT

The method used to estimate effects of trace elements released to the atmosphere by the powerplant stack in the original ERT study (ERT, 1978) was to multiply model predictions for SO_2 by the ratio of the trace element emission rate to that of SO_2. The use of such ratios in this analysis has not changed, but it has been necessary to revise the emission rates and the SO_2 model predictions as discussed previously.

The trace element feed rates to the boiler can be calculated from the peak coal consumption rate of about 40 000 t/d and the trace element concentration in the coal, as shown in Table 2-6. (The trace element concentrations are expressed on a dry basis so only the dry fraction of the coal consumption rate, about 76 percent, should be used.) Of this feed rate a certain percentage is emitted to the atmosphere. This percentage differs for each element based on its own chemical and physical properties and has been estimated in Table 3-1. In this way emission rates for each of the trace elements have been calculated and compared to the emission rates used in the original ERT analysis in Table 3-2.

(a) Concentrations

The estimate of ground-level trace element concentrations in the trace element appendix to the original ERT work was done only for the local-scale modelling and only for the case of a 366 m stack height. In this reassessment, trace element concentrations have also been restricted to the local-scale, because highest concentrations are expected within this radius. The case treated, however, is for a 244 m stack with a Meteorological Control System (MCS). In addition the earlier trace element appendix did not address 3-hour and 24-hour maximum concentrations, which have been addressed here.

TABLE 3-1

A COMPARISON OF THE FRACTIONS OF TOTAL TRACE ELEMENTS CONTAINED IN THE COAL WHICH WERE ASSUMED TO BE EMITTED IN THE PREVIOUS WORK AND THE FRACTIONS CURRENTLY ASSUMED

Element	Symbol	Previous Work Assumed Percent Emitted (%)	Current Value[1] Assumed Percent Emitted (%)
Antimony	Sb	0.57[2]	1.0
Arsenic	As	6.4	Not changed
Beryllium	Be	0.05[2]	1.5
Boron	B	1.2[2]	5
Cadmium	Cd	2.1	Not changed
Chromium	Cr	0.15	Not changed
Cobalt	Co	0.3[2]	Not changed
Copper	Cu	0.4	2
Fluorine	F	6.0	63
Lead	Pb	1.9	3
Manganese	Mn	0.2[2]	1.1
Mercury	Hg	148	100
Molybdenum	Mo	0.5[2]	5
Nickel	Ni	0.5[2]	1.0
Selenium	Se	1.0[2]	25
Silver	Ag	0.2[2]	Not changed
Thallium	Tl	0.1[2]	Not changed
Thorium	Th	0.11[2]	Not changed
Tin	Sn	0.5[2]	Not changed
Tungsten	W	0.1[2]	Not changed
Uranium	U	0.09[2]	1
Vanadium	V	0.3	Not changed
Zinc	Zn	1.5	Not changed

1 Selected as representative of literature values (Curtis, 1977; Lim, 1979; Meserole at al., 1978; Lövblad, 1977; Ondov et al., 1979; Gladney et al., 1978; Kaakinen et al., 1975) and Hat Creek coal characteristics.

2 For these elements emissions were not analysed in the original work. The values shown above are those which would result from analysis of test burns.

TABLE 3-2

TRACE ELEMENT EMISSION RATES FROM THE POWERPLANT
AS USED IN THE ORIGINAL ERT WORK AND AS CURRENTLY ESTIMATED

Element	Symbol	Emission Rate (kg/d) Previous Work	Current Estimate[1]
Antimony	Sb	Not analysed	0.15
Arsenic	As	17.2	18
Beryllium	Be	Not analysed	0.32
Boron	B	Not analysed	26
Cadmium	Cd	0.35	0.19
Chromium	Cr	5.2	3.4
Cobalt	Co	Not analysed	0.53
Copper	Cu	5.93	23
Fluorine	F	281	2300
Lead	Pb	4.36	5.5
Manganese	Mn	Not analysed	71.0
Mercury	Hg	7.07	4.0
Molybdenum	Mo	Not analysed	3.5
Nickel	Ni	Not analysed	7.3
Selenium	Se	Not analysed	6.1
Silver	Ag	Not analysed	0.02
Thallium	Tl	Not analysed	0.02
Thorium	Th	Not analysed	0.18
Tin	Sn	Not analysed	0.13
Tungsten	W	Not analysed	0.03
Uranium	U	Not analysed	0.73
Vanadium	V	16.1	10
Zinc	Zn	12.9	16

1 Calculated by multiplying coal consumption rate (40 000 t/d) by the dry fraction of the coal (0.76), and by the trace element concentrations (Table 2-6) and finally by the fraction of the trace elements which are emitted (Table 3-1). It should be noted that these emissions correspond to a 2000 MW powerplant operating at full load continuously.

Although model predictions for an MCS may not show the same property for SO_2 as for trace element concentrations, an analysis of the relative effects on trace element emissions of MCS control actions has been conducted. The methods used to effect this control by an MCS are switching to low sulphur coal and reduction of load. While the load reduction actions will clearly result in reduced trace element emissions, the effect of fuel switching on trace element emissions varies from element to element. A comparison of the change in emission rate during a fuel switching action for SO_2 and various trace elements is shown in Table 3-3. While there is considerable variability, the general nature is a reduction for most elements.

Trace element concentrations have thus been calculated using SO_2 model predictions and the ratio of emission rates between each trace element and SO_2. The maximum impacts are presented in Table 3-4. Annual-average concentrations are calculated for the isopleths shown in Fig. 3-1 and presented in Table 3-5.

(b) Deposition

In the previous work (ERT Appendix F) deposition of trace elements was calculated for the local-scale only and was based on ground-level concentrations and an assumed deposition velocity. However, since this time, an improved method has become available with the publication of the report on long range transport and the implications of acid precipitation (ERT Appendix I). It became apparent from this report that areas receiving largest values of deposition rates for major contaminants were outside this local-scale. Since this analysis of major component deposition (ERT Appendix I) was a more theoretical treatment of this process, it was decided to use the deposition patterns in the Appendix I report to calculate deposition patterns for trace elements in this reassessment. Within the acid precipitation

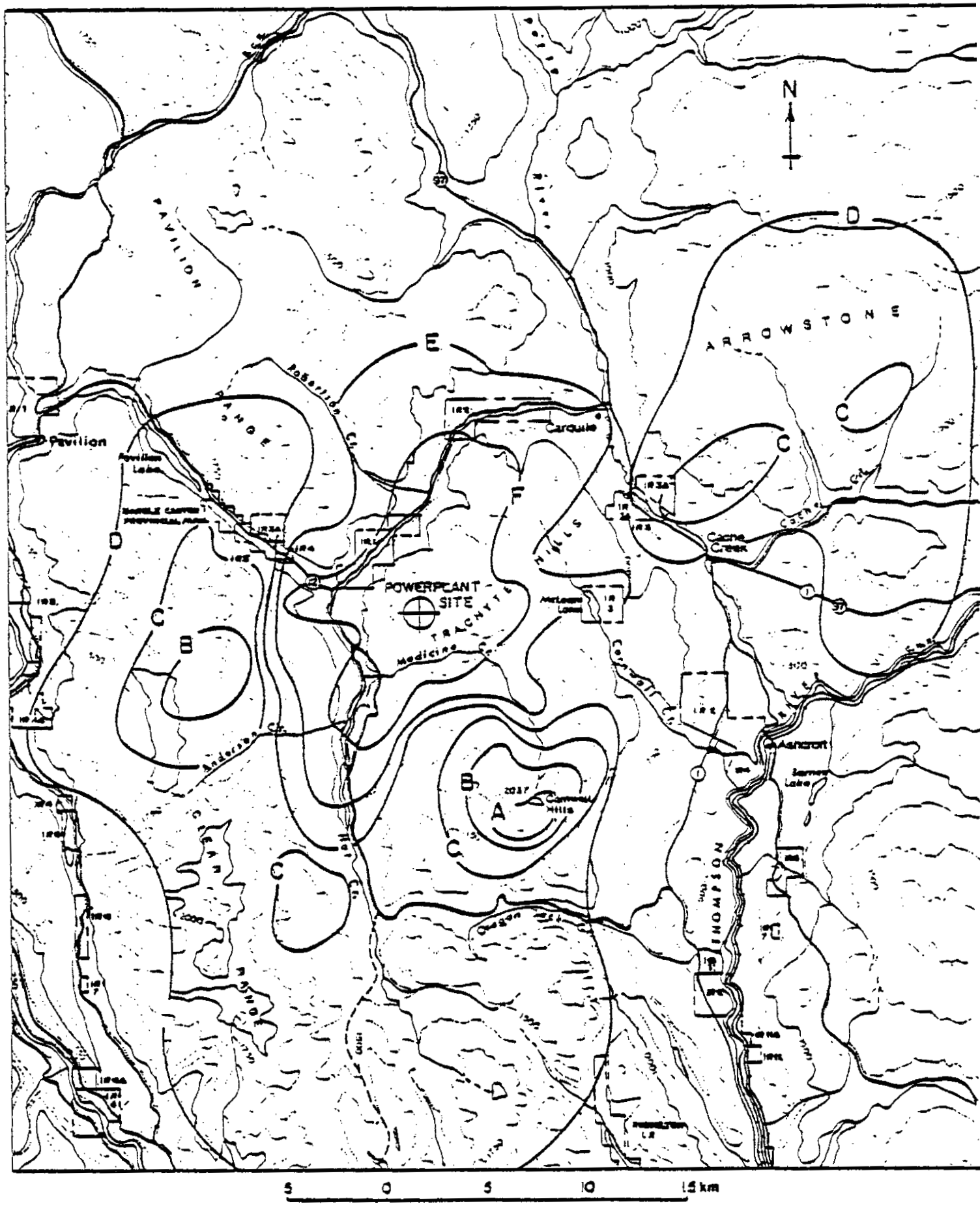

Figure 3-1 Coded Isopleths of Annual Average Concentrations resulting from Power Plant Emissions

TABLE 3-3

CHANGE IN EMISSION RATE FOR VARIOUS CONTAMINANTS
DURING FUEL SWITCHING

Contaminant	Symbol	Percent of Normal Emissions During Fuel Switching
Sulphur dioxide	SO_2	53
Antimony	Sb	NQ[1]
Arsenic	As	46
Beryllium	Be	92
Boron	B	137
Cadmium	Cd	75
Chromium	Cr	65
Cobalt	Co	65
Copper	Cu	58
Fluorine	F	60
Lead	Pb	67
Manganese	Mn	74
Mercury	Hg	77
Molybdenum	Mo	83
Nickel	Ni	38
Selenium	Se	65
Silver	Ag	NQ
Thallium	Tl	NQ
Thorium	Th	110
Tin	Sn	85
Tungsten	W	NQ
Uranium	U	75
Vanadium	V	61
Zinc	Zn	69

[1] NQ - not quantifiable due to inadequate data.

TABLE 3-4

MAXIMUM TRACE ELEMENT CONCENTRATIONS IN $\mu g/m^3$
RESULTING FROM POWERPLANT EMISSIONS[1]

Element	Symbol	3-hour	24-hour	Annual
Antimony	Sb	0.00029	0.00012	0.0000043
Arsenic	As	0.034	0.014	0.00052
Berylluim	Be	0.00061	0.00026	0.0000092
Boron	B	0.050	0.021	0.00074
Cadmium	Cd	0.00036	0.00015	0.0000054
Chromium	Cr	0.00065	0.0027	0.000097
Cobalt	Co	0.001	0.00042	0.000015
Copper	Cu	0.044	0.018	0.00066
Fluorine	F	4.4	1.8	0.066
Lead	Pb	0.0105	0.0044	0.00016
Manganese	Mn	0.136	0.057	0.002
Mercury	Hg	0.0077	0.0032	0.00011
Molybdenum	Mo	0.0067	0.0028	0.0001
Nickel	Ni	0.014	0.0058	0.00021
Selenium	Se	0.012	0.0049	0.00017
Silver	Ag	0.000038	0.000016	0.00000057
Thallium	Tl	0.000038	0.000016	0.00000057
Thorium	Th	0.00034	0.00014	0.000005
Tin	Sn	0.00025	0.0001	0.0000037
Tungsten	W	0.000057	0.000024	0.00000086
Uranium	U	0.0014	0.00058	0.000021
Vanadium	V	0.019	0.008	0.00029
Zinc	Zn	0.031	0.013	0.00046

1 No comparison is given here between previous work and these estimates are for the current work because the original ERT studies did not address these impacts. The concentrations are based on a 2000 MW powerplant operating at full load continuously.

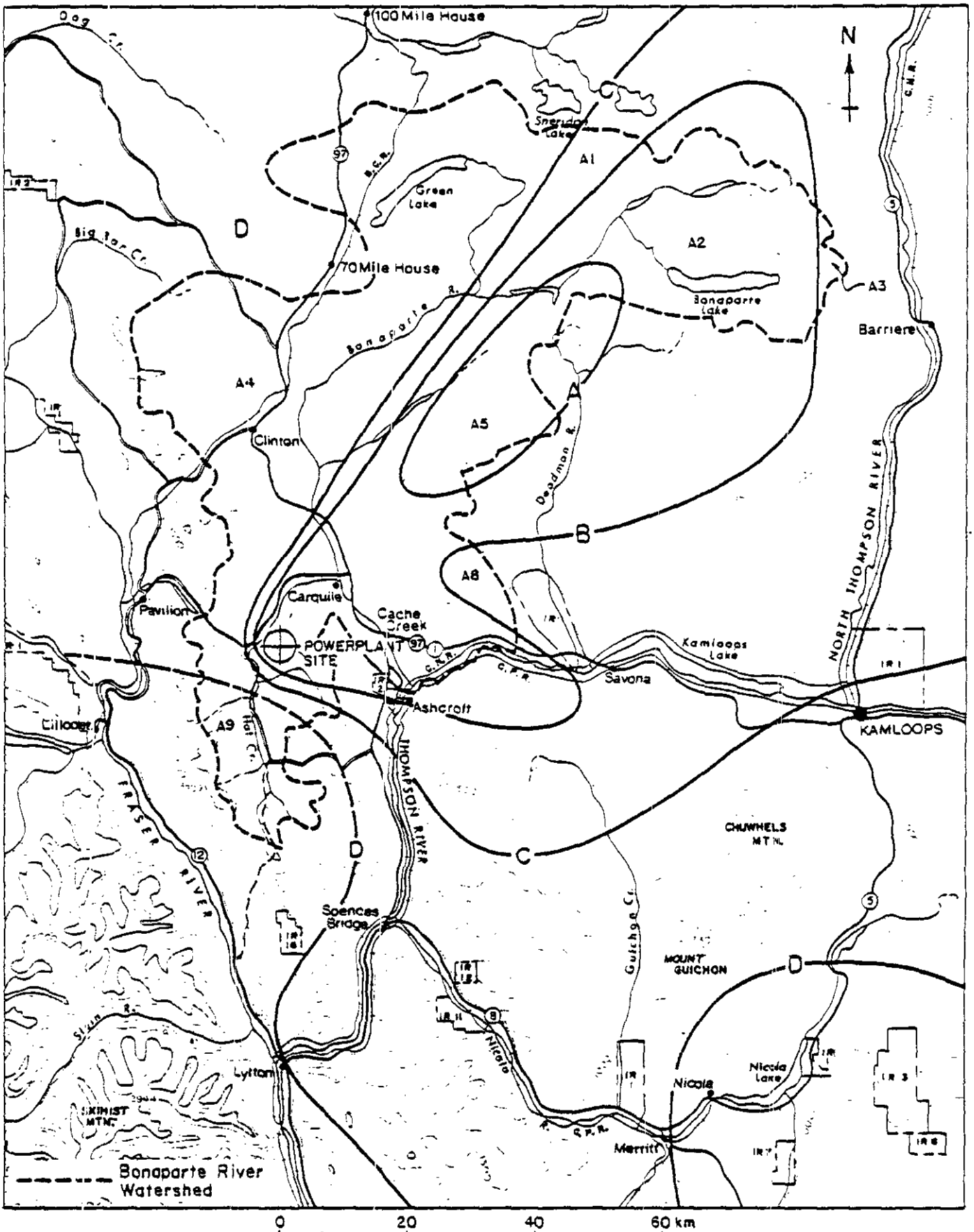

Figure 3-2 Coded Isopleths of Annual Average Trace Element Deposition Patterns resulting from Power Plant Emissions

TABLE 3-6

ANNUAL-AVERAGE TRACE ELEMENT DEPOSITION RATES IN $\mu g/m^2/a$ FOR CODED ISOPLETHS[1] RESULTING FROM POWERPLANT EMISSIONS

Element	Symbol	Coded Isopleth A	B	C	D
Antimony	Sb	0.58	0.44	0.29	0.15
Arsenic	As	70	52	35	17
Beryllium	Be	1.2	0.93	0.62	0.31
Boron	B	101	76	50	25
Cadmium	Cd	0.74	0.55	0.37	0.18
Chromium	Cr	13	9.9	6.6	3.3
Cobalt	Co	2.1	1.5	1.0	0.51
Copper	Cu	89	67	45	22
Fluorine	F	8800	6700	4500	2200
Lead	Pb	21	16	11	5.3
Manganese	Mn	280	210	140	69
Mercury	Hg	16	12	7.8	3.9
Molybdenum	Mo	14	10	6.8	3.4
Nickel	Ni	28	21	14	7.1
Selenium	Se	24	18	12	5.9
Silver	Ag	0.078	0.058	0.039	0.019
Thallium	Tl	0.078	0.058	0.039	0.019
Thorium	Th	0.70	0.52	0.35	0.17
Tin	Sn	0.5	0.38	0.25	0.13
Tungsten	W	0.12	0.087	0.058	0.029
Uranium	U	2.8	2.1	1.4	0.71
Vanadium	V	39	29	19	9.7
Zinc	Zn	62	47	31	16

1 See Fig. 3-2.

3.2 MINE - (Cont'd)

scientists. In order to develop trace element concentrations and deposition rates from these estimates it is necessary to assume that trace element concentrations in the particulate emissions are the same as those in the coal. This may not be the case since much of the dust is generated by exposed rock and soil areas as well as the handling of materials other than coal. However, a considerable amount will be coal dust, and thus the assumption has been adopted.

(a) Concentrations

Concentrations of trace elements in the ambient air at ground level around the mine resulting from mine dust are calculated by multiplying the ambient air particulate concentration by the fraction of each trace element in the coal. Concentrations of total suspended particulates will be maintained within 60 $\mu g/m^3$ on an annual average basis and 150 $\mu g/m^3$ on a maximum 24-hour basis by a dust control program. These values have been used in the calculation of trace element concentrations which follows. Table 3-7 shows annual-average concentrations and maximum 24-hour concentrations for trace elements.

(b) Deposition

Deposition of mine dust has been presented for annual average rates only. These results are calculated by multiplying the ambient concentration of 60 $\mu g/m^3$ by an assumed deposition velocity of 1.0 cm/s and then multiplying by the trace element content of the coal. The results of this calculation are presented in Table 3-8.

It is important to realize that trace elements in mine dust are still bonded in their original state. Unlike the trace elements from the powerplant, they have not undergone the processes of combustion. It is necessary for the mine dust related trace elements to be leached from the material they are bonded to in order to be released to the environment.

TABLE 3-7

AMBIENT TRACE ELEMENT CONCENTRATIONS RESULTING
FROM MINE DUST EMISSIONS IN $\mu g/m^3$

Element	Symbol	Maximum 24-hour	Highest Annual Average[1]
Antimony	Sb	0.000057	0.000023
Arsenic	As	0.0010	0.00041
Beryllium	Be	0.000080	0.000032
Boron	B	0.0019	0.00078
Cadmium	Cd	0.000034	0.000014
Chromium	Cr	0.0084	0.0034
Cobalt	Co	0.00066	0.00026
Copper	Cu	0.0043	0.0017
Fluorine	F	0.014	0.0055
Lead	Pb	0.00068	0.00027
Manganese	Mn	0.024	0.0097
Mercury	Hg	0.000015	0.0000059
Molybdenum	Mo	0.00026	0.000010
Nickel	Ni	0.0027	0.0011
Selenium	Se	0.000091	0.000036
Silver	Ag	0.000046	0.000018
Thallium	Tl	0.000057	0.000023
Thorium	Th	0.00060	0.00024
Tin	Sn	0.000095	0.000038
Tungstan	W	0.00011	0.000046
Uranium	U	0.00027	0.00011
Vanadium	V	0.013	0.005
Zinc	Zn	0.004	0.0016

[1] Annual averages are arithmetic averages.

TABLE 3-8

ANNUAL-AVERAGE DEPOSITION RATES FOR TRACE ELEMENTS RESULTING FROM MINE DUST IN $\mu g/m^2/a$

Element	Symbol	Highest Deposition Rate
Antimony	Sb	7.3
Arsenic	As	129
Beryllium	Be	10.1
Boron	B	246
Cadmium	Cd	4.4
Chromium	Cr	1072
Cobalt	Co	82
Copper	Cu	536
Fluorine	F	1734
Lead	Pb	85
Manganese	Mn	3059
Mercury	Hg	1.9
Molybdenum	Mo	3.2
Nickel	Ni	347
Selenium	Se	11
Silver	Ag	5.7
Thallium	Tl	7.3
Thorium	Th	76
Tin	Sn	12
Tungsten	W	15
Uranium	U	35
Vanadium	V	1577
Zinc	Zn	505

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SECTION 4.0 - ENVIRONMENTAL IMPACT OF TRACE ELEMENTS

4.1 TRACE ELEMENTS OF CONCERN

(a) Introduction

Coal contains at least some of every element in the periodic table and hence is similar in geochemical characteristics to the earth's crust (Ruch et al., 1973). During the combustion of coal the chemistry of the numerous trace elements varies widely and, in turn, reflects upon both the amounts emitted and the chemical species of the element. When coal is combusted, all elements are either volatile or non-volatile with some showing intermediate characteristics. (Ray and Parker, 1978; Curtis, 1977; Lim 1979). Basically, there are four types of behaviour exhibited by the elements:

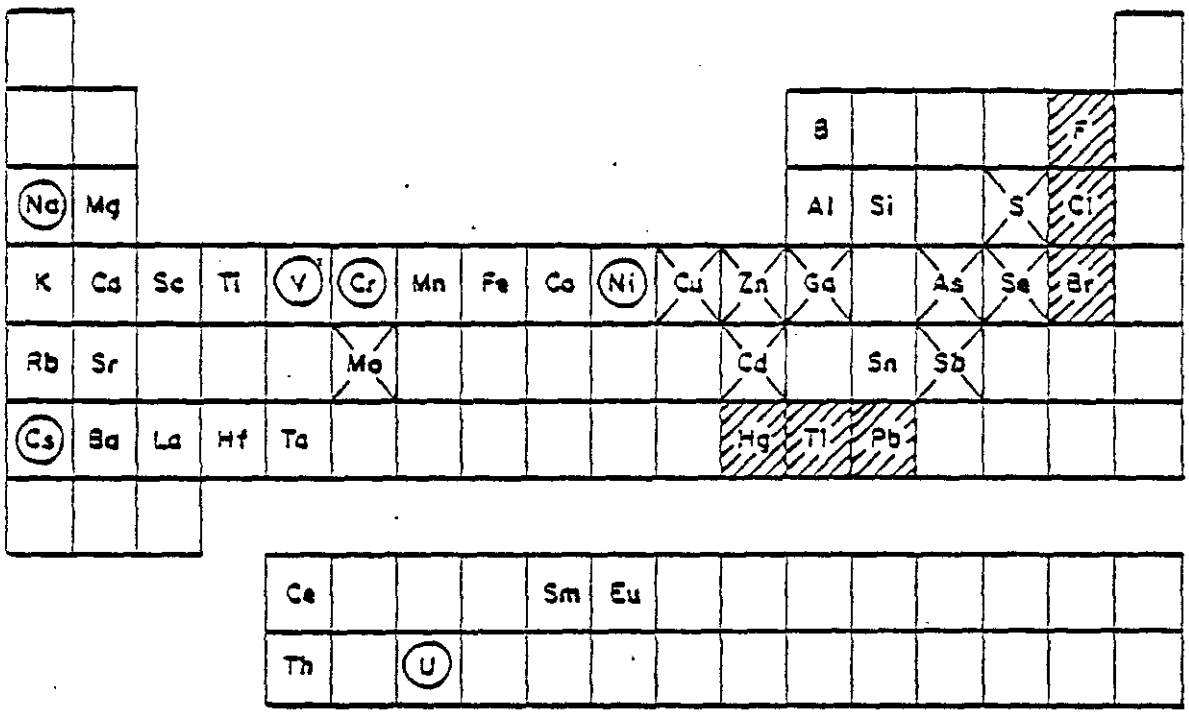
1. Group 1 - equal distribution in the ash and slag.

2. Group 2 - preferential concentration on smaller particles and relative depletion in bottom ash.

3. Group 3 - volatilized and emitted in the vapour phase.

4. Group 4 - behavioural characteristics between Groups 1 and 2. Fig. 4-1 summarizes the behaviour of some of the trace elements and shows their position in the Periodic Table.

Many trace elements pose a degree of potential hazard to the environment. The amounts and forms of these elements that are emitted from coal-fired powerplants are largely unknown and likely vary between facilities (Van Hook and Shultz, 1976). Information on these physical and chemical characteristics of materials released to the environment is a prerequisite to the study of



Group 1: Equal distribution in fly ash and slag

Group 2: Preferential concentration on smaller particulates

Group 3: Volatilized and emitted in the vapour phase

Group 4: Elements which show partitioning behaviour intermediate between Group 2 and Group 3

Figure 1: Characteristics of various elements from coal combustion and their position in the Periodic Table (taken from Lim, 1979 and Ray and Parker, 1978).

their movement in the biota (Torrey, 1978). Hence it is necessary to estimate the transport and transformation mechanisms of these elements as they are emitted from the powerplant to the receptor.

A more thorough understanding of the environmental fate of trace elements is necessary for the total assessment of associated pollution problems. The less volatile trace elements are largely concentrated in the slag and bottom ash while some condense on fly ash and are removed by electrostatic precipitation. These fractions have been previously described (Section 3.0). As they may not enter the atmosphere to any large degree they are associated with ash pond or other disposal areas. They may subsequently undergo transformations which allow them to enter biological systems. Airborne trace elements may enter the ecosystem by direct fallout and precipitation scavenging. The amounts entering the environment are a function of the variability in trace element concentrations of coals and the efficiency of flyash removal systems (Jones, 1978), as well as the conditions of combustion and the type of fly ash removal system.

Emitted trace elements from the coal-fired powerplant will ultimately return to the soil or sediment systems from where they originally came. The rates of entry of these elements into the environment and their transfer through various trophic levels are influenced by complex interactions of chemical, physical and biological factors (Crawford, 1978).

Not all trace elements pose potential environmental hazards in view of the fact that various organisms display tolerance or a metabolic need for some elements. The selection of various trace elements for detailed assessment as they relate to the Hat Creek Project depends on the elements' demonstrated toxicity and their ability to move and bioaccumulate throughout the various trophic levels of both the aquatic and terrestrial

biota. Ultimately, an assessment of trace element impacts to the Hat Creek biota were made on the basis of project trace element quantities arising from stack emissions and the leaching of overburden and waste dumps as well as coal stockpiles.

The remaining sections have been organized to address the following:

1. Selection of the trace elements that are to be addressed as they relate to the Hat Creek Project.

2. To prepare a critical review of trace element impacts specifically, to the aquatic and terrestrial environments arising from the burning of coal.

3. To assess the impacts of projected trace element emissions from the Hat Creek Project in relation to the natural environment at Hat Creek and pertinent information available from the literature.

(b) Trace Elements of Interest

The terminology "Trace Elements" originated from the fact that many stable elements occur in the environment and living organisms in such small quantities that determination of their precise concentrations was very difficult with the analytical methods formerly available (Clements, 1976). Most of the trace elements, however, that are present in biological and environmental materials can now be measured accurately and reliably to a degree with much lower detection levels than before (Clements, 1976; La Gayt, 1979). The adjective "trace" nevertheless, continues to be used in the description of these elements.

4.1 TRACE ELEMENTS OF CONCERN - (Cont'd)

According to Thrush (1968) most inorganic elements are referred to as trace elements with the exception of the eight abundant rock-forming elements: oxygen, silicon, aluminum, iron, calcium, sodium, potassium and magnesium. These elements, in addition to chlorine and titanium are major components of common rocks and soils (Hall et al., 1974). Their systematic toxicity to animals and humans, however has not been demonstrated or is unknown (Friberg, 1977). Hydrogen, phosphorus, sulphur and nitrogen have also been considered major elements of the earth's crust (Heinrichs and Mayer, 1977).

On the basis of elemental concentration in biological materials no clear division can be drawn between the trace elements and those classified as "major" (Clemente, 1976). Those elements that occur at micrograms/gram (µg/g) or micrograms/litre (µg/L) quantities in biological material are, in practice however, referred to as trace elements.

The occurrence and distribution of trace elements in the environment have been receiving increased attention in recent years due to the potential toxicity of many of these elements (Heinrichs and Mayer, 1977). Increases in coal combustion for the production of electricity have led to concern over the possibly hazardous effects of an attendant release of trace elements to the environment. It has been suggested that environmental mobilization of certain trace elements resulting from coal combustion may be approaching or even exceeding that due to natural causes (Bertine and Goldberg, 1971; Andren et al., 1975; Klein and Andren, 1975).

The potential toxicity of the trace elements in coal varies. The constant adaptation of organisms to their environments makes it impossible to easily or absolutely describe the

toxicity of given trace elements. Clemente (1976) generally agrees with this statement and claims that the classification of trace elements into different groups according to their toxicity is inaccurate and misleading. Even essential elements can be considered toxic at sufficiently high intake and the margin between levels that are beneficial, and those that are harmful may be very small. Nevertheless, some empirical catagorization of trace element toxicities is possible as demonstrated in Section 1.0. This approach is useful when addressing the relative toxicities of trace elements to organisms.

Ostensibly, at the present time there are 13 trace elements which are believed to be essential to human and animal life: copper, iron, iodine, zinc, manganese, cobalt, molybdenum, selenium, chromium, nickel, tin, fluorine and vanadium (World Health Organization, 1973; Underwood, 1975). The roles of these elements are summarized in Table 4-1. Boron is also an essential trace element being required by plants at low concentrations (Schwarz, 1974). According to Schwarz (1972) the other trace elements which can normally be found in biological materials can be classified into two other groups:

1. Likely to be essential or under special consideration.

2. Very unlikely to be essential.

Consequently, through elimination, the majority of trace elements are assumed to belong to the second category and are, therefore, not considered to be essential to human, animal or plant life. The trace elements found in coal have been segregated into various catagories on the basis of the above information in Table 4-2. Many of the trace elements listed in this table have been shown to be toxic to organisms.

TABLE 4-1

TRACE ELEMENTS ESSENTIAL TO ANIMALS[1]

Trace Element	Known Function
Chromium	Involved in lipid, protein, and glucose metabolism.
Cobalt	A component of Vitamin B_{12}.
Copper	A component of cytochrome oxidase and other enzymes.
Fluorine	Reduces incidence of dental caries and partially prevents osteoporosis.
Iodine	A component of thyroxine and triiodothyronine, hormones of the thyroid gland.
Iron	A component of cytochromes, succinate dehydrogenase, and catalase; functions in electron transfer, aerobic oxidation of carbohydrates, and protection against H_2O_2.
Manganese	A component of enzymes involved in urea formation and pyruvate metabolism.
Molybdenum	A component of enzymes involved in purine metabolism and sulfite oxidation.
Nickel	Precise role unknown.
Selenium	A component of glutathione peroxidase; protects against hemoglobin oxidation.
Silicon	Initiates mineralization process in bone, and may function as a biological cross-linking agent in connective tissue.
Tin	Precise role unknown.
Vanadium	Precise role unknown.
Zinc	A component of carbonic anhydrase and other enzymes; functions in CO_2 formation, regulation of acidity, protein metabolism, alcohol metabolism, and superoxide dismutation.

[1] Compiled from information in Underwood (1975).

TABLE 4-2

CATEGORIZATION AND ESSENTIALITY OF ELEMENTS FOUND IN COAL TO BIOLOGICAL MATERIALS

MAJOR		TRACE					
		Essential to Living Organisms		Very Unlikely to be Essential to Living Organisms			
aluminum	(Al)	boron	(B)	antimony	(Sb)	mercury	(Hg)
calcium	(Ca)	chromium	(Cr)	arsenic	(As)	plutonium	(Pu)
chlorine	(Cl)	cobalt	(Co)	barium	(Ba)	Polonium	(Po)
hydrogen	(H)	copper	(Cu)	beryllium	(Be)	radium	(Ra)
iron	(Fe)	fluorine	(F)	cerium	(Ce)	rubidium	(Rb)
magnesium	(Mg)	iodine	(I)	cadmium	(Cd)	scandium	(Sc)
nitrogen	(N)	manganese	(Mn)	cesium	(Cs)	samarium	(Sm)
oxygen	(O)	molybdenum	(Mo)	dysprosium	(Dy)	silver	(Ag)
phosphorus	(P)	nickal	(Ni)	europium	(En)	strontium	(Sr)
potassium	(K)	selenium	(Se)	gallium	(Ga)	tantalum	(Ta)
silicon	(Si)	tin	(Sn)	germanium	(Ge)	thallium	(Tl)
sodium	(Na)	vanadium	(V)	gold	(Au)	terbium	(Tb)
sulphur	(S)	zinc	(Zn)	hafnium	(Hf)	thorium	(Th)
titanium	(Ti)			indium	(In)	uranium	(U)
				lanthanum	(La)	tungsten	(W)
				lutetium	(Lu)	yttarbium	(Yb)
				lead	(Pb)	zirconium	(Zr)

4.1 TRACE ELEMENTS OF CONCERN - (Cont'd)

The manifestation of trace element effects in the biota can be assumed to be a function of tolerance. Tolerance of individual species may be related to the adjustive capacity of the organism as well as the fact that many trace elements are essential at low concentrations which may facilitate their metabolism and excretion (Schwarz, 1972, 1974; Prosser, 1973). As the essential trace elements have a natural affinity for biological materials, they must be considered as obvious inclusions into the discussion of which trace elements are important when considering the impacts of trace element emissions from the Hat Creek Project.

Clearly, the selection of specific trace elements which may be of concern at Hat Creek is a complex and difficult task. Many factors must be considered including a trace element's inherent toxicity and essentiality to biological materials as well as their redistribution from the burning of Hat Creek coal. This task was first addressed by Environmental Research and Technology (ERT). Environmental Research and Technology, Appendix F (1978) developed a rationale for selection of trace elements to be analyzed in Hat Creek receptors (environmental samples). Initially, receptor samples from the Hat Creek area were examined to include all of the elements analyzed by the methodologies of spark source mass spectroscopy and plasma emission spectroscopy. In all, concentrations for more than 60 elements were obtained. This list was shortened by ERT (1978, Appendix F) to 21 elements that were selected for detailed environmental review. Removed from the original list were elements normally found in relatively high concentrations in biotic materials that are comparatively non-toxic and those elements in minute to non-detectable quantities. This rationale appears reasonable, however it should be noted that many elements, although quite low in biotic samples, may be significantly increased in the ecosystem due to powerplant emissions and depositions (Crawford, 1978).

4.1 TRACE ELEMENTS OF CONCERN - (Cont'd)

The 21 elements chosen by ERT also have the following characteristics in common

1. relatively high concentrations in Hat Creek coal or ash,

2. volatilized during coal combustion,

3. potentially most toxic to Hat Creek receptors,

4. present in relatively high concentrations in Hat Creek sources or receptor materials as compared with values reported by others in similar ecosystem materials or

5. regulated by governmental agencies.

Table 4-3 shows the 21 trace elements selected for study by ERT and the parameters used to assess their importance. This list of 21 elements was reduced to nine elements of most environmental concern. Generally, if an element had checks in at least three of the five categories listed in Table 4-1, the element was selected as being of environmental concern. Using ERT's selection criteria nine elements including arsenic, cadmium, chromium, copper, fluorine, lead, mercury, vanadium and zinc were selected as being of most environmental concern.

The logic of ERT's (Appendix F, 1978) selection process would appear to be adequate in choosing certain trace elements for detailed environmental review. All of ERT's criteria have some merit although the third criterion might be subject to comment primarily because emitted trace elements would have to be deposited largely within the vicinity of Hat Creek. The nature of stack emissions from a coal-fired powerplant would be limiting to these depositions as such emissions are known to be carried many kilometres from the plant site (Dvorak and Lewis et al., 1978; Heit, 1978; Wangen and Williams, 1978).

TABLE 4-3

CHARACTERISTICS OF TRACE ELEMENTS SELECTED FOR DETAILED ENVIRONMENTAL REVIEW BY ERT

Element	Symbol	High Concentration in Coal or Ash	Volatilized During Combustion	High Potential Toxicity	High Concentration in Receptors	Regulated Guideline[1]
Antimony	Sb	X			X	
Arsenic	As	X	X	X	X	X
Beryllium	Be			X		X
Boron	B	X			X	
Cadmium	Cd			X	X	X
Chromium	Cr	X			X	X
Cobalt	Co	X			X	
Copper	Cu	X		X	X	
Fluorine	F	X	X	X	X	X
Gallium	Ga	X				
Lead	Pb	X		X		X
Lithium	Li	X			X	
Mercury	Hg		X	X	X	X
Nickel	Ni				X	X
Selenium	Se		X		X	X
Strontium	Sr	X		X		
Thallium	Tl			X		
Tin	Sn	X			X	
Vanadium	V	X		X	X	X
Zinc	Zn	X			X	X
Zirconium	Zr	X			X	

[1] Taken from Environmental Research and Technology, 1978, Air Quality and Climatic Effects of the Proposed Hat Creek Project, Appendix F.

4.1 TRACE ELEMENTS OF CONCERN - (Cont'd)

ERT's fifth criterion is a logical inclusion as regulation by a government agency for a specific trace element implies that sufficient reasons have been identified to distinguish the element as one of environmental concern and one that should be addressed. On the other hand, the large number of trace elements has precluded governmental screening for all of them and the fact that no guidelines exist for many elements should not be taken that they pose no potential threat to the environment. Consequently, the selection process employed herein has considered most elements regardless of the status of governmental jurisdiction.

Hat Creek coal contains a similar spectrum of trace elements to other coals (McCullough, 1978; Section 2.0). Many of the trace elements are of insufficient toxicity to pose any potential threat to the Hat Creek environment. Of major concern are those trace elements that are volatilized during coal combustion and are preferentially absorbed or condensed onto the small fly ash particles. These trace elements subsequently enter the environment and are dispersed in gaseous and fine particulate form both locally and regionally. In fact the anthropogenic contribution of trace elements to the environment from the combustion of coal is significant for many trace elements (Allaway, 1968; Bertine and Goldberg, 1971; Klein and Andren, 1975; Klein et al., 1975; Newkirk, 1976). Heit (1978) has reported that some volatilization studies indicate a preferential release of arsenic, cadmium, mercury, lead and thallium to the environment out the stack of coal-fired powerplants.

Other mass balance and particulate studies have shown that many of the elements as expected are predominantly concentrated in the ash (Ag, Al, Ba, Be, Ca, Ce, Cr, Co, Cu, Dy, Eu, Fe, Ge, Hf, K, La, Lu, Mg, Mn, Na, Ni, Rb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, U, V, W) while a few are released into the environment as particulates or gases in varying degrees (Au, As, B, Cd, Ga,

Hg, Mo, Ni, Pb, Sb, Se, Te, Tl, V, Zn) (Ruch et al., 1973; Davidson et al., 1974; Klein et al., 1975; Radian Corporation, 1975; Lindberg et al., 1975; Curtis, 1977; Meserole et al., 1979). Some discrepancies exist among different investigators on the partitioning of trace elements in the slag, fly ash and gaseous phases. The above discussion, however, does provide a general overview of the situation in spite of these differences.

The trace element content and species in vapours and particulate matter produced by the combustion of fossil fuels is largely unknown (Bolton et al., 1975; Lee et al., 1975; Heit, 1978). It is known, however, that mercury, selenium and arsenic are emitted as gases in significant quantities. The metals As, Tl, Cd, Se, Pb and Sb are enriched in fly ash particles of respirable size. These elements are concentrated on the surface of the fly ash due to their vaporization and recondensation on the particle surface (Natusch and Wallace, 1974; Davidson et al., 1974). Although many trace elements are largely collected in the boiler bottom ash and fly ash, they must be considered in the ultimate selection for study as certain quantities will be released to the environment.

Newkirk's (1976) estimation of trace element amounts released into the global environment in 1970 is reproduced in Table 4-4 to provide an appreciation for the significance of trace element emissions. Even though the trace elements are present in very small quantities in coal, Newkirk's (1976) data show that the large amount of coal burned each year can result in significant emissions of trace elements.

Answering the question as to which trace elements found in coal and their subsequent emissions are significant to the general well-being of the environment is difficult in view of the large number of elements contained in coal (Table 4-2). As pointed out earlier, not all of the trace elements are necessarily

TABLE 4-4

ROUGH ESTIMATE OF AIRBORNE TRACE ELEMENTS
RELEASED FROM COAL-FIRED POWERPLANTS IN 1970[1]

Element	Concen. in Coal Used for Estimate (μg/g)	Stack Emission: Total, Coal-Fired Plants, Element Basis (tons/year)	Stack Emission: Per 10^8 Btu in Coal (lb)	Stack Emission: Per m^3 of Flue Gas (STP) (mg)
As	5	800	2.3×10^{-4}	0.2
B	55	1 600	4.4×10^{-4}	0.53
Ba	64	1 900	5×10^{-4}	0.6
Be	2	100	3×10^{-5}	0.04
Co	12	360	10^{-4}	0.12
Cr	20	600	1.6×10^{-4}	0.2
Cu	12	360	10^{-4}	0.12
Ga	5	150	4×10^{-5}	0.05
Ge	8	240	6.4×10^{-5}	0.08
Hg	2	600	1.6×10^{-4}	0.2
Mn	30	900	2.4×10^{-4}	0.3
Mo	6	180	5×10^{-5}	0.06
Ni	20	600	1.6×10^{-4}	0.2
Pb	9	270	7×10^{-5}	0.09
Rb	25	750	2×10^{-4}	0.25
Sc	8	240	6.4×10^{-5}	0.08
Se	3	90	3×10^{-5}	0.03
Sn	2	60	1.6×10^{-5}	0.02
Sr	85	2 500	7×10^{-4}	0.8
Ti	400	12 000	3×10^{-3}	4
V	33	1 000	2.6×10^{-4}	0.33
Zn	40	1 200	3×10^{-4}	0.4
Zr	76	2 300	6×10^{-4}	0.77

[1] Compiled from Heit, 1978.

toxic nor are some of environmental concern since they are not emitted in large quantities from coal-fired powerplants. The logic in selecting the various trace elements should be reflective of the elements' toxicity, essentiality to biological materials and the amounts emitted to the environment.

No distinct causal relationships have been shown to exist between a pathological entity and trace element contamination resulting from the burning of coal (Klein and Russell, 1973; Cannon and Swanson, 1975; Horton and Dorsett, 1976). The potential hazards have been logically deduced from relationships exhibited between mortality and/or reduction in the quality of life processes in organisms during exposures to trace element emissions arising from coal combustion (Piperno, 1975). The major bodies of toxicological data are quite heterogeneous including both the aquatic and terrestrial environments and are largely derived from acute and subacute experimentation (Piperno, 1975). Application of these results to the problems associated with trace element emissions from coal-fired powerplants is, therefore, difficult.

Dose-response relationships for trace elements are not well defined and even less so for those organisms comprising natural ecosystems. Jones (1978) has classified the potential toxicity of some significant trace elements in coal into three broad categories - high potential, medium potential, and low potential for both terrestrial and aquatic organisms. Table 4-5 summarizes the classifications, but Jones points out that the scheme can only be considered a "best estimate" based on the experience, knowledge, and intuition of those judging. The generalizations above have been made despite the fact that trace element impacts on the biota are also a function of the chemical state of the element and its interaction with receptors. Such

TABLE 4-5

POTENTIAL TOXICITY OF TRACE ELEMENTS IN COAL[1]

Element	Terrestrial		Aquatic	Comments
	Plant	Animal		
As	Low	Low	Low	
B	High	Medium	Low[2]	Know enough in toxicity for terrestrial ecosystems, in some instances may be beneficial.
Be	Medium	High	High[2]	Speciation important.
Cd	High	High	High	
Co	High	Medium	High	
Cr	High	Medium	Medium	Cr^{+6} very toxic-need to know speciation.
Cu	High	Medium	High	Complexing in soil reduces toxicity, in some instances may be beneficial.
F	High	High	Low	
Hg	Medium	High[2]	High	Enriched in plants, toxicity in food cycle.
Mn	Low	Low	Low	Potential for net beneficial effects.
Mo	Low	Medium	Low	High enrichment in plants-beneficial or adverse effects.
Ni	High	High	Medium	Very mobile in plants.
Pb	Low	Medium	Medium	
Sb	Medium	High[2]	Low[2]	
Se	Medium	High	Low[2]	Interacts with other trace metals, e.g. Ni, Hg.
Sn	Low	Low	Low	
Ti	High	High	Medium[2]	
V	High	Low[2]	Medium[2]	
W	Medium	Medium[2]	Low[2]	Very mobile in plants.
Zn	Low	Medium	Medium	Potential for net beneficial effect.

1 Modified from Jones (1978).

2 Uncertain.

interactions influence trace element availability and hence the relative amounts that may affect organismic life processes.

The general significance of 12 trace elements arising from emissions due to coal combustion in the terrestrial environment is summarized in Table 4-6. Jones (1978) primarily used the predictive model of Vaughan et al. (1975) to rank the effects of these trace elements. Extrapolations to other coals are difficult since the conditions of runoff, weathering patterns, mineralogy and land-use patterns may differ. The pollution in a given region will, therefore, be a function of both the coal's characteristics and the environment within which the contaminants are deposited.

Of the 13 trace elements essential to animals, twelve are included within Tables 4-5 and 4-6, the notable exception is iodine. Iodine is essential to the function of the thyroid gland and its homologues in animals (Prosser, 1973). The element has a rapid passage through biological systems and concentrates in a small mass of tissue (Garner, 1972). In spite of iodine's ability to enter and accumulate in various trophic levels of the biota it has not been identified as an environmental contaminant in emissions arising from the burning of coal. Consequently, it will be deleted from further discussion. The remaining essential elements can exhibit toxic effects in sufficiently high concentrations. These will be addressed in this report in view of their essentiality, potential toxicity and the fact that they will be in emissions from the combustion of Hat Creek coal.

Bromine belongs to the same group of elements as iodine and fluorine, namely the halogens. It can sometimes be substituted for chlorine, but is not a normal constituent of animals (Prosser, 1973). In certain environments, bromine is much more abundant than iodine yet the latter is used more by animals. The

TABLE 4-6

SIGNIFICANCE OF TRACE ELEMENT EMISSIONS IN TERRESTRIAL ECOSYSTEMS[1]

Rank[2]	Element	Comments
1	Cd	Very high toxicity to both plants and animals
2	Ni	Very mobile in plants
3	Tl	Very mobile in plants
4	Cu	Can be very toxic but formation of complexes reduces toxicity
5	F	Gaseous forms highly toxic to plants, accumulative toxicity in plants and animals
6	V	High enrichment factor
7	Zn	Effects probably positive
8	Co	Reasonably high enrichment factor
9	Mo	High enrichment factor, positive effects for plants or negative for animals, depending on region
10	W	Very mobile in plants
11	Hg	High enrichment factor, toxicity in food chain
12	Se[3]	Interacts with Ni, Hg, etc.

1 Compiled from Jones (1978).

2 Ranked in descending order of biological impact and need for research, and based on consideration of toxicity, atmospheric deposition, availability, and uptake.

3 Se - Not sure where to rank, but needs to be considered in terms of interactions.

element is relatively non toxic and will not be considered a contaminant in Hat Creek coal-combustion emissions in view of its relative innocuous nature to plants and animals.

According to Heit's (1978) literature review, the trace elements released from coal which are of greatest environmental concern in at least one of their chemical forms are: arsenic, beryllium, cadmium, copper, chromium, fluorine, lead, mercury, nickel, selenium, silver, thallium, tin and zinc. Heit's sources considered the information available on these elements' toxicity to humans, released amounts, and ecological effects.

Consideration of the data presented in Heit's (1978) report and Tables 4-5 and 4-6, reveals there are 21 trace elements that have been identified as being of environmental concern due to redistribution from burning coal. These elements are represented by those listed in Table 4-5 (Jones, 1978). Comparison with Table 4-2 shows that there are many trace elements remaining whose potential impacts to the environment are not well understood with respect to distribution arising from the combustion of coal.

Generally, these remaining elements have not been considered threats to the environment although the natural radionuclides uranium-235 (U-235) and thorium-238 (Th-238) along with their daughter products have elicited some concern (Wilson and Jones, 1974; McBride et al., 1977; Lim, 1979; Christiansen, 1979). The majority of radionuclides in coal consist of U-238, Th-232, Ra-226, Po-210 and Pb-210 (Zimmermeyer, 1978; Dvorak and Lewis et al., 1978).

Thorium and uranium are the parent products that decay into various daughter products. The daughters can be assumed to be in secular equilibrium with the parent. In secular equilibrium the activity of the daughters is roughly equal to that of the

parent. In many instances, however, uranium and/or thorium can be out of equilibrium with their daughters due to the different chemical properties between the elements that affect their geochemical partitioning (Peyton, 1977).

The potential environmental impact of these elements is usually addressed on the basis of their radiotoxicity rather than their chemical toxicity (Welford and Baird, 1967). Uranium, thorium and their daughters are emitted in relatively low quantities from coal-fired powerplants although water percolation through ash disposal areas leaches out quantities of these elements (Peyton, 1977). The concentrations of these radionuclides entering the environment from coal-fired powerplants have not been reported to be hazardous to the biota on the basis of their chemical toxicity. The movements of these radionuclides through the environment, however, depend on their chemical forms and the characteristics of the receiving ecosystem (Dvorak and Lewis et al., 1978). Accumulation of radioactivity in biological receptors is therefore, dependent on the elements' chemistry and the receptors' physiology. Consequently, the chemical nature and occurrence of, at least, the parent elements (uranium and thorium) should be considered in the assessment of trace element impacts to the environment associated with the combustion of coal. These two elements are added to the list (Table 4-5) of trace elements for discussion as being of potential environmental concern from the combustion of coal.

For the remaining elements: Au, Ba, Cs, Dy, Eu, Ga, Ge, Hf, In, La, Lu, Pu, Ru, Rb, Sc, Sm, Sr, Ta, Tb, and Yb no data was uncovered to indicate any were of concern with respect to environmental contamination as a result of burning coal for electricity. There were, however, many litarature references to the toxicity for many of these elements under controlled laboratory conditions.

These studies, although providing valuable toxicity information, are not pertinent to the effects of these elements in the biota within the context of coal-fired powerplants. At any rate, the environmental redistribution from coal combustion for most of these elements is undoubtedly limited as they are reported to remain in the collectible ash of combusted coal, thus minimizing their attendant stack emissions (Curtis, 1977). The general dearth of information in the literature for these elements is the rationale which has precluded their inclusion with the trace elements which are recognized as being of potential hazard to the environment associated with coal-fired powerplants.

From the above discussion the following trace elements have been identified as warranting concern in regards to contamination of the Hat Creek environment from the proposed project:

Ag	Mo
As	Ni
B	Pb
Be	Sb
Cd	Se
Co	Sn
Cr	Th
Cu	Tl
F	U
Hg	V
Mn	W
	Zn

The general impacts of these trace elements to the biota, namely the elements' movement and/or accumulation in both abiotic (soil, sediment and water) as well as biotic receptors (animal and plants), are elaborated upon in Appendix C.

4.2 TOXICITY OF TRACE ELEMENTS

The combustion of coal in conventional powerplants produces particulates in the size range of 0.01 to 100 μm. Electrostatic precipitators will remove up to 99 percent or more of the particulate matter. Larger particles are more efficiently removed (Lee et al., 1975).

Particulate matter released from the stacks of coal-fired powerplants can potentially affect vegetation and wildlife. Particulate matter from an industrial source has been shown to prevent stomatal pore closure which interferes with plant respiration (Richs and Williams, 1974). The authors also postulated that the build-up of particulates on leaf surfaces could affect the photosynthetic capacity of the plant.

The particulate emissions may affect terrestrial vertebrates by direct inhalation or through ingestion of contaminated vegetation (Dvorak and Lewis et al., 1978). Of concern are the smallest particulates (≤1 μm) that can bypass respiratory filters and can be deposited deep into the pulmonary regions of the lung (Natusch et al., 1974; Davidson et al., 1974; Fennelly, 1975).

The chemical composition of inhaled particulates determines their toxicity (Dvorak and Lewis et al., 1978). Certain potentially toxic trace elements present in coal are preferentially concentrated on the smaller particulates (Natusch et al., 1974; Davidson and Lewis et al., 1975). Linton et al., (1976) have indicated that, in the smaller particulates, a greater fraction of the trace element's surface area is more readily available for interaction than in the larger particulates.

Trace elements absorbed to particulates emitted from coal-fired powerplants reach the soil by direct deposition, the washing of plant or other particulate-intercepting surfaces and the decomposition of plant litter. These elements may be retained in the surface or

leached to lower soil horizons perhaps reaching groundwater and affecting aquatic systems. Weathering of trace elements by wind and water erosion will also occur. The ultimate toxicity of trace elements to plants remaining in the rooting zone is dependent on a number of complex factors including the physico-chemical properties of the trace elements, the soil, plant roots, biological characteristics of the soil and climatic factors such as temperature and precipitation (Vaughan et al., 1975; Dvorak and Lewis et al., 1978).

The cation exchange capacity (CEC) of the soil (sum total of the exchangeable cations that a soil can absorb) controls the availability of trace elements. Generally the heavier clay soils have higher CEC's than light, sandy soils low in organic matter. Cations will, therefore, be less available in the former soil type and are bound more tightly in neutral or slightly alkaline soils while in acidic soils they are more available due to increased solubility (Brady, 1974). According to Lagerwerff (1972) soil pH affects the oxidation-reduction conditions of the soil so that in acidic soils the more mobile, lower valency trace elements predominate over the less mobile higher valency forms. Soils with a pH $\geq$6.5, therefore, have less potential cation toxicity problems.

Precipitation of other ions, organic matter reactions, soil drainage, soil microbiota and plant roots also affect the behaviour of trace elements in soils. Generally a significant amount of trace element deposition, especially the cationic forms, is retained in the surface soil layers and is not readily leached to lower horizons except in very acid or sandy soils (Little and Martin, 1972).

The impact of soil-deposited trace elements is also dependent, to a certain degree, on endogenous levels. For example, trace elements added to soils as a result of coal combustion are likely to have a greater impact to terrestrial systems if the facility is located

in an area where endogenous soil concantrations are higher than average.

Trace elements emitted as vapours may directly affect the above-ground portions of plants. It is not fully understood whether those elements deposited as particulates on leaf surfaces can enter the cuticle and be subsequently translocated (Zindahl and Arvik, 1973). These deposited trace elements may, however, be washed off plant surfaces by precipitation thereby entering the soil.

The uptake and accumulation of trace elements by plants also depends on soil fertility and the nutritive status of the plants. Phosphate, an essential nutrient for example, has been shown to affect trace element uptake (Miller and Koeppe, 1971). In neutral or alkaline soils plants with shallow, spreading root systems may be exposed to more trace elements than plants with deeper roots as trace elements are retained in the upper soil horizon. Species specific profiles of trace element uptake and accumulation can also be identified.

The impacts of trace elements on plants is also determined by the species' tolerance to various elements (Bradshaw, 1975). Some plants can accumulate large quantities of particular trace elements without any apparent toxicity. These species are generally termed accumulator or indicator species (Dvorak et al., 1978). Tolerance may be related to exclusion of the trace element from metabolic sites within the plant.

The general toxic mechanism of trace elements on plants is perturbance of some metabolic function (namely photosythesis and respiration) often manifested by growth reduction and visual symptoms of chlorosis, necrosis and discolorations.

4.2 TOXICITY OF TRACE ELEMENTS - (Cont'd)

The presence of trace elements in edible plant parts is significant for the passage of these elements to herbivorous wildlife and other grazing animals. The extent that certain trace elements are translocated within the plant is dependent on many complex interacting factors as previously discussed.

Vegetative community type also affects trace element impacts. The constant cropping of high value crops, for example, slowly removes trace elements from the soils on which they are grown (Kubota and Allaway, 1972). Accumulated trace elements in forage crops can be passed on to man via livestock. A portion of these will obviously be returned to the soils through defecation. In natural areas where a lower percentage of the vegetation is consumed a more rapid accumulation of trace elements with time may occur.

Trace elements emitted from a coal-fired powerplant may enter animals (wildlife and livestock) in three ways

1. vapor and particulates can be inhaled,

2. deposited on the soil and vegetation and

3. seepage from ash disposal and mine sites can introduce trace elements into ground and surface waters.

Dvorak and Lewis et al. (1978) state that the effects of trace elements on wildlife i.e.

1. inhalation and

2. ingestion

are difficult to determine due to a general lack of information.

4.2 TOXICITY OF TRACE ELEMENTS - (Cont'd)

Much information has been gathered through laboratory studies with domestic animals which may not reflect the situation in the natural environment.

Drinking water may be contaminated by leachates from ash disposal and coal mining areas as well as particulate emission fallout. Trace elements may be introduced to wildlife through drinking such waters. Assuming wildlife have similar physiological tendencies and tolerances, drinking water standards established for livestock can be applied to wildlife.

Knowledge of the trace element content of forage plants for herbivorous animal diets is required to calculate the trace element commitment from dietary intake. Some appreciation of digestion rates and accumulation of trace elements on vegetation would also be required.

Food habits of the receptor wildlife species should also be appreciated. Wildlife typically display variations in home range sizes. Trace element doses via dietary intake are therefore increased for browse species, with small home ranges within the heaviest zone of trace element deposition and concentration.

Certain species of wildlife inhabit the terrestrial-aquatic interface. Waterfowl and shorebirds for example, will receive trace element doses from both environments.

Trace elements from the combustion of coal can be expected to augment those entering the aquatic environment from natural sources. These sources include: precipitation, runoff, groundwater, the atmosphere and the system's sediments (Dvorak and Lewis et al., 1978). Trace elements released through coal combustion enter aquatic systems either by direct discharge or indirect input from groundwater, terrestrial litter, runoff and atmospheric fallout.

4.2 TOXICITY OF TRACE ELEMENTS - (Cont'd)

The behaviour of trace elements in aquatic systems depends on a number of physical and chemical parameters (Stumm and Morgan, 1970). The elements form associations with water molecules (hydration) or with organic molecules (chelation). Acidity, or pH of the water as well as the oxidation-reduction (redox) potential also influences the activity of trace elements. In aquatic systems the trace element concentration is divided among various inorganic and organic complexes as well as biological materials. The ultimate concentration of these forms is a function of temperature, salinity, solubility, water hardness, chemical speciation, biological activity, and other environmental factors (Kinkade and Endman, 1975).

In sediment systems trace elements, especially heavy metals, are associated with organic compounds or clay particles. The major method of metal transport is through organometallic particulates, the dissolved fraction being a relatively minor contribution (Gibbs, 1973; Trefry and Presley, 1976). Precipitation and adsorption-desorption reactions, in part, determine the ionic forms of trace elements in water (Dvorak et al., 1978).

Microorganisms in aquatic systems affect trace element concentrations. A number of heavy metals are required as essential nutrients and catalysts in biochemical reactions (Karlson, 1970). These organisms are also active in the processing and conversion of trace elements in the aquatic biota. They affect the biogeochemical cycles of some elements and are capable of processing others to methylated compounds (Kuznetsov, 1970; McEntire and Neufeld, 1975; Chau et al., 1976).

Trace element concentrations are also affected by aquatic plants. These plants have the capacity to sequester and accumulate various trace elements (Leland et al., 1978; Eriksson and Mortimer, 1975). Some species of aquatic plants concentrate trace elements far above the background concentration. The ratio of the amount in the

plant to that of the ambient water concentration is referred to as a "concentration factor". These high concentration factors are significant for aquatic plant species that are browsed upon by fish and other aquatic species as well as wildlife such as waterfowl and certain species of ungulates.

Aquatic invertebrates take up trace elements in varying degrees depending upon their metabolism, their feeding behaviour and the chemical form of the elements in the environment. Fluctuations in trace element concentrations in these animals are reflective of changing environmental conditions or alterations in contaminent concentrations (Dvorak and Lewis et al., 1978).

Invertebrates often accumulate trace elements to much greater levels compared with those concentrations in the ambient environment. Concentration factors may range from values of less than 10 to 100 000 times (Vaughan et al., 1975).

Tolerance of individual species also affects the impact of trace elements in the aquatic biota. Many of these organisms have adapted tolerance mechanisms to trace elements. In highly contaminated areas the structure and function of the invertebrate community are altered to the point where the numbers of tolerant species increase while the overall population diversity decreases (Gaufin, 1973). The responses of some aquatic invertebrates can be so specific that they can be used as monitors of trace element contamination (Nehring, 1976).

Fish occupy the top trophic level in the aquatic biota and, in many ways, reflect the conditions of subordinate food-chain levels. Trace elements enter fish through two routes: one, by active or passive absorption through the gills, and secondly, by ingestion. Either route may assume a prominent role but this depends on the chemical form of the trace element in the biota, indigenous fish species, metabolic patterns and forage bases as well as food habits.

4.2 TOXICITY OF TRACE ELEMENTS - (Cont'd)

The chemical form of the trace elements can vary with pH, alkalinity, hardness and temperature which will also affect uptake rates. Temperature can also alter the metabolic rates of fish (Hochachka and Somero, 1973) which will affect the uptake of trace elements. Fluctuations in pH alters the amount of dissolved trace elements in the aquatic environment. When the solution is acidic, many heavy metals and other trace elements are liberated from sediments and related complexes which makes them available for bronchial uptake. Various other factors that affect trace element uptake include dissolved oxygen and carbon dioxide concentrations and the presence of organic ligands as well as other trace elements.

Retention and elimination of trace elements appears to be related to the source of uptake. Losses of some heavy metals in fish were slower when the original source of the element was the food rather than water (Pentreath, 1976; Rvohtula and Miettinen, 1975). Retention of trace elements is influenced by various factors including: age, size, metabolic rate and feeding habits.

Trace elements in the water column can affect fish in two general ways: 1) direct lethal effects when concentrations are high, and 2) indirect sublethal effects when concentrations or exposures are chronic (Sprague, 1973). In the ecological context the overall effects of sublethal exposures to trace elements are more significant. These are the concentrations that are more likely to persist in receiving bodies of water. The potential trace element impacts on the aquatic biota associated with coal combustion powerplants should be assessed individually for each facility. Generalizations of impacts are too difficult to make in view of the many mixed and complex factors contributing to trace element toxicity.

Bioaccumulation and biomagnification of trace elements in the aquatic environment have been observed. A number of factors influence these processes including the physicochemical form of the trace

4.2 TOXICITY OF TRACE ELEMENTS - (Cont'd)

element, the nature of the organisms and their habitat, substrate-sediment associations, and food habits (Dvorak, A.J. and B.G. Lewis et al., 1978). Sediments act as both a sink and a reservoir for trace elements while attendant concentrations in the water column are comparatively lower. Benthic organisms absorb trace elements from the sediments, grazers and lower-order consumers seem to concentrate the elements to the highest degree. The greatest bioaccumulation or concentration factors have been observed in sediment or detrital feeders.

Members of higher tropic levels seem to discriminate as trace element concentrations are usually lower in predators than in their prey. Trace elements will eventually return to the sediments or move downstream unless some factors are accounting for trace element removal from the aquatic system.

The above discussion has been presented to provide an appreciation of the phenomena affecting trace element movements through the aquatic and terrestrial biota after their release from coal combustion. Reference to specific trace elements has not been made but each of the 23 selected elements are reviewed individually in Appendix C (C1-C23).

4.3 ASSESSMENT OF BACKGROUND TRACE ELEMENTS FOR HAT CREEK BIOTA

(a) Introduction

Concern has been expressed that the techniques used for analyses of certain trace elements for Hat Creek receptors may not be adequate to characterize actual levels. Le Geyt (1979) has reviewed the sampling program as well as sample preparation and subsampling techniques for trace elements associated with the Hat Creek project. Although Le Geyt was unable to comment on the method of plasma emission spectroscopy, the semi-quantitative analytical technique of spark source mass spectrometry was addressed. Generally, if one recognizes the constraints of the

latter method, and rejects tin results as well as makes an allowance for the uncertainties associated with the method, the data are reasonable. Le Geyt also points out that spectral analyses for a particular element may be significantly in error. It was also apparent that some discrepancies existed with the analyses for boron, vanadium, zinc, chromium and molybdenum.

Trace element data have been collected for water for 1976, 1977, 1978, 1979 and 1980. The dates of collection are summarized in Table 4-7. Generally, for 1976 the semi-quantitative techniques of spark source mass spectrometry (SSMS) and plasma emission spectroscopy (PES) were used for all elements except for fluorine which was analyzed by specific ion electrode (SIE) and mercury and lead which were quantified by atomic absorption spectrophotometry (AAS). In 1977 analyses on biota were obtained by AAS. In 1977, 1978 and 1979, receptor samples were analyzed exclusively by quantitative techniques including cold vapour ultra violet absorption for mercury, specific ion electrode for fluoride, inductively coupled plasma torch for boron and variations of atomic absorption spectrophotometry for the remainder. Samples from 1980 were collected only for water in Hat Creek and the Bonaparte River and were analysed by AAS (B.C. Ministry of the Environment, 1980; Appendix D).

In order to place the trace element data collected for Hat Creek receptors in their proper perspective the measurements have been assessed with respect to Le Geyt's (1979) report. Each receptor is assessed in the following discussion with an evaluation of the trace element data included.

(b) Water

Water samples were collected by ERT (Appendix F, 1978) in 1976 and 1977 and analyzed for trace elements by Commercial Testing and Engineering Co. Ltd. (CTE) in Golden, Colorado. Some

TABLE 4-7

HAT CREEK RECEPTORS ANALYZED FOR TRACE ELEMENTS

SPECIMEN	YEAR					
	1976	1977		1978	1979	1980
	October	January	May	October	May	-
Aquatic						
Water	X	X	X	-	-	X
Sediment	X	X	X	-	-	-
Fish	X	-	X	-	-	-
Terrestrial						
Soils	X	X	X	X	X	-
Lichens	X	X	X	X	X	-
Grasses	X	-	X	X	X	-
Shrubs	X	-	X	X	X	-
Small Mammals	X	-	X	-	-	-

Year of collections shown - receptor sampling indicated by an X.

additional data were obtained in the hydrology study conducted by Beak Consultants Ltd. (1978) for the same years. The sampling schemes and details of the analytical techniques are summarized in the hydrology study prepared by Beak (1978) and Appendix F of the ERT (1978) report. CTE used the quantitative methods of atomic absorption for mercury and lead and the specific ion electrode for fluoride in the sampling periods. All remaining elements in the 1976 program were analyzed by plasma emission spectroscopy. The January 1977 water samples were analyzed by SSMS while May 1977 samples were analyzed by atomic absorption spectrophotometry. Plasma emission spectroscopy is a semi-quantitative method, Le Geyt (1979) did not evaluate the technique used by ERT (Appendix F, 1978) but presented a discussion of the method's precision and accuracy. The data collected with this method can be considered representative if one keeps in mind the concentrations of the trace elements that can be effectively quantified. Data collected by spark source mass spectrophotometry are representative if one follows the conclusions of Le Geyt's (1979) assessment summarized in the introduction of this section. Trace element concentrations determined by atomic absorption spectrophotometry (AAS) are quantitative and can be considered valid within the limits of precision for the technique.

Assessment of the SSMS technique has revealed that variations exist with the measurements for boron, chromium, molybdenum, tin, vanadium and zinc. Le Geyt (1979) has presented evidence to show that all tin data analyzed by SSMS should be rejected and that the other elements should be critically assessed. The levels of Cr, V and Zn collected in 1977 should be used to represent background water concentrations since they were all analyzed by quantitative methods.

Beak's (1978) data were all analyzed using quantitative techniques. The data are considered to be representative of water borne trace element concentrations. The program included both ground and surface waters, the major water courses of the latter group included Hat Creek, Bonaparte River, and the Thompson River. The data presented by Beak (Hydrology, 1978) have been considered in the impact assessment for trace elements generated from the burning of coal at Hat Creek.

(c) Sediments

Trace element data for sediments have only been analyzed for 1976 and 1977. Details of the sampling program are presented in, ERT's report (Appendix F, 1978). Mercury and lead determinations were made by atomic absorption spectrophotometry, and fluoride by specific ion electrode, both of which are quantitative techniques. The validity of results obtained with these techniques has been addressed by Le Geyt (1979). The data can be considered accurate within the context of Le Geyt's (1979) evaluation. The remaining elements for 1976 were analyzed by spark source mass spectrophotometry. The data are reasonably acceptable if one recognizes the scope of the technique as Le Geyt (1979) has indicated. Sediment samples collected in January and May 1977 were analyzed for trace elements by atomic absorption spectrophotometry which provided a semi-quantitative estimate of trace elements in the sediments.

Trace element data for stream sediments are probably more accurately represented by those shown for January and May 1977 because quantitative techniques were used. The trace element data collected by SSMS in 1976 is suspect because of variations observed in a number of the elemental analyses for vegetation and soils. Comparisons for trace element levels determined by SSMS with those by more quantitative methods showed that boron, molybdenum, chromium, zinc, vanadium and tin yielded variable and

questionable results. If the tin data are incorrect for sediments, as Le Geyt (1979) has indicated they are for soils and vegetation due to contamination, there are no data for this element in fish at Hat Creek. The other trace element data must be critically assessed in view of Le Geyt's (1979) evaluation of the analytical techniques used.

No data are available for B in 1977 as the sampling program was discontinued for the element. Consequently there are no reliable background data for Boron in sediments. Measurements for Cr, V, and Zn were made in 1977 by quantitative methods, these data can, therefore, be used to represent sediment concentrations. Molybdenum data were not collected for stream sediments, hence no background information is available for the element. Absence of Mo data from this receptor is of importance since the element has been identified as being of environmental significance with regards to a coal-fired powerplant.

(d) Fish

Fish samples collected in October 1976 were analyzed by specific ion electrode for fluoride and spark source mass spectrometry for all other elements. Samples obtained in January and May 1977 were again determined by specific ion electrode for F but the remaining elements were analyzed by atomic absorption spectrophotometry.

The reliability, precision and accuracy of these methods have been reviewed by Le Geyt (1979). The techniques, specific ion electrode and atomic absorption spectrophotometry, more accurately represent trace element concentrations for fish in Hat Creek as the methods are quantitative compared with the semi-quantitative technique of spark source mass spectrophotometry. Consequently, the data from January and May 1977 can be considered

relatively reliable and accurate determinations of trace elements in fish.

Analyses for tin in fish were only made in 1976 by SSMS. These data appear to be incorrect as evidence of gross contamination during analysis was apparent (Le Geyt, 1979). Essentially, this means there are no tin data for fish at Hat Creek since samples were not analyzed past 1976. It is not possible, therefore, to characterize background Sn levels in fish which may be important for the development of an adequate monitoring scheme. The variability of the chromium, zinc, boron, vanadium and molybdenum results by SSMS throws some doubt upon the reliability of these analyses for the same period. Evaluation of the reliability for data for 1976 is subject to the criticisms put forward by Le Geyt (1979).

Boron data were not collected in 1977 for fish which essentially results in a lack of background information for this element in fish as the 1976 data are suspect. Analyses for Cr, V and Zn were, fortunately, continued in 1977 by quantitative analytical techniques. These data should be used in reference to background levels in fish.

(d) Soil

Samples of soil were collected by ERT (Appendix F, 1978) in October 1976 and January and May, 1977. B.C. Hydro in its Environmental Studies Programme (1978) collected soil data for October 1978 and May and September 1979.

The analytical techniques employed for the soils collected by ERT (Appendix F, 1978) parallel those for the fish, and similar comments can be made with respect to the reliability, accuracy and precision of the methods. Soil data collected in

1978 and 1979 were analyzed by Chemex Labs employing the following quantitative techniques for the trace elements:

mercury - cold vapour ultra violet absorption;
fluoride - specific ion electrode;
boron - inductively coupled plasma torch;
all remaining elements - variations of atomic absorption spectrophotometry.

Comparison of the data obtained from CTE and Chemex Labs indicates that most of the analyses are comparable, with the exception of those for tin which are many times higher in the CTE results than those presented by Chemex. A similar observation can be made for tin in vegetation, according to Le Geyt (1979) the data are unreliable and represent some contamination during analysis. Recent analyses have shown that Sn levels are within a "normal" range thus verifying that some Sn contamination of the earlier samples have taken place. Variable results were also observed for boron, molybdenum, chromium, zinc and vanadium in 1976. These discrepancies were apparently due to significant interferences for these elements associated with the SSMS technique (Le Geyt, 1979). With the exception of these data, the trace element content of soils at Hat Creek can be most accurately represented by the values reported in B.C. Hydro's Environmental Studies Programme (1978) as analyzed by Chemex Labs. The data obtained from 1976 and 1977 can also be used if one does not include the results for tin and if one keeps in mind the reliability and precision of SSMS used for the 1976 samples.

Boron analyses were not continued past 1976 in the ERT (Appendix F, 1978) program so no reliable data exist for this element in that particular study. The data for Cr, V and Zn collected in 1977 by ERT (Appendix F, 1978) are reasonably valid

as analyses were performed by quantitative techniques and compare favourably to those observed in the B.C. Hydro Environmental Studies programs (1978, 1979).

(e) Vegetation

Samples of vegetation were collected by ERT (Appendix F, 1978) in October, 1976 and January and May 1977 for trace element analyses. An additional series of samples were collected in October 1978 and May and September 1979 by B.C. Hydro as part of their Environmental Studies Program (1978). These samples were analyzed by Chemex Labs.

The analytical techniques used for the vegetation collected by ERT (Appendix F, 1978) and analyzed by CTE in Golden, Colorado are similar to those employed for the fish and soil samples. Briefly, in 1976 fluoride was analyzed by specific ion electrode (SIE), mercury and lead by AAS with the exception of F which was again determined by SIE. The analytical methods employed by Chemex Labs were all quantitative and are summarized in the soils section. The accuracy, precision and reliability of these methods have been previously discussed by Le Geyt (1979) and are briefly referred to in the introduction of this section.

A comparison of the 1976 SSMS data with the quantitative 1978 data (Chemex Labs) revealed a number of discrepancies. Boron and molybdenum generally were lower and higher respectively while tin values were extremely high in the 1976 data and according to Le Geyt (1979) are incorrect and show evidence of gross contamination. Chromium, vanadium and zinc also showed some variation.

The remaining data seem to be in reasonable agreement with the exception of fluoride. The 1978 ERT report (Appendix F) states that F was analyzed by specific ion electrode but Le Geyt (1979) has indicated the samples were analyzed by spark source

mass spectrophotometry (SSMS). Fluoride analyses by SSMS are not reliable although CTE personnel consider the values determined by SSMS to be approximate (Le Geyt, 1979).

The data which can most accurately be used to represent trace element levels in vegetation at Hat Creek are those collected by Chemex Labs in 1978 and 1979. The SSMS and atomic absorption (AA) data collected in October 1976 and January and May 1977 can also be used if one does not include the analyses of boron or tin for 1976.

The data for Cr, V and Zn in the 1977 ERT program were analyzed by quantitative methods and are reasonably representative. Information provided from B.C. Hydro's environmental studies (1978, 1979) most accurately represented trace element concentrations for vegetation.

(f) Small Mammals

Trace element data for small mammals have only been collected in October, 1976 and January and May 1977 by ERT (Appendix F, 1978). The data were analyzed by SIE for fluorine, AAS for mercury and lead and SSMS for the remaining trace elements in 1976. The 1977 samples were all analyzed for trace elements by AAS except for F which was determined by the SIE technique.

Trace element analyses conducted under ERT's program (Appendix F, 1978) have been shown to be in error for tin with variable results reported for boron, molybdenum, chromium, zinc, vanadium as well as fluoride. These discrepancies were largely associated with interferences in the SSMS technique. Review of ERT's (Appendix F, 1978) tin data show that the small mammals at Hat Creek had tin concentrations roughly an order of magnitude higher compared with those reported elsewhere. Assuming the same contamination existed in tin SSMS analyses for small mammals as

for soils and vegetation it is likely these data are unreliable. Data were not collected for the element past 1976, consequently no reliable data for tin exist for small mammals. No information is available for Mo in small mammals as data for the element were never collected.

Analyses for B were not continued past 1976, thus no reliable background information exists for this element in small mammals.

(g) Conclusions

Of the 23 elements selected for discussion in this report (see Section 4.1(b)), reliable background data for Hat Creek receptors are available for only the following 14 elements: antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, fluorine, lead, manganese, mercury, nickel, vanadium and zinc. Certain of these data, however, more accurately represent background levels in Hat Creek receptors depending on the assay technique.

4.4 TRACE ELEMENT SOURCES FROM THE PROJECT

The principal sources of trace elements associated with the coal mine are coal, overburden, waste rock and mine dust. The coal burned in the plant will result in various forms of gaseous and ash emissions. The leachings of disposal areas for slag and precipitated fly ash are also trace element contributors. Also a certain amount of trace elements will enter the local Hat Creek environment as a result of cooling tower drift.

(a) Overburden and Waste Rock

Overburden and waste rock materials will be placed in above ground storage piles or basins where weathering and chemical reactions can dissolve various trace elements. Details of the

overburden dump construction and location have been given in the report prepared by Beak (Volume 3A, 1979).

Overburden and waste rock leachate quality was estimated by Acres Consulting Services (1978). Extraction tests were performed on crushed test materials. Details of the overburden and waste rock sampling program have been previously described (Acres Consulting Services, 1978).

Projected leachate characteristics (Beak, Volume 3A, 1979) are shown in Table 4-8 based on averaging the projections of leachate quality of overburden and waste rock given in Table 6 to 9 Volume 3 of Beak's (1978) report. The volumes of the seepage loss to regional groundwater from the Houth Meadows Dump range from 0.86 m^3/d to 86.0 m^3/d. Roughly 58 percent or 50 m^3/d will enter the Houth Meadows groundwater regime while the remainder will enter the Marble Canyon aquifer. Surface runoff from the dumps of Houth Meadows and Medicine Creek will be directed through sedimentation ponds prior to entering Hat Creek. The quality of the dump runoff depends on the contact time of precipitation but the least estimate would approximate that shown in Table 4-8. Runoff from the Medicine Creek reclaimed dump should be similar to natural Medicine Creek water (Table 4-9).

(b) Coal and Low Grade Waste Stockpiles

Runoff and leachates from these stockpiles will be collected and stored in a leachate storage pond. A coal stockpile at the mine mouth will be about 32 ha (80 acres) of which about 20 ha (70 acres) will be used for coal storage. The low grade waste dump is anticipated to be roughly 128 ha (317 acres) containing 46 x 10^6 t of low grade waste-coal during plant operation. The proposed drainage control for these areas will consist of collection of runoff by ditching and diverting the water to the closest lagoon. A relatively impermeable base will line the low grade waste stockpile to prevent groundwater contamination.

TABLE 4-8

PROJECTED WASTE DUMP LEACHATE CHARACTERISTICS[1] FOR TRACE ELEMENTS

Trace Element	Concentration (mg/L)
Arsenic	0.07
Boron	0.04
Cadmium	< 0.002
Chromium	0.13
Copper	1.5
Fluoride	0.06
Lead	0.02
Mercury	0.0015
Vanadium	0.01
Zinc	0.15

Raw data from Acres Consulting Services Limited leachate tests on overburden and waste rock.

Note: Estimated by Beak from Total Extractable Tests and multiplying by ration of filterable residue extracted in 24 hours to Total Extractable Filterable Residue.

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[1] At low pore volume displacement (see example calculation).

Leachate characteristic in mg/L =

$$\frac{\text{(Extractable component at Day 1 in mg/kg) x (weight of sample in kg)}}{\text{(Volume of extract at Day 1 in litres)}}$$

From Beak (Volume 3A, 1979).

TABLE 4-9

PROJECTED QUALITY OF INTERCEPTED SURFACE WATER
FOR TRACE ELEMENTS[1] MEDICINE CREEK AREA

Trace Element	Value (mg/L)
Arsenic	< 0.005
Boron	< 0.1
Cadmium	< 0.005
Chromium	< 0.01
Copper	< 0.005
Fluoride	0.12
Lead	< 0.01
Mercury	< 0.0005
Vanadium	< 0.005
Zinc	0.009

[1] Based on average of available Medicine Creek water quality data 21/5/77.

From Beak (Volume 3A, 1979).

Estimates of the runoff and leachate water quality for the coal and low grade waste stock piles are shown in Table 4-10. The results are based on actual samples collected from B.C. Hydro's bulk sample program on site stockpiles. These waters will be contained throughout the construction and operation phases of the Hat Creek Project.

Under normal conditions it is likely that runoff and leachates from the coal stockpile would be non-existant as the average short duration rainfall would likely be totally infiltrated into the stockpile and would subsequently evaporate (Beak, Volume 3, 1978). The pile will be designed to handle runoff which will be collected in ditches and directed to the nearest lagoon. Due to the dry climate the low grade waste stockpile will probably be unsaturated and hence not likely produce any continuous leachate seepage. The leachates expected would originate during spring snowmelt runoff and during rainstorms. These waters will, however, be collected and stored in a leachate storage pond and not discharged.

(c) Ash Disposal

Disposed ash will be a mixture of conditioned fly ash and damp bottom ash. It is projected some seepage will come from the dump (Beak, Volume 3A, 1979). Surface runoff from the ash disposal area in mid-Medicine Creek will be contained during the first 15 years by an embankment across the valley below the fill. Runoff and dump seepage that is collected will be returned via the pump station and pipeline to the powerplant waste water retention pond. In subsequent years, ash pond runoff and runoff from the lower Medicine Creek mine waste dump will be prevented from mixing by maintaining a till berm across the lower perimeter of the ash disposal fill (Beak, Volume 3A, 1979). Ash runoff will then be pumped back to the powerplant waste water retantion pond. On the basis of the current plan there will be no direct discharge of

TABLE 4-10

PROJECTED LOW GRADE COAL AND COAL LEACHATE CHARACTERISTICS
FOR TRACE ELEMENTS

Trace Element	Low Grade Coal[1] (mg/L)	Coal[2] (mg/L)
Arsenic	0.005	0.005
Boron	0.7	0.31
Cadmium	N.D.	N.D.
Chromium	0.010	0.01
Copper	0.007	0.04
Fluoride	N.D.	0.10
Lead	N.D.	N.D.
Mercury	0.0003	0.0003
Vanadium	0.006	0.04
Zinc	0.18	0.11

N.D. Not determined

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1 Based on one sampling of leachate collected from storage pile constructed as part of the bulk sample program. Data supplied by B.C. Hydro. Sampling data 28/4/78.

2 Based on three (3) samplings of leachate collected from coal storage pile constructed as part of the bulk sample program. Raw data supplied by B.C. Hydro.

From Beak (Volume 3A, 1979).

runoff from the ash area to surface waters or creeks. Seepage to substrates will enter the Medicine Creek regional groundwater regime. The maximum seepage to groundwater is estimated at being from 7.0 to 15 m^3/d. The projected quality of this seepage is shown in Table 4-11. It has been suggested that the most impermeable ash should be placed next to the base fill to minimize seepage from the ash dump.

(d) Mine Dust

Fugitive dust resulting from coal mining and transport activities will comprise natural soil, overburden, waste rock materials and coal. The trace element content in the coal and overburden materials is not significantly different from that in the surrounding soil materials. In fact, ERT (Appendix F, 1978) has pointed out that soil concentrations of trace elements may even be higher.

Ambient concentrations of trace elements associated with fugitive dust from the plant have been estimated in Section 2. Concentrations were determined by multiplying the ambient air particulate concentrations by the various elements. Annual average and maximum 24-hour concentrations are given in Table 3-7 of this report.

(e) Cooling Tower Drift

Thompson River water will be the source of cooling water which will be concentrated by a factor of 14 as it is recycled through the cooling system (B.C. Hydro, 1978). A portion of the concentrated circulating water (approximately 0.008 percent) will be carried to areas near the cooling tower as winds disperse some of the water away from the tower (ERT, Appendix F, 1978). The predicted concentrations of selected trace elements in cooling

TABLE 4-11

PROJECTED COMBINED ASH LEACHATE QUALITY FOR TRACE ELEMENTS[1]

Trace Element	Concentration (mg/L)
Arsenic	< 0.6-2.4
Boron	< 3.0-3.6
Cadmium	< 0.10
Chromium	< 0.12-0.20
Copper	< 0.23-0.33
Fluoride	3.3-4.9
Lead	< 0.05
Mercury	< 0.0013-0.0023
Vanadium	< 0.18-0.22
Zinc	0.82-2.5

[1] Based on fly ash to bottom ash ratio of 75/25, conditioned and wetted with recycled powerplant waste waters to 20 percent and 40 percent moisture respectively.

tower drift are shown in Table 4-12 which also describes Thompson River water quality and the predicted total amount of trace element drift associated with the cooling towers. Although there are no estimates of ambient concentrations arising from cooling tower drift, it is possible to predict soil depositional zones. The deposition of trace elements in these zones has been predicted for the data shown in Table 4-12 along with the predicted salt deposition due to drift from various cooling tower designs. These salt depositional zones are shown in Fig. F7-2 of the ERT report (Appendix F, 1978).

The ratio of trace element concentrations to TDS (total dissolved solids or salt) concentration in drift is used to determine trace element deposition rates in various depositional zones. Projected increases in soil trace element concentrations can then be calculated for the salt depositional zones. Trace element depositions from cooling tower drift will augment those depositing from stack emissions. Estimates of these amounts are provided in Section 4.6.

(f) Powerplant Stack Emissions

These emissions have recently been re-evaluated (Section 3.0). The sources of changes to the emission assessment are due to revised amounts of trace element content in coal as well as an improvement in the methods used to estimate concentration and deposition patterns.

Section 2 gives estimates of local ground level trace element concentrations on the basis of a 244 m stack with meteorological control system (MCS). Maximum trace element concentrations have been calculated for 3-hour, 24-hour and annual (Table 3-4). Local annual average ambient concentrations of trace elements are calculated for the isopleths shown in Fig. 3-1, presented in Table 3-5.

TABLE 4-12

CHEMICAL CHARACTERISTICS OF COOLING WATER
AND COOLING TOWER DRIFT

Element	Thompson River[1] (mg/L)	Cooling Tower Drift[2] (mg/L)	Predicted Amount in Drift (kg/a)[3]
Total dissolved solids (TDS)	109	1526	155 652
Arsenic (As)	0.05	0.7	71
Cadmium (Cd)	0.005	0.007	7.1
Chromium (Cr)	0.002	0.028	2.9
Copper (Cu)	0.01	0.14	14
Fluoride (F)	0.1	1.4	142
Lead (Pb)	0.05	0.7	71
Mercury (Hg)	0.001	0.014	1.4
Vanadium (V)	0.006	0.084	9
Zinc (Zn)	0.031	0.43	44

1 Thompson River will be source of cooling water; TDS value from a 1975 study; trace element values from samples collected in May 1977.

2 Cooling water recirculation buildup factor assumed to be 14 (B.C. Hydro, 1978).

3 Estimated drift is 194 L/min; see ERT Appendix D - Assessment of Atmospheric Effects and Drift Deposition due to Alternate Cooling Tower Designs.

From ERT (Appendix F, 1978).

4.4 TRACE ELEMENT SOURCES FROM THE PROJECT - (Cont'd)

It became apparent (Section 3.0) that the most significant areas of deposition would occur outside of the local scale due to long range transport (ERT, Appendix I, 1979). The deposition of trace elements has been done on the basis of annual average SO_2 deposition rates. The deposition patterns correspond to the coded isopleths of Fig. 2-2, while deposition rates are shown in Table 3-5.

4.5 ASSESSMENT OF AMBIENT TRACE ELEMENT CONCENTRATIONS FROM THE PROJECT ON THE BIOTA

The main interest in gaseous and particulate trace element emissions from coal-fired powerplants has been directed largely toward the impacts on human health, economically important crops and ornamental plants as well as the health of livestock (Dvorak and Lewis et al., 1978). The effects of these trace element emissions on the natural environment namely wildlife, vegetation, soils and the aquatic biota, have received a comparatively small amount of attention.

Once the trace elements are in the atmosphere there are numerous conversions and reactions that can take place to alter the chemical forms of these elements. The airborne trace elements will have variable reaction times, hence their impacts must be considered not only locally (plant site-specific) but also regionally. A number of trace elements are known, for example, to be deposited relatively close to the plant site while others can be carried many kilometres away from the point-source emission (Section 4.2).

The potential impacts of airborne trace elements are greater in the terrestrial biota due to their aerial distribution. Under fumigation conditions, for example, all trophic levels of the terrestrial ecosystem would be exposed to airborne trace elements. The aquatic ecosystem, on the other hand, is little affected by ambient trace element concentrations. Elements deposited in the terrestrial

environment, however, may ultimately impact upon aquatic receptors via leachate and surface water dissolution of trace elements.

The effects of airborne trace elements on the terrestrial biota have been largely determined under laboratory conditions using acute levels in fumigation chambers (Dvorak and Lewis et al., 1978). Data for chronic exposure under natural conditions are less available even though such data would be more reflective of the operating coal-fired electrical facility. Vegetation would be the first major biotic component to be affected by airborne trace elements. It is likely that annual and perennial plant species would be affected differently. A population of annual plants, for example, would be affected sooner and perhaps more severely by factors impairing sexual reproduction and/or seed germination than would a population of perennial plants. Such changes (chronic or acute) could lead to alterations in community structure, productivity, stability and a number of other factors. The animal component would be impacted by secondary effects due to habitat changes or food species changes caused by pollutant effects on vegetation. Herbivores would likely be the first animal trophic level affected since they are dependent on vegetation for both food and habitat. The effects of airborne trace elements on wildlife are expected to be more variable than those on livestock because of the general migratory nature of the former group.

It has been proposed that there are three general levels of effects of air pollution on ecosystems (Dvorak and Lewis et al., 1978). Under conditions of low dosage (first level) the vegetation and soils function as an important sink for air contaminants. When exposed to the secondary or intermediate doses, individuals of the various biotic components may be adversely and subtly affected while exposure to high pollutant doses, the third level, may induce mortality.

4.5 ASSESSMENT OF AMBIENT TRACE ELEMENT CONCENTRATIONS FROM THE PROJECT ON THE BIOTA - (Cont'd)

The impacts of airborne trace elements on the biota arising from the combustion of Hat Creek coal, both locally (Hat Creek) and regionally are assessed below.

(a) Aquatic Biota

As discussed previously, the effects of ambient concentrations of airborne pollutants generally do not impact upon aquatic systems. The maximum ambient trace element concentrations ($\mu g/m^3$) resulting from powerplant emissions have been given in Section 3.0, Table 3-5 while Table 3-6 and Fig. 3-1 provide the annual average concentrations and the coded isopleths corresponding to these conditions.

Certain organisms which inhabit the terrestrial aquatic interface such as amphibians and various forms of aquatic vegetation (macrophytes) that have aerial plant parts could be affected. Comparison of the concentrations shown in Tables 3-5 and 3-6 with the ambient air quality objectives for trace elements (Table 4-13) indicates that ambient concentrations are below those of the guidelines. The 24-hour average for fluorine (F), however, of 1.9 $\mu g/m^3$ is very close to the guideline level of 2.0 $\mu g/m^3$ for the same averaging time. There are a dearth of data describing the effects of F on amphibians and aquatic macrophytes. Weinstein (1977) reports, however, that selected macrophytes (Impatiens sp. and Plantago sp.) display differing tolerances to F.

The abundance of aquatic macrophytes in the Hat Creek vicinity is low due to the rocky substrata of the streams and intermittant nature of some of the watercourses (Beak, Fisheries and Benthos Study, 1977). The effects of 1.9 $\mu g/m^3$ of F over a 24-hour period are projected to be insignificant on these vegetative forms. The maximum average ambient concentrations of F and those coded to the isopleths of Fig. 3-1 will not affect macrophytic vegetation.

TABLE 4-13

AMBIENT AIR QUALITY STANDARDS FOR TRACE ELEMENTS

Element	Agency			
	B.C. Pollution Control Branch (Average Concentration Ranges Without Time Specification[1] (μg/m³)	Province of Ontario Ambient Air Quality Objective 24-h Averages except as Noted[2] (μg/m³)	U.S. Ambient Standards[3] (μg/m³)	USEPA Sponsored Panel Safe 24-h Ambient Air Quality Levels[4] (μg/m³)
Antimony	0.10 to 0.50	-	-	-
Arsenic	0.10 to 1.0	25	-	5.9
Beryllium	-	-	0.01 (30-day average)	0.005
Cadmium	0.05 to 0.10	2.0	-	1.2
Chromium	0.50 to 0.10	-	-	4.6
Copper	0.25 to 2.0	-	-	10.0
Fluorine	0.10 to 2.0	Expressed as HF April 15 - October 15 0.86 for 24 h (gaseous) 1.72 for 24 h (gaseous plus particulate) October 16 - April 14 1.38 for 24 h (gaseous plus particulate	-	47 47
Lead	1.0 to 2.5	5.0	-	4.7
Manganese	-	-	-	11.4
Mercury	0.10 to 1.0	2.0	1.0 (24 h average)	0.8
Molybdenum	0.10 to 2.5	-	-	
Nickel	0.01 to 0.10	2.0	-	3.7
Selenium	0.10 to 0.50	-	-	5.4
Uranium	0.01 to 6.0	-	$(1 \times 10^{-13})^{0.4}$ μcuries/mL)[5]	-
Vanadium	0.05 to 1.0	2.0	-	6.8
Zinc	1.0 to 2.5	2.0	-	34

1 B.C. Pollution Control Board (1979).
2 Ministry of the Environment, Ontario (1976).
3 USEPA, 1973; U.S. Government, 1977.
4 Wilcox (1973).
5 Conversions based on the specific activity of naturally occurring uranium being 6.77×10^{-1} μcuries/gm (U.S. Government, 1977).

The remaining trace elements' average ambient concentrations are roughly an order of magnitude below any guideline level. Further, data available from the literature survey indicate there will not be any adverse effects to the biota at any of the expected concentrations. Consequently, their impacts as gaseous pollutants to amphibians and aquatic vegetation in the Hat Creek area are projected to be negligible.

Regional ambient concentrations of trace elements are much lower than those described for the local Hat Creek area (Section 3.0, Table 3-6 and Fig. 3-1). The deposition of trace elements in the regional area is, however, greater than in the local area as described in the ERT (Appendix I, 1979) acid rain report. These deposition patterns are based upon the annual average dry and wet SO_2 depositions. These deposited trace elements will subsequently enter surface and groundwaters. The impacts of deposited trace elements to the aquatic biota are discussed in Sections 4.6(d) and (e) below.

(b) Terrestrial Biota

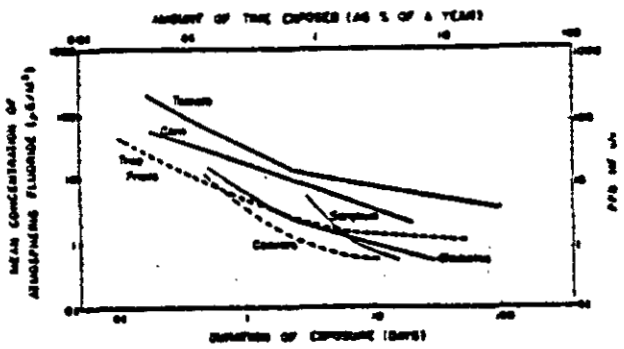
As it has been pointed out above, terrestrial vegetation would be the first biotic component that could be affected by ambient trace element concentrations. The impact assessment for ambient trace element concentrations is limited to the local environment (Hat Creek) since these concentrations are much higher in this area than the regional or offsite zones (Section 3.0). Those elements of greatest potential toxicity are those that display phytotoxicity to vegetation or are readily accumulated through leafy tissues. The principal elements of this group include boron, fluorine, lead and mercury. These elements may enter plants through the leaves and can be translocated within the plant. Of the above elements, F is the most significant in terms of impact to the vegetative species as a result of the Hat Creek

Project. The fluorine concentration of Hat Creek coal is relatively high (Section 2.0) and hence will result in significant gaseous emissions of the element from the combustion of Hat Creek coal (Section 3.0).

Resulting maximum average ambient concentrations for F have been given (Tables 3-5 and 3-6), these levels are in compliance with the guideline concentrations shown in Table 4-13. On this basis, vegetation will likely be protected from acute injury although they will probably accumulate the element in their tissues proportionately to the increase in ambient concentrations. This relationship holds true for F concentrations over the range 0.6 to 40 $\mu g/m^3$ in grasses (Weinstein, 1977). It is presumed a similar response will be elicited by the plants at the F concentrations projected for Hat Creek. The resultant accumulations should not, however, be of sufficient magnitude to significantly affect the growth or reproduction of indigenous vegetation at Hat Creek. The projected maximum 24-hour concentration of 1.9 $\mu g/m^3$ is of the same order of magnitude which has demonstrated toxicity to beans. A concentration of 2.1 $\mu g/m^3$ was shown to inhibit the growth of beans but the exposure was continuous over the first generation of the plants. It is unlikely that the 24-hour projected maximum F concentration of 1.9 $\mu g/m^3$ will produce any long-lasting or deleterious affects to the vegetation in the vicinity of Hat Creek in view of the intermittent nature of exposure. Fig. 4-2 shows the dose-response relationships for foliar injury to different plant species (McCune, 1969). Comparison of projected ambient F concentrations with this figure reveals that the estimated levels should not affect Hat Creek vegetation even during long-term exposure. If sufficient data were available a series of different curves could be drawn for criteria based on photosynthetic carbon dioxide assimilation, growth, fruiting, quality or F content. It is obvious from Fig. 4-2 that coniferous trees are more sensitive to F than most

Figure 4-2

Dose - Response Relationships for Foliar Injury to Different Plant Species.



From McCune (1969) as summarized in Weinstein (1977).

plants. These trees contribute significantly to the forest industry of British Columbia and the impacts of the projected ambient F concentrations on these sensitive and economically valuable species has been assessed (TERA Appendix A3, prepared by Reid Collins Ltd., 1978).

The projected ambient concentrations of B, Hg and Pb are quite low (Tables 3-5 and 3-6). These elements are phytotoxic to plants but at much higher concentrations than those projected from the combustion of coal at Hat Creek. Even though the estimated ambient levels are quite low, some accumulation of these elements by local vegetation is expected to occur. Boron concentrations in plants of 300 mg/kg or greater can produce injury (Temple et al., 1978). The background B levels for vegetation at Hat Creek ranges only from 2.01 to 39.33 mg/kg (Section B-3 of Appendix B). It is unlikely that significant accumulations could occur by the plants from the ambient concentrations projected to produce injury. Similarly, the project ambient concentrations of lead and mercury are so low that it is improbable local plants will accumulate the elements to toxic levels.

The airborne toxicity of the remaining trace elements to vegetation has been discussed in Section 4.2. No evidence exists which indicates that the maximum ambient concentrations of these trace elements could adversely affect the vegetation in the Hat Creek area.

Gaseous trace elements may also be inhaled by livestock and wildife that are near the plant site. Although the major routes of trace element entry into these animals is by ingestion some will undoubtedly enter via inhalation. The trace elements that enter the lungs are primarily those that are gaseous or volatilized and adsorbed to particulates of submicron size. Such elements include Hg, Se, Be, Pb, As, F, B and Ni. The submicron

4.5 ASSESSMENT OF AMBIENT TRACE ELEMENT CONCENTRATIONS FROM THE PROJECT ON THE BIOTA - (Cont'd)

particulates bearing these trace elements can deposit into the deep alveolar portions of the lung where they have access to the bloodstream and subsequent transport to the internal organs (Natusch and Wallace et al., 1974). The ambient guideline concentrations of trace elements are designed to protect humans respiring similar concentrations for the time periods indicated. If we assume that these guidelines are adequate to protect other mammals such as livestock and wildlife species, the estimated maximum concentrations of ambient trace elements will not impact upon these animals.

There are not sufficient data for avian species to adequately determine whether the projected ambient levels are hazardous. It is expected those levels that are safe for mammals would also protect birds.

The maximum 24-hour and annual average ambient concentrations resulting from mine dust have been estimated. These concentrations have been given in Section 3.0 (Table 3-7). The ambient levels projected are below all guideline values and hence, are not anticipated to have any adverse affect on the local biota.

Generally, there is a lack of information addressing the effects of airborne trace elements to animals, whether they be domestic or wild. This should be considered in the development of monitoring programs to assess airborne trace element impacts during the operation of the Hat Creek Project.

4.6 RECEPTOR ACCUMULATION OF TRACE ELEMENTS AND IMPACTS FROM THE PROJECT ON THE BIOTA

(a) Soils

There will be minor increases of trace elements in the local and regional soils due to powerplant and cooling tower

emissions and subsequent deposition. The deposition rates for emitted trace elements have been discussed previously (Section 3.0, Table 3-6). The more recent deposition rates have been calculated on an improved method from earlier studies on the basis of information that has come available with the publication of the report on the long range transport and the implications of acid precipitation ERT (Appendix I, 1979). It was realized that the major deposition zones of trace elements occurred outside the local area while ground-level ambient concentrations were higher in the local area. For the purposes of this impact analysis the isopleths of regional-annual SO_2 deposition (Fig. 3-2) have been extended to include the plant site. This approach provides a much more conservative estimate of soil accumulations in the local area as trace element depositions, regionally, were typically greater than the local area. The deposition rates shown in Table 3-6 have been used to calculate the estimated soil enrichment of trace elements due to stack emissions after 35 years of powerplant operation, assuming an overall capacity of 65 percent. Table 4-14 provides the projected soil enrichment within the isopleths shown in Fig. 3-2.

Several assumptions were employed to facilitate the calculation of these predictions:

1. Soils in the Hat Creek and regional areas are of a sandy loamy texture whose bulk density is approximately 1.75 g/cm^3 (Dvorak and Lewis et al., 1978).

2. All deposited trace elements will remain in residence in the top 3 cm of soil which approximates the most biologically active area.

TABLE 4-14

TRACE ELEMENT SOIL ACCUMULATIONS,

AFTER 35 YEARS OPERATION (ASSUMING 65% CAPACITY

ELEMENT		Isopleth Code - Concentration per Code $ug \cdot kg^{-1}$			
		A	B	C	D
ANTIMONY	(Sb)	0.23	0.18	0.14	0.07
ARSENIC	(As)	28.67	21.61	14.33	7.28
BERYLLIUM	(Be)	0.523	0.387	0.25	0.011
BORON	(B)	43.68	32.99	21.63	10.82
CADMIUM	(Cd)	0.32	0.25	0.16	0.07
CHROMIUM	(Cs)	5.28	4.03	2.68	1.34
COBALT	(Co)	0.91	0.68	0.46	0.20
COPPER	(Cu)	38.45	29.12	19.57	9.56
FLUORINE	(F)	4029.94	3033.26	2036.58	996.68
LEAD	(Pb)	8.65	6.59	4.32	2.21
MANGANESE	(Mn)	116.93	86.68	60.74	29.35
MERCURY	(Hg)	6.83	5.23	3.41	1.59
MOLYBDENUM	(Mo)	6.14	4.32	2.96	1.37
NICKEL	(Ni)	12.06	9.1	6.14	3.19
SELENIUM	(Se)	10.01	7.28	5.23	2.5
SILVER	(Ag)	0.034	0.025	0.015	0.009
THALLIUM	(Tl)	0.034	0.025	0.015	0.009
THORIUM	(Th)	0.296	0.205	0.148	0.073
TIN	(Sn)	0.21	0.16	0.11	0.06
TUNGSTEN	(W)	0.05	0.04	0.02	0.01
URANIUM	(U)	1.206	0.91	0.614	0.32
VANADIUM	(V)	16.45	12.56	8.24	4.16
ZINC	(Zn)	28.85	21.61	14.33	7.28

Isopleth Codes shown in Fig. 3-2

Values represent trace element accumulations after 35 years assuming a 65% plant capacity.

Assumes that all deposited elements will remain in residence in top 3 cm of soil and that neither uptake by vegetation nor erosion of soil to watershed drainages will occur. Assumes a soil bulk density of 1.75 g/cm^3.

Annual soil accumulations calculated by the formula: $X = \frac{R}{10^6\ cm^2} \cdot \frac{1}{d} \cdot \frac{1}{Db}$

Where: X = concentration of trace element in mg/kg

R = deposition rate in ug/m^2 / unit time

d = depth of penetration in cm

Db = bulk density of soil in g/cm^3

For 35 years at 65% plant capacity values multiply the results of the above calculations by 35 x 0.65.

3. Neither trace element uptake by vegetation nor erosion of soil to watershed drainages will occur.

The deposition of nine trace elements (arsenic, cadmium, chromium, copper, fluorine, lead, mercury, vanadium and zinc) onto soils has been estimated from cooling tower drift characteristics. The deposition zones of these trace elements followed those of the salt deposition zones illustrated in Fig. F7-2 of the ERT report (Appendix F, 1978). All of these zones were found to be located within the B isopleth of trace element deposition (Fig. 3-2). Trace element soil accumulations from this source annually and after 35 years operation at 65 percent capacity are shown in Table 4-15. The assumptions contributing to these calculations are similar to those described for soil accumulations arising from stack emissions. Consequently, trace element contributions from cooling tower drift have been added to those in the B isopleth to provide the total trace element soil accumulation given in Table 4-16. Generally, trace element enrichments in Hat Creek soils represent less than 1 percent of background trace element levels even after the 35-year lifetime of the powerplant. The one exception was mercury which may be enriched by as much as 11.4 percent. Expressed as a percentage this increase appears to be quite large. The quantities of Hg, however, accumulated in the soils range only from 1.59 to 6.83 mg/kg x 10^{-3} (Table 4-14)). Such concentrations of Hg are within the normal ranges reported for natural soil components (Appendix B.12).

The trace element contents of soils in offsite areas, namely Pavilion Mountain, Cornwall Mountain, Lower Hat Creek, Arrowstone Creek and Ashcroft are similar to those levels observed in Hat Creek soils. Trace element soil-enrichment in these areas due to stack emissions can, therefore, be approximated to those described for Hat Creek.

TABLE 4-15

PROJECTED ANNUAL AND 35 YEAR (ASSUMING 65% CAPACITY) INCREASE OF SELECTED TRACE ELEMENTS IN SOIL DUE TO COOLING TOWER DRIFT (mg/kg)

ELEMENT		ANNUAL				AFTER 35 YEARS - ASSUMING 66% CAPACITY			
		SALT DEPOSITIONAL ZONES ($kg \cdot km^{-2} \cdot a^{-1}$)*							
		4700	2240	560	112	4700	2240	560	112
ARSENIC	(As)	0.041	0.019	0.0049	0.0009	0.94	0.446	0.112	0.022
CADMIUM	(Cd)	0.0003	0.0019	0.000049	0.000009	0.009	0.0043	0.0011	0.0002
CHROMIUM	(Cr)	0.0016	0.00076	0.00019	0.000038	0.037	0.017	0.0043	0.0008
COPPER	(Cu)	0.008	0.0039	0.0009	0.00019	0.186	0.088	0.022	0.0043
FLUORINE	(F)	0.08	0.039	0.009	0.0019	1.86	0.88	0.22	0.043
LEAD	(Pb)	0.041	0.019	0.0049	0.0009	0.94	0.446	0.112	0.022
MERCURY	(Hg)	0.0008	0.0003	0.00009	0.000019	0.0184	0.0088	0.002	0.00043
VANADIUM	(V)	0.004	0.0023	0.00059	0.00011	0.112	0.053	0.013	0.0026
ZINC	(Zn)	0.025	0.013	0.0029	0.00057	0.57	0.291	0.068	0.013

See Fig. F7-2 for areal extension of these zones - ERT (Appendix F, 1978).

Trace element deposition flux ($kg \cdot km^{-2} \cdot a^{-1}$) = salt deposition rate x element to salt concentration ratio in drift (see table F4-3 of ERT Report Appendix F, 1978).

Assumes that all desposited elements will remain in residence in top 3 cm of soil and that neither uptake by vegetation nor erosion of soil to watershed drainages will occur. Assumes a soil bulk density of 1.75 g/cm^3.

Then, soil concentration increase per year = depositional flux x 1 km^2 ; (0.03 x 10^6 m^3 x 1.75 g/cm^3 x 10^6 cm^3/m^3)= kg/52.5 x 10^6 kg = mg/52.5 kg. Therefore, soil increase (mg/kg/a) = deposition flux for 35 year buildup with 65% capacity multiply projected annual values by (35 x 0.65).

Calculations for annual values based on cooling towers operating at design capacity for 365 days/year (worst case ses t).

TABLE 4-16

TRACE ELEMENT ACCUMULATION AFTER 35 YEARS OPERATION (ASSUMING 65% CAPACITY) FROM STACK EMISSIONS AND COOLING TOWER DRIFT

ELEMENT		TRACE ELEMENT ACCUMULATIONS IN B ISOPLETH (mg/kg)	TRACE ELEMENT ACCUMULATIONS (mg/kg) IN SALT DEPOSITIONAL ZONES ($kg.km^{-2}.a^{-1}$) FROM COOLING TOWER DRIFT			
			4700	2240	560	112 *
ARSENIC	(As)	0.0216	0.9616	0.4676	0.1336	0.0436
CADMIUM	(Cd)	0.0002	0.0092	0.0045	0.0013	0.0004
CHROMIUM	(Cr)	0.0040	0.0410	0.0210	0.0083	0.0048
COPPER	(Cu)	0.0291	0.2561	0.1171	0.0511	0.0334
FLUORINE	(F)	3.033	4.8930	3.9130	3.2530	3.0760
LEAD	(Pb)	0.0066	0.9466	0.4526	0.1186	0.0286
MERCURY	(Hg)	0.0052	0.1902	0.0140	0.0072	0.0056
VANADIUM	(V)	0.0126	0.1246	0.0656	0.0256	0.0152
ZINC	(Zn)	0.0216	0.5916	0.3126	0.0896	0.0346

*Assumed that all salt deposition zones lie completely within the B isopleth of annual SO_2 deposition.

Attendant trace element accumulations (mg/kg) are given for the B isopleth (taken from Table 4-15).

Values of trace element accumulations shown for salt deposition zones are derived by adding the concentrations in the B isopleth to those for the salt deposition zones from Table 4-15.

The soils in the Hat Creek area are charactarized by being alkaline and of a sandy/loamy texture. Soil types such as these readily bind trace elements that occur most often as cations (Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Sn, V and Zn) (Berry and Wallace, 1974). Arsenic, molybdenum and selenium, on the other hand, occur as divalent anions in the soil solution. These elements can be expected to be more mobile in Hat Creek soils as they are more soluble in neutral to alkaline soils (Allaway, 1968). Deuel and Swoboda (1972), however, have estimated that only about 1 percent of applied As was recovered in the soluble water phase with the remainder tied down by the soil. The remaining elements, Sb, B, F, Hg, Ag, Tl, Th, W and U, according to the litarature (Section 4.2) will be relatively immobile in alkaline soils approximating those of Hat Creek. Uranium, as the uranyl ion (UO_2^{2+}), however, is soluble in water and hence may be available in soils.

During the 35-year operation of the powerplant it is believed the soils in the Hat Creek area and offsite locations will be able to absorb and fix a large portion of the trace elements that are deposited on them. As they are alkaline with an assumed high cation exchange capacity and rainfall is relatively low these soils will have a protective effect on the contamination of groundwater and will also protect plants from exposure to levels of available trace elements. The soils in the study areas will, therefore, act as a "sink" for most of the trace elements. Even those elements that will display some mobility and availability (As, Mo and Se) are anticipated to have a slight impact due to the extremely small percentage of their enrichment. The attendant percentages are 0.30 for As, 0.46 for Mo and 1.0 for Se. The contribution of trace elements to soils as a result of mine dust deposition are expected to be negligible. There is no real

difference in trace element content between the coal-dust particles and soils near the mine. Therefore no trace element enrichment of soils can occur via this source.

It is reiterated that the above calculations are fairly conservative and that the actual enrichment of the soils is probably less than the values shown above. The ultimate enrichment of soils resulting from the project do not alter the soil content beyond those reported as "natural" (Tables B.1 to B.23).

(b) Terrestrial Vegetation

The uptake and accumulation of trace elements from soils and nutrient solutions by plants has been reviewed in Section 4.2.

The vegetation at Hat Creek will likely accumulate the essential micronutrient trace elements such as B, Ca, Mn, Mo and Zn in amounts proportional to those added to the soils. These enrichments have been assessed in Section 4.6(a) and were shown to be generally less than 1 percent of the background concentration. The accumulation of these elements by indigenous plant species should, therefore, not exceed this percentage. By similar mechanisms the plants could accumulate unessential trace elements such as Cd, Ni, Be, Cr, Pb, Hg, Se, Ag, Tl, Sn, U as UO_2^{2+} and V. If soil concentrations are sufficiently increased, plants will continue to accumulate the elements and concentrations toxic to the plant or its consumers may be reached. There is little or no accumulation of Co, F, Sb, Th, Tl or W by plants from soils.

The conservative enrichment of soils (about 1 percent after 35 years) as a result of the Hat Creek Project will preclude the accumulation of trace elements to toxic proportions in the plants.

Arsenic, selenium and molybdenum are expected to have the greatest availability in soils of all the trace elements. These elements are anionic in soils and hence are more soluble in the solutions of such soils. In the semi-arid region of Hat Creek where soil moisture is low the migration of As, Mo and Se through soils and diffusion into plants of even these soluble trace elements will be limited. If one again assumes that all of the deposited trace element amounts are available to the plants, the resulting change in plant tissue levels is expected to be negligible because of the limited enrichment in soil quantities.

Some discrimination of trace elements uptake is displayed by plants. Many trace elements such as As, Be, Cr, Ni, Pb and V are accumulated by the roots, but are not readily translocated to the above ground plant parts. Other elements such as Cd, Cu and Zn are more freely translocated. The movement of these elements from Hat Creek soils to vegetation is expected to occur in a similar fashion but it is not known if the translocation characteristics of these elements reduces or increases their toxicity to plants. The movements are, however, significant when considering which trace elements are transported to the aerial portions of plants which then become available to herbivorous animals. It is unlikely that significant impacts will occur in view of the relatively small amounts of trace elements that are anticipated to reach biological receptors.

(c) Wildlife

Wildlife could be exposed to trace elements through the ingestion of contaminated plant material. In the previous section it was shown, however, that accumulations of trace elements by plants from the soils and from the atmosphere are anticipated to be relatively minor. Consequently, it is unlikely that

herbivorous animal species would in turn accumulate trace elements in their tissues to a significant level. The possible movements of a number of selected trace elements in wildlife are discussed below with respect to the project. From the literature review (Appendix C) it became apparent that not all of the 23 trace elements originally listed are of environmental concern, due to certain elements' immobility in the biota and the projected low emission rates of others.

The elements B, Mn and Mo can accumulate in plant tissues but they are relatively innocuous when ingested by browsers. Increases in the concentration of these elements in plants as a result of the project are expected to be negligible. Hence, the ingestion of these plants by herbivorous wildlife or the consumption of forage crops grown in the zones of highest deposition (Fig. 3-2) are not expected to result in significant accumulations by consumers. Antimony, thorium and tungsten are bound relatively tightly to soils and uptake of them by plants in all areas is not expected to occur. These elements are poorly absorbed from the gastrointestinal tract and are not expected to be of concern to wildlife or domestic animals during the operation of the plant.

The volatile trace elements, As, Be, Cd, F, Hg, Ni, Pb, Se, Tl and V may be inhaled by wildlife and domestic animals but the ambient concentrations are projected to be below PCB* guidelines. Animals will not be endangered from exposure to the ambient concentrations projected. As gases or very fine particulates these elements will enter the gas exchange systems of plants and become accumulated in the tissues. Plant accumulations via this route are not expected to be significant.

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* Pollution Control Board, Ministry of Environment, B.C. Government.

Fluorine will probably accumulate in browse vegetation in proportion to the ambient air concentration but much of the F will be absorbed by soil and water. Increased F levels in plant tissues will not be sufficient to significantly alter background levels. Fluorine compounds diffuse easily across gut walls of animals and are readily incorporated into growing bones. Most of the F that is not incorporated into hard body tissues is excreted by animals. The projected low concentrations of F in plants grown within the greatest depositional zones (Fig. 3-2) should not cause fluorine toxicosis in animals. The remaining volatile elements, As, Be, Cd, Ni, Pb, Se, Tl and V are accumulated by plants from the air but display varying movements in plant tissues (Section 4.2).

Cadmium is considered potentially dangerous because of the inability of animals to excrete it. The element has a relatively long biological half-life and can be an accumulative poison in animals (Dvorak et al., 1978). It has been estimated that only 7 percent of Cd fallout will be incorporated into living vegetation while a majority of the remainder is bound to dead vegetation. Thus, contamination of plants ingested by animals during the project will be negligible and should not be high enough to be a potential health concern. Cadmium will be most available to animals whose food base is litter or detritus as a large amount of the deposited Cd remains in these receptors.

Lead is highly absorbed by soil but some of the airborne Pb arising from stack emissions can be absorbed by plant leaves. Lead in the soils at Hat Creek will be unavailable to plants as they are alkaline and bind the metal. The main route of entry into animals will be from the ingestion of vegetation that has accumulated Pb from the atmosphere. Lead ingested by animals is not readily transported across gut walls, and only a small fraction of the Pb taken in by animals is stored in bones. These

observations suggest that Pb will not be accumulated by animals to significant proportions as a result of powerplant emissions. Lead is not methylated in the terrestrial system, a fact that will limit the element's movement in this system.

Vanadium is more soluble in alkaline media, hence many plants including grazing crops such as clover and alfalfa may accumulate the V deposited on the basic soils in the Hat Creek area. Some of the element is taken up by plants from the airborne route. Vanadium will be widely distributed in Hat Creek and other environs but at low levels. The amount of V in plants, however, is not expected to be harmful to wildlife or domestic animals ingesting the vegetation.

Nickel is accumulated by plants from the atmosphere but is relatively immobile in alkaline soils, although plants have been shown to accumulate the metal under certain conditions. Nickel that is ingested is poorly absorbed and excreted mostly in the feces. The movement of Ni through the terrestrial ecosystem to animals will be limited at Hat Creek due to the basic nature of the soils and the animals' capability to excrete the element.

Selenium is accumulated by plants and is more available in neutral or alkaline soils. It is essential to animals and is readily absorbed but is eliminated in the feces and urine. Animals can be poisoned through the ingestion of contaminated vegetation. The consumption of vegetation containing 5 mg/kg or greater of Se has been shown to be toxic to browsers. Levels below 1 mg/kg appear to provide an adequate margin of safety against adverse effects. The element will be widely distributed to the Hat Creek area and will be relatively mobile. The low levels emitted, however, should preclude its accumulation to toxic levels in plants and animals.

Thallium is not accumulated by plants to any great extent especially in alkaline soils. It is relatively toxic to both plants and animals. The projected ambient concentrations and biotic accumulations are not expected to adversely affect animal life at Hat Creek.

The elements Co, Cr, Cu, Sn, Th, U, W and Zn are concentrated in the ash and are not emitted to the same extent as the volatile elements. The majority of their potential impacts result from leachates of ash disposal ponds not stack emissions.

Cobalt is not accumulated by plants to any great extent so its movement through the terrestrial food chain is limited. The movement of Cr in the environment as a function of the project is difficult to predict because of the element's ubiquitous nature. Once deposited the element may be available for biotic uptake especially if oxidation to hexavalent Cr occurs. This form can readily penetrate biological membranes so it would likely be accumulated by plants. Animals can, however, eliminate the element from their systems, and it is usually not considered to be an environmental hazard. Copper will be largely unavailable to plants at Hat Creek because it is highly absorbed by soils; a portion will become accumulated in plants via the airborne route. It can be taken up by animals but it is also eliminated. Copper is not anticipated to be a problem to the health of wildlife or domestic animals as a result of the project.

The methylated form of tin is toxic to animals and most of the inorganic tin is not absorbed. Most of what is accumulated is in the kidneys and liver. Some accumulation of Sn by plants can occur from soils in contaminated areas. The projected levels of soil enrichment as a result of the Hat Creek Project should not be sufficient to significantly alter the levels of background Sn in plants. Tin is methylated in aquatic sediments which is

volatilized and can enter the terrestrial ecosystem. This process is anticipated to provide very little Sn. The element should be monitored in view of the discrepancies observed in the analytical data for plants and animals.

The general concern for Th as an environmental contaminant has been due to its natural radioactivity. Its occurrence in the terrestrial ecosystem is expected to be limited since accumulation in plants does not occur and it is bound to alkaline soils. Some leaching may occur from ash disposal areas. Uranium is a member of the naturally radioactive elements. Unlike Th it can be readily accumulated by plants as the uranyl ion (UO_2^{2+}). The amounts of UO_2 ultimately becoming available to wildlife and domestic animals is considered to be negligible.

Tungsten will be limited in its movement through the terrestrial ecosystem. It is bound by soils and is virtually excluded by plants. Stack emissions are estimated to be very low as the majority of the W remains within the plant and ash. These characteristics preclude the element from being an environmental concern for animals due to the project.

Zinc should be relatively immobile and unavailable to plants in the Hat Creek area as the element is bound by alkaline soils. Zinc may be accumulated from the atmosphere by plants, many plants have a high affinity for Zn and accumulate the element in concentrations much higher than those of other trace elements. Zinc will be widely distributed in the Hat Creek area but its mobility through the food chain will be limited because it is bound by alkaline soils. Although Zn is required by animals it is poorly absorbed across gut walls and can be eliminated. In view of the above, it is unlikely Zn will be a problem for animals in the Hat Creek area although potential changes in plant concentrations should be monitored.

4.6 RECEPTOR ACCUMULATION OF TRACE ELEMENTS AND IMPACTS FROM THE PROJECT ON THE BIOTA - (Cont'd)

(d) Water Quality

Trace elements naturally existing in coal, overburden and waste rock will be released to the environment during coal mining and power generation (Fig. 3-2). The principal source of trace element additions to the aquatic environment is from the deposition of trace elements arising from the stack as airborne emissions. Minor additions will result from surface water runoff and leachates originating from coal stockpiles, overburden and waste rock piles as well as ash disposal sites.

A worst-case example was examined in order to obtain some estimate of the impact of trace elements from stack emissions on the aquatic system. The following conservative assumptions were made to simplify the calculations:

1. All of the trace elements that fall on the Bonaparte River watershed make their way into the aquatic system.

2. All trace elements that enter the water dissolve completely.

Trace element depositions followed the isopleth codes shown in Fig. 3-2, attendant deposited amounts corresponded to those occurring in a 1-year period with the powerplant operating at full capacity. These total depositions were then divided by the total amount of surface water runoff in the Bonaparte River watershed (Beak, 1979; Volume 2) to provide an estimate of trace element concentration for any given time during the plant's operation, considering that there is no accumulation. These concentrations are shown in Table 4-17. The levels were then added onto those observed for Hat Creek and the Bonaparte River to obtain projected water concentrations of the 23 trace elements during plant operation. These data are summarized in Table 4-18.

TABLE 4-17

PROJECTED TRACE ELEMENT ADDITIONS TO THE BONAPARTE RIVER

FROM THE HAT CREEK POWER PLANT

ELEMENT		CONCENTRATION µg/L	ELEMENT		CONCENTRATION µg/L
ANTIMONY	(Sb)	0.013	MOLYBDENUM	(Mo)	0.437
ARSENIC	(As)	1.426	NICKEL	(Ni)	0.51
BERYLLIUM	(Be)	0.025	SELENIUM	(Se)	0.489
BORON	(B)	2.15	SILVER	(Ag)	0.002
CADMIUM	(Cd)	0.016	THALLIUM	(Tl)	0.002
CHROMIUM	(Cr)	0.263	THORIUM	(Th)	0.025
COBALT	(Co)	0.043	TIN	(Sn)	0.04
COPPER	(Cu)	1.89	TUNGSTEN	(W)	0.002
FLUORINE	(F)	198.51	URANIUM	(U)	0.059
LEAD	(Pb)	0.437	VANADIUM	(V)	0.702
MANGANESE	(Mn)	6.16	ZINC	(Zn)	1.412
MERCURY	(Hg)	0.42			

Calculated from total amount of trace elements deposited within the Bonaparte River Watershed (Fig. 3-2).

Total amounts deposited (mg/a) were then divided by the total amount of surface water runoff ($120 \times 10^6 m^3 \times 10^3 L$) for the watershed to derive concentrations (µg/L).

Assumes that all elements falling within the Bonaparte River Watershed make their way into the surface water and are completely dissolved.

TABLE 4-13

TRACE ELEMENT CONCENTRATIONS OBSERVED IN THE BONAPARTE RIVER AND HAT CREEK RELATIVE TO THE PROJECTED WATER CONCENTRATIONS DURING OPERATION OF THE HAT CREEK POWER PLANT

ELEMENT		WATER CONCENTRATIONS (µg/L)			*Projected Trace Element Additions (µg/L)	**Projected Water Concentrations in the Bonaparte River (µg/L)
		[a] Hat Creek	[b] Bonaparte River	[c] Hat Creek		
ANTIMONY	(Sb)	—	—	<2.2	0.013	< 2.213
ARSENIC	(As)	<5.0	<5.0	<18.07	1.425	< 6.425
BERYLLIUM	(Be)	—	—	0.90	0.025	0.925
BORON	(B)	—	—	3.10	2.15	5.25
CADMIUM	(Cd)	<5.0	<5.0	<3.0	0.016	< 5.016
CHROMIUM	(Cr)	<10.0	<10.0	<9.13	0.253	< 10.253
COBALT	(Co)	—	—	4.0	0.043	4.043
COPPER	(Cu)	<5.0	<5.0	<7.7	1.39	< 6.39
FLUORINE	(F)	—	—	133.5	198.51	332.01
LEAD	(Pb)	<10.0	<10.0	54.57	0.437	< 10.437
MANGANESE	(Mn)	—	—	0.012	6.16	6.172
*** MERCURY	(Hg)	<0.05-0.07	<0.05	<0.05-0.07	0.42	(0.47-0.49)
MOLYBDENUM	(Mo)	<20.0	<20.0		0.437	< 20.437
NICKEL	(Ni)	—	—	9.2	0.51	9.71
SELENIUM	(Se)	<3.0	<3.0	2.3	0.489	< 3.489
SILVER	(Ag)	—	—	0.001	0.002	0.003
THALLIUM	(Tl)	—	—	<1.1	0.002	< 1.102
THORIUM	(Th)	—	—	0.007	0.025	0.032
TIN	(Sn)	—	—	<51.5	0.04	< 52.0
TUNGSTEN	(W)	—	—	0.001	0.002	0.003
URANIUM	(U)	—	—	0.005	0.059	0.063
VANADIUM	(V)	<5.0	<5.0	<4.5	0.702	< 5.702
ZINC	(Zn)	<7.0	<22.0	29.5	1.412	< 24.412

(a) Overall annual means (1976 and 1977) of trace element concentrations for Hat Creek summarized from Beak (1978) Hydrology Inventory Report, Volume 2, Table 4.16.

(b) Overall annual means (1976 and 1977) of trace element concentrations for Hat Creek summarized from Beak (1978) Hydrology Inventory Report, Volume 2, Table 4.15.

(c) Overall annual means for October 1976, January and May 1977 of trace element concentrations for Hat Creek summarized from Environmental Research and Technology (1978) Appendix F.

* Projected trace element additions as a result of the Hat Creek Project taken from Table 4.6.4.1 of this report.

** Values represent the summation of projected trace element additions and trace element levels observed in the Bonaparte River. Values for Hat Creek as described by ERT (1978) Appendix F were used to approximate trace element concentrations where values for these elements were missing for the Bonaparte River.

*** Earlier estimates of Hg concentrations (a, b and c) in these water courses have been replaced by the values shown in view of more recent and accurate data provided by the B.C. Ministry of the Environment (1980, Appendix D). The final Hg concentration in the Bonaparte River is calculated to be $0.0521 µg/L. Details of the calculations are given in Table 4-25.

Existing concentrations of mercury in the two water courses have recently been reevaluated (B.C. Ministry of the Environment, 1980) in view of earlier Hg measurements which were considered to be erroneously high representations of Hg concentration in the streams. These latter values ranged from <0.29 to <0.40 µg/L (Beak, Volume 2, 1978; ERT, Appendix F, 1978) and were obtained with an analytical method employing a detection limit of 0.25 µg/L. This limit is higher than the recommended guideline limit of 0.20 µg/L for the protection of fish and other aquatic life (Table 4-23). Consequently, it was not possible to relate Hg levels in the two watercourses to this guideline figure.

It was deduced that should Hg concentrations be as high as these earlier values, evidence of Hg contamination in the two watercourses would have been obvious. In addition, measurements of the Hg content of indigenous fish species (Appendix B-12) were within "normal" ranges and are not indicative of a mercury pollution problem.

The data provided by the British Columbia Ministry of the Environment (1980, Appendix D; Table 4-18) using a much lower Hg detection limit in water (0.05 µg/L) indicates that actual levels are below 0.05 and 0.07 µg/L for the Bonaparte River and Hat Creek respectively. These values have been used in this assessment to provide an estimation of projected Hg concentrations in Hat Creek and the Bonaparte River arising from the Hat Creek Project.

Regular measurements of the Hg concentration in Hat Creek and the Bonaparte River are continuing using the Ministry of the Environment's methods in order to eventually provide a data base which more accurately represents existing concentrations of the element.

The contributions of trace elements arising from coal stockpiles, overburden and waste rock piles as well as ash disposal sites have been assessed by Beak (Volume 3A, 1979). The projected water quality of the leachates and runoff from these areas was given in Sections 4.4(a) to 4.4(d). With the adoption of the zero discharge approach for all low quality waters (leachates, seepages, mine water and coal pile runoff) many of the previous concerns and potential impact sources are now non-existent. In order to project the probable change in the quality of Hat Creek water during the operation phase a water quality balance was performed by Beak (as previously in Volume 3, 1978). Beak (Volume 3A, 1979) investigated three case situations.

Case 1 - Dry weather condition when the predominant sedimentation lagoon inflow and outflow will be water from dewatering wells. Hat Creek will be at low flow.

Case 2 - Spring runoff condition when the predominant lagoon inflow and outflow will be surface runoff and dewatering activities. Hat Creek flows will be elevated.

Case 3 - Summer rainstorm condition (a 10-year, 24-hour rainfall) when surface runoff to lagoons will be large. Hat Creek flows will be elevated.

The basis of the above water balances have been described in Table 9-14 of Beak (Volume 3A, 1979). The resulting water quality from these balances is given in Tables 4-19 to 4-21.

The projections of water quality for the Bonaparte River and Hat Creek from the various sources has been compared with a number of regulatory agency guidelines for agricultural uses

TABLE 4-19

TRACE ELEMENT WATER QUALITY PROJECTIONS - CASE 1*

Parameter (mg/L)	Projected North Lagoon Effluent	Average Existing Hat Creek	Projected Hat Creek
Arsenic	<0.005	<0.005	<0.005
Boron	<0.10	<0.10	<0.10
Cadmium	<0.005	<0.005	<0.005
Chromium	<0.01	<0.01	<0.01
Copper	<0.005	<0.005	<0.005
Fluoride	0.2	0.16	0.17
Lead	<0.01	<0.01	<0.01
Mercury	<0.0003	<0.0004	<0.0004
Vanadium	<0.006	<0.005	<0.006
Zinc	<0.04	<0.007	<0.01

*Dry Weather Condition (Year 35). The only discharge to Hat Creek via the sedimentation lagoon is the dewatering flows from the pit surficials and from the slide area. Hat Creek discharge assumed to be 0.12 m^3/s.

From Beak (Volume 3A, 1979).

TABLE 4-20

TRACE ELEMENT WATER QUALITY PROJECTIONS - CASE 2*

Parameter (mg/L)	Projected Effluent North Lagoon	Projected Effluent Med. Ck. Lagoon and Rim Reservoir	Average Existing Hat Creek	Projected Hat Creek After Mixing
Arsenic	<0.007	<0.017	<0.005	<0.006
Boron	<0.10	<0.09	<0.10	<0.10
Cadmium	<0.005	<0.005	<0.005	<0.005
Chromium	<0.013	<0.04	<0.01	<0.011
Copper	<0.04	<0.28	<0.005	<0.016
Fluoride	0.17	0.11	0.16	0.16
Lead	<0.01	<0.012	<0.01	<0.01
Mercury	<0.0004	<0.0007	<0.0004	<0.0004
Vanadium	<0.005	<0.006	<0.005	<0.006
Zinc	<0.017	<0.035	<0.007	<0.009

*Spring Runoff Condition (Year 35). Discharges to Hat Creek via the sedimentation lagoon include prorated mean surface runoffs and the dewatering flows from the pit surficials and from the slide area. Hat Creek discharge was assumed to be 0.48 m^3/sec. Surface runoff and dewatering rates are from CMJV estimates. Flow attenuation in the lagoons has been assumed as negligible.

From Beak (Volume 3A, 1979)

TABLE 4-21

TRACE ELEMENT WATER QUALITY PROJECTIONS - CASE 3*

Parameter (mg/L)	Projected Effluent North Lagoon	Projected Effluent Med. Ck. Lagoon	Projected Pit Rim Dam Discharge	Existing Hat Creek	Projected Hat Creek After Mixing
Arsenic	<0.008	<0.03	<0.019	<0.005	<0.007
Boron	<0.10	<0.08	<0.09	<0.10	<0.10
Cadmium	<0.005	<0.004	<0.005	<0.005	<0.005
Chromium	<0.015	<0.05	<0.03	<0.010	<0.013
Copper	<0.07	<0.47	<0.26	<0.005	<0.035
Fluoride	0.16	0.10	0.13	0.16	0.16
Lead	<0.01	<0.014	<0.012	<0.010	<0.012
Mercury	<0.0004	<0.0008	<0.0006	<0.0004	<0.0005
Vanadium	<0.005	<0.007	<0.006	<0.005	<0.006
Zinc	<0.014	<0.052	<0.03	<0.007	<0.01

*Summer Rainstorm Condition (Year 35). Discharges to Hat Creek via sedimentation ponds include surface runoff caused by a 10 year 24 hour rainfall, dewatering flows from pit surficials and from the slide area. Hat Creek discharge was assumed to be 1.68 m^3/s. Surface runoff and dewatering rates are from CMJV estimates. Flow attenuation has been assumed to occur in the lagoons. Discharge from Pit Rim Dam, into which the Medicine Creek sedimentation lagoon overflows, is assumed to be 0.12 m^3/s (pump capacity) into Hat Creek Canal.

From Beak (Volume 3A, 1979).

TABLE 4-22

WATER QUALITY CRITERIA FOR AGRICULTURAL USES (IRRIGATION AND LIVESTOCK WATERING)

ELEMENT	B.C.Pollution Control Branch mg/l (Effluent Quality) *	U.S.E.P.A. 1972 Water Quality Criteria		U.S.E.P.A. 1976 Water Quality Criteria		Min. of Environment Ontario, 1974		Environment Canada Inland Waters Directorate 1979	
		Livestock	Irrigation	Livestock	Irrigation	Livestock	Irrigation	Livestock	Irrigation
ANTIMONY	0.25-1.00								
ARSENIC	tribasic 0.05-0.25 total 0.1-1.0	≤ 0.2 mg/l	≤ 0.10 mg/l for continuous use ≤ 2 mg/l for use up to 20 years.		≤0.10 mg/l for crops	absent - 0.05 mg/l	<1.0-10.0 mg/l	≤0.5 mg/l As	Sensitive crop: ≤0.2 mg/l for sandy loam; ≤1.0 mg/l for clay. Tolerant crop: ≤1.0 mg/l for sandy loam; ≤ 2.0 mg/l for clay.
BERYLLIUM		addressed but no limit recommended	≤0.10 mg/l for continuous use ≤0.50 mg/l for use up to 20 yrs.		≤0.10 mg/l for continuous use ≤0.60 mg/l on neutral-alkaline soils		<0.5-1.0 mg/l		
BORON		≤5.0 mg/l	1-2 mg/l for tolerant and intolerant species ≤2.0 mg/l in alkaline soils up to 20 years.		<0.75 mg/l for long term use on sensitive crops.		0.3-0.5 mg/l		
CADMIUM	0.01-0.1	≤0.05 mg/l	≤0.01 mg/l for continuous use ≤0.05 mg/l for use up to 20 yrs.			absent -0.05 mg/l	≤0.005-0.05 mg/l	≤0.02 mg/l total Cd	≤0.01 mg/l total Cd
CHROMIUM	0.05-0.30	≤1.0 mg/l	≤0.10 mg/l for continuous use ≤1.0 mg/l for use up to 20 yrs.			absent-0.05 mg/l (hexa-valent)	≤5.0 - 2.0 mg/l	≤1.0 mg/l total Cr	≤0.1 mg/l total Cr

TABLE 4-22 - (Cont'd)

WATER QUALITY CRITERIA FOR AGRICULTURAL USES (IRRIGATION AND LIVESTOCK WATERING)

ELEMENT	B.C.Pollution Control Branch mg/l (Effluent Quality)	U.S.E.P.A. 1972 Water Quality Criteria		U.S.E.P.A. 1976 Water Quality Criteria		Min. of Environment Ontario, 1974		Environment Canada Inland Waters Directorate 1979	
		Livestock	Irrigation	Livestock	Irrigation	Livestock	Irrigation	Livestock	Irrigation
COBALT	0.5-1.00	≤1.0 mg/l	≤0.05 mg/l for continuous use ≤5.0 mg/l for use up to 20 yrs.				<0.2-10.0 mg/l		
COPPER	0.05-0.3	≤0.5 mg/l	≤0.20 mg/l for continuous use ≤5.0 mg/l for use up to 20 yrs.				<0.2 mg/l		
FLUORIDE	2.50-10.0	≤2.0 mg/l	≤1.0 mg/l for continuous use ≤1.5 mg/l for use up to 20 yrs.			1.2 - 2.4 mg/l			
LEAD	0.05-0.2	<0.1 mg/l	≤5.0 mg/l for continuous use ≤10 mg/l for use up to 20 yrs			absent- 0.05 mg/l	5.0 - 20 mg/l		
MANGANESE	0.1-1.0	limit of acceptability not necessary	<0.20 mg/l for continuous use ≤10 mg/l for use up to 20 yrs				<2.0 - 20.0 mg/l		
MERCURY	Nil-0.005	<0.01 mg/l						≤0.003 mg/l total Hg	no limit recommended

TABLE 4-22 - (Cont'd)

WATER QUALITY CRITERIA FOR AGRICULTURAL USES (IRRIGATION AND LIVESTOCK WATERING)

ELEMENT	B.C.Pollution Control Branch mg/l (Effluent Quality)	U.S.E.P.A. 1972 Water Quality Criteria		U.S.E.P.A. 1976 Water Quality Criteria		Min. of Environment Ontario, 1974		Environment Canada Inland Waters Directorate 1979	
		Livestock	Irrigation	Livestock	Irrigation	Livestock	Irrigation	Livestock	Irrigation
MOLYBDENUM	0.50-5.0	addressed but no limit recommended	≤0.01 mg/l for continuous use ≤0.05 mg/l for short term use				<0.005 - 0.05 mg/l		
NICKEL	0.2-1.00		≤0.20 mg/l for continuous use ≤2.0 mg/l for use up to 20 yrs.				<0.5 - 2.0 mg/l		
SELENIUM	0.05-0.5	≤0.05 mg/l	maximum concentrations = 0.02 mg/l for continuous use.			absent - 0.01 mg/l	<0.05 - 0.05 mg/l		
SILVER	0.05-0.5								
THALLIUM									
THORIUM									
TIN			excluded by plant: no unit provided						

TABLE 4-22 - (Cont'd)

WATER QUALITY CRITERIA FOR AGRICULTURAL USES (IRRIGATION AND LIVESTOCK WATERING)

ELEMENT	B.C.Pollution Control Branch mg/l (Effluent Quality)	U.S.E.P.A. 1972 Water Quality Criteria		U.S.E.P.A. 1976 Water Quality Criteria		Min. of Environment Ontario, 1974		Environment Canada Inland Waters Directorate 1979	
		Livestock	Irrigation	Livestock	Irrigation	Livestock	Irrigation	Livestock	Irrigation
TUNGSTEN			excluded by plants no limit provided						
URANIUM	as UO_2 2.00-5.0								
VANADIUM		≤ 0.1 mg/l	≤0.10 mg/l for continuous use ≤1.0 mg/l for use up to 20 yrs.				<200 - 500 mg/l		
ZINC	0.2-1.0	≤25 mg/l	≤2.0 mg/l for continuous use ≤10.0 mg/l for use up to 20 yrs.				<10.0 - 10.0 mg/l		

*Guidelines taken from PCB Guidelines.

(irrigation and livestock). The agencies and guideline concentrations are shown in Table 4-22. The livestock guidelines have been applied for those which are presumed to be acceptable by wildlife. Projected receiving water quality in the Bonaparte River as a result of stack emissions meets all regulatory agency criteria for use in crop irrigation and livestock watering.

The results of Beak's (Volume 3A, 1979) three case assessments of water quality from coal and waste disposal areas have also been compared with the guidelines shown in Table 4-22. The lagoon effluent quality in Case 1 meets the lowest Pollution Control Branch objectives, for Case 2 elevated levels of Cu from the Medicine Creek sedimentation lagoon effluent may be possible. Predictions indicate somewhat elevated levels of copper could be expected from the Medicine Creek sedimentation lagoon discharge in Case 3. Once diluted with other runoff entering the pit rim reservoir, the Cu levels in the discharge to Hat Creek would be reduced. The Cu concentration may, however, still exceed the lower range of (0.05 mg/L) suggested by the Pollution Control Branch.

In all three cases there are predictions of marginal increases in trace element concentrations for Hat Creek. Comparison of these projections with the levels suggested for irrigation and livestock watering (Table 4-22) shows that all predicted concentrations meet the respective guideline levels.

Livestock and most wild animals will be restricted from drinking lagoon and reservoir waste waters. Birds, especially waterfowl, have been observed using such areas for watering and staging sites (Dvorak and Lewis et al., 1978). Besides drinking the water, waterfowl at Hat Creek could be expected to ingest trace elements through the consumption of sediments. Geese and ducks for example, eat sediment materials because of the detritic

organics and certain types of aquatic macrophytes that are concentrated in the sediments. The sediments in the reservoir and lagoons are expected to contain high levels of trace elements which could contribute significantly to the total body burdens of waterfowl using these areas. It is anticipated, however, that periodic measurements of selected trace elements in lagoon sediments will be performed to monitor any changes.

(e) Fish and Other Aquatic Life

Projected trace element concentrations for the Bonaparte River and Hat Creek have been given in Tables 4-18 to 4-22 in the previous section. These predictions have been compared with the recommended criteria for the protection of fish and other aquatic life shown in Table 4-23. The effluent guidelines of the Pollution Control Branch do not apply as the concerns for aquatic life are for receiving water quality and not effluent water quality. The guideline criteria are expressed as either absolute recommended quantities or as an application factor value. The latter factor is to be used in the multiplication of the 96-hour LC50* for the most sensitive species in the receiving water system of the fish species described in the Hat Creek studies (Beak, Fisheries and Benthos Study, 1977). Rainbow trout were the dominant species. This species is a member of the salmonid family and has been found to be one of the most sensitive to toxic trace elements (Section 4.2). Consequently, if the predicted trace element concentrations are suitable for habitation by rainbow trout the remainder of the aquatic organisms in Hat Creek and the Bonaparte River should be protected.

* LC50 means concentration that is lethal to 50 percent of the test organisms in 96 hours.

WATER QUALITY CRITERIA FOR FISH AND OTHER AQUATIC LIFE

TABLE 4-23

ELEMENT	AGENCY				
	B.C. Pollution Control Branch (Effluent Quality) 1979.	U.S.E. P.A. 1972 Water Quality Criteria	U.S.E.P.A. 1976 Quality Criteria for Water	Min. of the Environment Ontario 1974	Environment Canada Inland Water Directorate 1979
Antimony	NA	0.02x96.h LC50 for most sensitive species and > 0.2mg/l hazard in marine environments			
Arsenic	NA	x0.01 96-h LC50 for most sensitive species; ≥ 0.05 mg/l hazardous; < 0.01 mg/l acceptable in marine environments.	0.05 mg/l for domestic water should be safe for aquatic life.	0.01x 96-h LC50; ≤ 0.01 mg/l under any circumstances.	≤ 0.05 mg/l
Beryllium	NA	<0.1mg/l minimal risk; ≥1.5 mg/l hazardous	0.01 mg/l in soft water; 1.1 mg/l in hard water.		
Boron	NA	x0.1 96-h LC50 for most sensitive species and > 5.0 mg/l hazardous; ≤5.0mg/l acceptable in marine environments	in the order of naturally occuring concentrations are acceptable. (NO.01 mg/l)		
Cadmium	NA	hard water (100 mg/l $CaCO_3$) 0.03 -0.003 mg/l soft water (<50 mg/l $CaCO_3$) 0.004-0.0004 mg/l	for salmon: 0.0004mg/l in soft H_2O; 0.0012mg/l in hard H_2O for others: 0.004mg/l in soft H_2O; 0.012 mg/l in hard H_2O	0.002 x 96-h LC50	0.002 mg/l as total Cd
Chromium	NA	<0.05 mg/l at any time or place	0.1 mg/l	0.01 x 96-h LC50	0.04 mg/l as total Cs
Cobalt	NA				
Copper	NA	0.1 x 96-h LC50	0.1 x 96 h LC50	/0.083x96-h LC50; for continuous exposure, 3-7% of 96-h LC50	
Fluorine	NA	0.1x96-h LC50 for most sensitive species; >1.5 mg/l hazardous, ≤0.5 mg/l minimal risk		/0.5x96-h LC50 at any time or place	

... 2/

TABLE 4 - 23 - (Cont'd)

WATER QUALITY CRITERIA FOR FISH AND OTHER AQUATIC LIFE

ELEMENT	AGENCY				
	B.C. Pollution Control Branch (Effluent Quality) 1979.	U.S.E. P.A. 1972 Water Quality Criteria	U.S.E.P.A. 1976 Quality Criteria for Water	Min. of the Environment Ontario 1974	Environment Canada Inland Water Directorate 1979
LEAD	NA	≤0.03 mg/l at any time or place	0.01 x 96-h LC50	24-h average ≠0.01 x 96-h LC50	
MANGANESE	NA	0.02x96-h LC50 for most sensitive species; >0.1 mg/l hazardous, ≤0.02 mg/l minimal risk in marine environments.			
MERCURY	NA	≤0.5 mg/kg body burden; ≤0.2 µg/l at any time or place, average ≤0.05 µg/l	≤ 0.00005 mg/l	discharges should be avoided	0.0001 mg/l for protection of fish consumers 0.0002 mg/l to protect aquatic life
MOLYBDENUM	NA	0.05x96-h LC50 for most sensitive species; 24 hour average ≤0.02x96-h LC50 in marine environments.			
NICKEL	NA	0.02x96-h LC50 for most sensitive species	0.01x96-h LC50	≠0.02x96-h LC50 at any time or place.	
SELENIUM	NA	0.01 x 96-h LC50 for most sensitive species; ≥ 0.01 mg/l hazardous, ≤0.005 mg/l acceptable in Marine environments.	0.01 x 96-h LC50		
SILVER	NA	≠0.05x96-h LC50 for most sensitive species; ≥0.005 mg/l hazardous, ≤0.001 mg/l acceptable in marine environments.			

TABLE 4-23 - (Cont'd)

WATER QUALITY CRITERIA FOR FISH AND OTHER AQUATIC LIFE

ELEMENT	AGENCY				
	B.C. Pollution Control Branch (Effluent Quality) 1979.	U.S.E. P.A. 1972 Water Quality Criteria	U.S.E.P.A. 1976 Quality Criteria for Watdr	Min. of the Environment Criteria for Water	Environment Canada Inland Water Directorate 1979
THALLIUM		≥0.1 mg/l hazardous; ≤0.05 mg/l acceptable in marine environments.			
THORIUM					
TIN					
TUNGSTEN					
URANIUM	NA	0.01 x 96-h LC50 for most sensitive species; >0.5 mg/l hazardous, ≤0.1 mg/l acceptable in marine environments.			
VANADIUM		∱ 0.05 x 96-h LC50 in marine environments			
ZINC	NA	≤ 0.005 x 96-h LC50	≤0.01 x 96-h LC50 for sensitive resident species	∱ 0.01 x 96-h LC50 at any time or place.	

The hardness of the receiving waters in the Hat Creek and the Bonaparte River is relatively high. On the basis of absolute amounts all of the predicted trace element concentrations in the Bonaparte River (Table 4-18) with the exception of mercury are below the guideline criteria shown in Table 4-23. Mercury levels, for example, are approximately an order of magnitude higher than those recommended.

The criteria for certain elements, however, are also expressed as application factors to be used in multiplying the 96-hour LC50. These elements include: antimony, arsenic, cadmium, chromium, copper, fluorine, lead, manganese, molybdenum, nickel, selenium, silver, uranium, vanadium and zinc. The application factors for these elements are given in Table 4-23. Applying these factors to the 96-hour LC50 data for rainbow trout and other species of comparable sensitivity, as discussed in Section 4.2, yielded "acceptable" concentration ranges shown in Table 4-24. Comparison of these limits with the attendant estimations of trace element content in the Bonaparte River shows that these latter values are lower than the calculated acceptable ranges presented in Table 4-24. Many trace elements were at least an order of magnitude below the calculated safe levels including As, Sb, B, Cd, Cr, Cu, Mn, Mo, Ni, Sc, Ag, U and V. Some projected trace element levels were in the same range as the calculated acceptable values including F, Pb and Zn. This information suggests that F, Pb and Zn may pose potential toxicity problems to indigenous fish life as a result of trace element emissions from all sources.

It must be kept in mind that the above calculations of projected trace element concentrations in the Bonaparte River resulting from powerplant stack emissions arising from the Hat Creek Project are conservative estimates in view of the assumptions made (Section 4.6(d)). Projected Hg concentrations

TABLE 4-24

TRACE ELEMENT SAFE CONCENTRATIONS DERIVED FROM 96-HOUR LC50 DATA AND GUIDELINE APPLICATION FACTORS.

Element	Guideline Application Factors (Table 4.6.5.1)	96-Hour LC50 data for fish in Hardwater (mg/L)	Species*	Acceptable Concentration Range (mg/l)
Antimony (Sb)	0.02	17.0	fathead minnow	0.34
Arsenic (As)	0.01	11.0	fathead minnow	0.11
Boron (B)	0.1	3600-5600	mosquito fish	360-560
Cadmium (Cd)	0.002	7.2	fathead minnow	0.01
Chromium (Cr)	0.01	27.3	fathead minnow	2.73
Copper (Cu)	0.083-0.10	0.33	rainbow trout	0.03-0.033
Fluorine (F)	0.1-0.5	>5.0	rainbow trout	0.5-2.5
Lead (Ph)	0.01	0.14-4.1	rainbow and brook trout	0.014-0.41
Manganese (Mn)	0.02	>10.0	rainbow trout.	0.20
Molybdenum (Mo)	0.05	37.	fathead minnow	18.50
Nickel (Ni)	0.01-0.02	24-44.5	fathead minnow	0.24-0.89
Selenium (Se)	0.01	NAD**	-	-
Silver (Ag)	0.05	0.1-1.0	rainbow trout	0.005-0.05
Uranium (U) (as UO_2)	0.01	135	fathead minnow	1.35
Vanadium (V)	0.05	NAD	-	-
Zinc (Zn)	0.005-0.01	4.21-7.21	rainbow trout	0.021-0.072

*Fathead minnows and brook trout are included as they have shown similar sensitivities as rainbow trout to trace elements.

**NAD - no applicable data.

are, therefore, actually higher in the Bonaparte River than one would reasonably anticipate resulting from stack emissions. It is not logical to assume, for example, that all of the deposited Hg would eventually find its way into the aquatic ecosystem. Mercury will be accumulated in various environmental receptors which will affect the ultimate amounts of the element entering the aquatic environment (Appendix, B-12).

Few data are available alluding to the complex behaviour of Hg in the natural environment. Huckabee and Blaylock (1974) have, however, attempted to describe the redistribution of the element resulting from coal combustion.

According to Huckabee and Blaylock (1974) as much as 50 percent of the Hg emitted from coal combustion may find its way into aquatic systems where 99 percent of this value accumulates in sediments. Huckabee and Blaylock's (1974) figures have been used in the further analysis of projecting more realistic impressions of Hg concentrations in the Bonaparte River resulting from stack emissions of the Hat Creek Project. By using Huckabee and Blaylock's (1974) factors the final projected concentration of Hg in the Bonaparte River is ≤0.0521 µg/L (Table 4-25). This level compares favourably with the EPA's recommended average guideline value of 0.05 µg/L (Table 4-23). The projected concentration is also below the 0.10 to 0.20 µg/L range recommended for the protection of fish consumers and aquatic life respectively (Environment Canada, 1979, Table 4-23). The projected increase in Hg concentration is minor being 4.2 percent.

TABLE 4-25

CALCULATION OF FINAL MERCURY CONCENTRATIONS (µg/L)
IN THE BONAPARTE RIVER RESULTING FROM POWERPLANT
EMISSIONS FROM THE HAT CREEK PROJECT

[1]Contributions From Stack Emissions (µg/L)	Amount (µg/L) Reaching Water Column (50%)	Amount (µg/L) Entering Sediments From Water Column (99%)	Final Amount (µg/L) Remaining in Water Column (0.21-0.2079)	Existing Hg Concentration (µg/L) in the Bonaparte River	Projected Concentration (µg/L) in the Bonaparte River
0.42	0.21	0.2079	0.0021	<0.05	≤0.0521

Note: Percentage factors taken from Huckabee and Blaylock (1974).

[1] Table 4-17

4.7 SELECTION OF TRACE ELEMENTS FOR CONTINUING DETAILED ENVIRONMENTAL STUDIES

Based on the present information available, the expected increases in trace elements in the areas surrounding the powerplant are not expected to cause any significant impacts on the aquatic or terrestrial biota including crops and livestock. Certain elements have been identified that are readily mobile in ecosystems or are widely distributed or that display relatively high toxicity to biotic receptors. Other elements are, conversely, relatively immobile and have low toxicity or may be emitted in low quantities.

The following section identifies those elements of concern with respect to the Hat Creek Project. It is implicit that the elements identified will be included in any monitoring schemes suggested.

(a) Rationale

The parameters that have determined a specific element's significance to the biotic receptors of Hat Creek and other environments are listed below, as well as the element's volatility, ambient concentration, mobility, methylation potential, toxicity and bioaccumulation. Each element is assessed individually on the basis of these parameters and a recommendation with regards to monitoring is made.

Antimony
- volatilized during coal combustion, will be widely distributed in the environment
- projected receptor concentrations are low, it is moderately toxic to all organisms but not at the concentrations projected. It is relatively immobile in food chains. Monitoring should not be required

Arsenic
- volatilized during coal combustion, will be widely distributed
- mobile in alkaline soils, methylated by soils and sediments, mobility through food chains
- severely toxic to plants, moderately toxic to animals

4.7 SELECTION OF TRACE ELEMENTS FOR CONTINUING DETAILED ENVIRONMENTAL STUDIES - (Cont'd)

- water is most common transfer route to wildlife
- should be monitored in both the aquatic and terrestrial environments

Beryllium

- volatilized during coal combustion
- widely distributed
- relatively immobile in alkaline soils
- not readily translocated in plants
- moderately toxic to plants and animals but not at levels projected
- monitoring should not be required

Boron

- only a small percentage is emitted from the stack
- not widely distributed
- accumulated by plants
- relatively immobile in soils
- low toxicity to animals
- interacts with fluorine in plants
- should be monitored in terrestrial plants due to its potential interaction with F

Cadmium

- volatilized during coal combustion
- widely distributed
- accumulated by animals
- relatively toxic to mammals, more toxic to fish
- moderately toxic to plants
- accumulated by plants
- should be monitored in both the aquatic and terrestrial environments

Chromium

- small amount emitted upon coal combustion
- widely distributed
- plants can accumulate large amounts without injury
- hexavalent Cr accumulated by animals
- can be mobile in soils in the hexavalent form
- relatively toxic to animals
- should be monitored in both the aquatic and terrestrial environments

Cobalt

- small amount emitted during coal combustion
- not widely distributed
- immobile in alkaline soils
- not readily accumulated in plants
- can accumulate in animals

4.7 SELECTION OF TRACE ELEMENTS FOR CONTINUING DETAILED ENVIRONMENTAL STUDIES - (Cont'd)

- moderately toxic to fish, can be severely toxic to animals but not at projected levels
- monitoring should not be required

Copper

- small percentage emitted during coal combustion
- widely distributed
- readily accumulated by plants and animals
- relatively toxic to plants and animals especially fish
- relatively immobile in alkaline soils
- should be monitored in both the aquatic and terrestrial environments

Fluorine

- volatilized during coal combustion and emitted in relatively large quantities, high in concentration for Hat Creek coal
- widely distributed
- readily taken up by aerial portion of plants
- toxic to herbivorous species if they ingest highly contaminated vegetation, can cause fluorosis
- much less toxic to fish than heavy metals
- relatively immobile in alkaline soils
- should be monitored but only in the terrestrial environment, especially plants

Lead

- volatilized during coal combustion
- widely distributed
- can be taken up by plants from the atmosphere
- accumulated by animals
- methylated in aquatic sediments
- relatively toxic to fish
- relatively immobile in soil
- should be monitored in both the aquatic and terrestrial environments

Manganese

- small amount emitted from coal combustion
- not widely distributed
- relatively immobile in soils
- readily absorbed by plants
- less toxic to fish and animals than heavy metals
- monitoring should not be required

Mercury

- volatilized during coal combustion
- widely distributed
- methylated in soils, plants and sediments

- relatively immobile as inorganic form in soils
- methylmercury biomagnifies in food chains
- very toxic to plants and animals
- should be monitored in both the aquatic and terrestrial environments

Molybdenum

- volatilized during coal combustion
- widely distributed
- mobile in alkaline soils
- accumulated by plants and animals but not in edible tissues
- low toxicity to plants and animals
- monitoring should not be required

Nickel

- volatilized during coal combustion
- widely distributed
- relatively immobile in soils
- not readily accumulated by animals but plants accumulate the metal
- relatively toxic to plants and animals especially fish
- should be monitored in both the aquatic and terrestrial environments although projected concentrations are low

Selenium

- volatilized during coal combustion
- widely distributed
- mobile in alkaline soils
- readily accumulated by plants and is toxic to them
- accumulated by animals
- relatively nontoxic to animals
- monitoring should not be required although the element's tendency to be mobile in alkaline soils should be remembered

Silver

- small amount emitted during coal combustion
- not widely distributed
- not readily accumulated by plants or animals
- very toxic to fish but not at projected levels
- immobile in alkaline soils and not readily accumulated by plants
- monitoring should not be required

Thallium

- volatilized during coal combustion
- widely distributed
- accumulates in animals and is quite toxic
- toxic to plants

4.7 SELECTION OF TRACE ELEMENTS FOR CONTINUING DETAILED ENVIRONMENTAL STUDIES - (Cont'd)

- presumed to be as toxic as Cu to fish
- relatively immobile in alkaline soils
- amounts of Tl emitted and projected in receptors are so low monitoring should not be required

Thorium

- small percentage emitted from coal combustion
- immobile in alkaline soils
- not readily accumulated by plants or animals
- moderately toxic to plants and animals
- monitoring should not be required

Tin

- small percentage emitted from coal combustion
- relatively immobile in alkaline soils
- methylated in sediments
- accumulated by plants and animals
- moderately toxic to animals
- may enter food chains in the methylated form but its fate is not completely understood
- should be monitored in both the aquatic and terrestrial environments due to its potential for movement in the food chain and because of discrepancies in Sn measurements from inventory studies

Tungsten

- small amount emitted from coal combustion
- not widely distributed
- relatively immobile in soils and virtually excluded by plants
- not usually found in animal tissues
- moderately toxic to animals
- monitoring should not be required

Uranium

- small amount emitted from coal combustion and from mine dust
- widely distributed
- soluble in water as UO_2^{2+})
- mobile in alkaline soils as uranyl ion - UO_2^{2+}
- accumulated by plants and animals as UO_2
- moderately toxic to animals as UO_2
- should be monitored in both the aquatic and terrestrial environments in view of its mobility and radio activity

Vanadium

- volatilized during coal combustion
- widely distributed
- accumulated by plants but mostly in roots
- relatively mobile in alkaline soils

- readily absorbed by animals from the gut
- should be monitored but only in the terrestrial environment in view of its mobility

Zinc
- small amount emitted during coal combustion
- widely distributed
- relatively immobile in alkaline soils
- readily accumulated by plants and animals
- relatively non-toxic to birds and mammals but may be very toxic to fish
- should be monitored in both the aquatic and terrestrial environments

(b) Monitoring

The previous section presented a short précis of the individual trace elements and a recommendation regarding monitoring. The following 13 elements are suggested for monitoring in biotic receptors during plant operation: arsenic, boron, cadmium, chromium, copper, fluorine, lead, mercury, nickel, tin, uranium, vanadium and zinc.

Receptor monitoring has been previously addressed by ERT (Appendix F, 1978). Their report described suggested receptor locations as well as the trophic levels to be monitored. It was pointed out that:

> "By focusing monitoring efforts on vegetation and major abiotic receptors such as water, soil and stream sediment, a sufficient data base can be obtained to evaluate effects of mining and powerplant activities in the Hat Creek area. Furthermore, since the primary intake of trace elements by animals is via the food chain (initiating, of course, with producers), trace element investigations on vegetation will provide a basis for postulating impacts to animals. Accordingly, the following receptors that were sampled in the initial baseline program should be considered for use in the monitoring program:

4.7 SELECTION OF TRACE ELEMENTS FOR CONTINUING DETAILED ENVIRONMENTAL STUDIES - (Cont'd)

Terrestrial	Aquatic
Soil	Water
Grass	Stream sediment
Shrubs	
Lichens	"

ERT's (Appendix F, 1978) perception of what a monitoring program should investigate appears to be adequately defined although there are some additions suggested. There is no proposed monitoring of any animals in the terrestrial ecosystem. In view of the potential for trace element entry into waterfowl and herbivorous species monitoring of wildlife and perhaps domestic animals is also recommended. Carnivorous animals should also be considered as they reside at the top of the terrestrial food chain. For the aquatic system, notable trophic levels absent in the proposed ERT monitoring scheme are primary producers (algae, macrophytes, etc.) and fish, both carnivorous and herbivorous forms. To provide a complete monitoring program the above elements are recognized essentials. Consideration should be given to the above for constructing a monitoring program with regards to trace element emissions arising from the Hat Creek Project.

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APPENDIX A

ANALYSES OF HAT CREEK COALS

FROM DDH-74-025

K. Fletcher

2 April 1976

Analyses of Hat Creek Coals

K. Fletcher
April 2nd, 1976

Introduction

Twenty-four coal samples from diamond drill hole 74-025, together with five composites from the same hole, have been analyzed for Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn by atomic absorption spectrophotometry and for Mo by colorimetry. X-ray fluorescence was used to provide a semi-quantitative check for the presence of As and Se.

Analytical methods

Powdered coal samples, received from Commercial Testing and Engineering Co. Ltd., were analyzed by the following methods.

1) Atomic absorption:

2.000 g samples were weighed into porcelain crucibles, ignited for 3 hours at 550°C in a muffle furnace, and then allowed to cool and reweighed to determine the ash content. 0.500 g of the resulting ash was transferred to a teflon dish and evaporated to dryness with 5 ml HF and 2.5 ml of 4:1 HNO_3-$HClO_4$ acids mixture. The residue was dissolved by warming with 6 ml of 6 M HCl, transferred to a 25 ml volumetric flask and diluted to volume with distilled water. Solutions were then analyzed by atomic absorption, against standards prepared in 1.5 M HCl, for Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn.

To provide an estimate of the accuracy of the method, National Bureau of Standards Coal 1632 was also analyzed. Results, summarized in Table 1, are judged to be satisfactory. Duplicate analyses of Hat Creek coals (Table 2) suggest that analytical precision is probably generally better than ± 10% of the amount present.

2) Determination of molybdenum:

A number of problems were encountered in the determination of molybdenum and several different methods were tried. The following procedure, given in detail after Table 8, was finally chosen. 1.000 g coal samples were weighed into a Ni crucible and ignited in a muffle furnace at 600°C for 3 hours. The ash was then mixed with a Na_2CO_3-NaCl-Na_2O_2 flux and fused at 900°C for 30 minutes. After cooling the melt was leached overnight with water, filtered into a volumetric flask and Mo determined spectrophotometrically as its thiocyanate complex.

No standard coal is available for Mo: results of duplicate analyses are summarized in Table 3.

3) X-ray fluorescence:

To check for the presence of abnormal concentrations of As or Se the powdered coal samples were loaded directly into sample holders for the Phillips PW1540 X-ray spectrometer. Secondary fluorescence was excited with a Mo source tube and scanned, using a LiF analyzing crystal, between 25° and 36°2Ø. The As and Se $K_{\alpha 2}$ lines are at 34.04° and 31.96° 2Ø respectively.

4) Estimation of "sulphide" metals:

As a guide to the proportions of Cu, Ni, Pb, Zn and Fe present as sulphides (or carbonates and any other readily leachable forms) coals were leached using a sulphide selective method. 0.2 g of $KClO_3$ crystals are mixed with 0.200 g of powdered coal, and 2 ml of HCl (concentrated) added. The nascent chlorine generated oxidises sulphides to sulphates. After 30 minutes the solution is diluted to 10 ml with distilled water and analyzed by atomic absorption.

Results

Se and Cd were not detected in any of the samples and concentrations are probably less than 5 and 0.2 ppm respectively. Semi-quantitative estimates of As content range from <5 to 25 ppm and Br, although not deliberately sought for, appears to range from <10 ppm up to at least 130 ppm (Table 4).

Results for the remaining elements are listed individually in Tables 5, 6 and 8, and are summarised in Table 7. In general trace metal concentrations are relatively uniform and are well within the range of values to be expected in geological materials of this type. A relatively high proportion of all the elements investigated with the sulphide selective leach appear to be present as sulphides or some other relatively labile form.

The one very striking exception to the general uniformity of the data is the abnormally high Cu (4700 ppm) and Mo (20.0 ppm) content of sample #25-24. Similar concentrations were also found in the composite sample #25-404 which represents 95 feet of core and includes the footage of sample #25-24. All the Cu is extracted from these two samples with the sulphide selective leach (Table 8) and a heavy mineral separate, prepared from #25-404 with bromoform (SG 2.9), was found to consist mainly of tarnished chalcopyrite ($CuFeS_2$).

Discussion

On the basis of results obtained for hole 74-25 the trace elements most likely to present environmental problems are Cu and Mo. Cu concentrations in samples 25-24 and 25-404 are comparable to those in many porphyry copper deposits! In the corresponding ash, concentrations are between 0.8 and 1% Cu.

Environmental problems could arise in a number of ways:

1) oxidation of the chalcopyrite causing acidity and the release of Cu into surface or groundwaters;

2) leaching of Cu from ash waste dumps;

3) Cu-toxicity to vegetation growing on waste dumps preventing or hindering re-vegetation;

4) high uptake of Cu by vegetation (from either coal or ash) resulting in a potential toxicity hazard to wildlife or livestock;

5) settling of Cu-rich fly ash or blown dust onto vegetation resulting in a potential toxicity hazard to wildlife or livestock.

Furthermore, assuming the coal contains 0.5% Cu all of which is present as chalcopyrite, it seems likely that the analysis of 0.14% for "pyritic" sulphur is sample 25-404 is too low. S contents may therefore be higher in some coals than the available data indicate .

In view of the remarkably high Cu content of the 95 ft. composite 25-404, considerably more work is needed to determine the full extent, mineralogy and chemistry of the Cu-rich zone. The effects of combustion on the distribution of Cu and its availability to plants should be examined. The possibility of economically separating and recovering the copper may have to be considered if the Cu-rich zone is sufficiently extensive.

Mo also presents a potential environment hazard in that concentrations in the ash (Table 6) and to a lesser extent the coal, are within the range associated with molybdenosis in cattle. A problem could arise in two ways:

1) uptake of abnormally high Mo values (>3 ppm dry weight) by forage grown on ash dumps

2) direct ingestion of Mo-rich dust from the surface of vegetation.

Further studies should therefore be made of distribution of Mo and of factors likely to influence its uptake by plants grown on waste materials.

Of the remaining elements it seems unlikely that concentrations of Cd,

Co, Fe, Ni, Pb and Zn would present any particular environmental hazard unless they were greatly concentrated at some stage during combustion. The same is probably true of As and Se. However because of their volatile character, and in the case of Se some uncertainty as to the amount present, both these elements warrant further study. Data is also required for Hg and F.

K. Fletcher

Table 1. Comparison of recommended values and results obtained in this study for NBS Coal - 1632 (all values in ppm unless otherwise indicated)

Element	Recommended value	This study
Cd	0.19 ± 0.3	nd
Cu	18 ± 2	16
Mn	40 ± 3	31
Ni	15 ± 1	15
Pb	30 ± 9	35
Zn	37 ± 4	33
Fe (%)	0.87 ± 0.03	0.63

Table 2. Duplicate analyses of coal samples (values in ppm unless otherwise indicated)

Element	Sample # 25-3		25-5		25-39		25-402	
Cu	43	42	50	50	49	48	50	52
Mn	680	673	179	175	206	209	210	238
Ni	53	53	46	45	53	53	53	55
Pb	3	7	7	7	6	9	4	6
Zn	53	53	75	70	60	61	55	55
Fe (%)	2.77	2.71	1.75	1.90	2.32	2.24	1.86	1.93

TABLE 3: Duplicate Mo analyses

Sample #	Mo content (ppm)	
25-11	2.6	3.0
25-33	2.6	2.5
25-63	2.5	2.6
15278	1.9	1.8

Table 4. Semi-quantitative estimates of As and Br by X-ray fluorescence

Sample #	As (ppm)	Br (ppm)
25-1		
-3	nd	85
-5	nd	55
-7	10	>130
-9	15	105
11	nd	85
13	10	85
15	nd	nd
17	15	>115
19	10	130
24	5	60
27	nd	65
30	20	90
33	25	>120
36	15	130
39	nd	65
42	15	80
45	10	55
48	20	>110
51	25	>110
54	10	20
57	10	25
60	15	15
63	10	50

Table 5. Trace element and ash content of Hat Creek coals (all values in ppm unless otherwise indicated)

Sample #	Cu	Mn	Ni	Pb	Zn	Fe(%)	Ash (%)
25-1	18	24	12	nd	8	0.22	14.0
25-3	43	680	53	3	53	2.77	45.1
25-5	50	179	46	7	75	1.75	52.6
25-7	29	565	25	2	30	2.43	31.4
25-9	41	206	45	9	43	1.79	41.7
25-11	44	660	51	8	53	2.65	45.0
25-13	48	218	46	12	52	2.11	50.3
25-15	55	370	48	7	61	2.42	55.4
25-17	40	164	44	4	30	1.27	22.8
25-19	62	410	41	9	65	2.07	43.9
25-24	4782	380	50	nd	77	3.51	54.3
25-27	52	192	52	10	60	2.27	59.9
25-30	28	13	30	4	21	0.42	21.2
25-33	41	184	29	5	33	1.11	30.7
25-36	54	403	40	7	63	2.06	43.8
25-39	49	206	53	6	61	2.32	59.3
25-42	57	64	44	11	43	0.99	54.6
25-45	33	202	28	4	28	1.06	27.5
25-48	40	45	30	3	21	0.49	25.2
25-51	39	44	29	4	21	0.49	25.4
25-54	21	213	16	nd	15	0.59	20.0
25-57	15	320	13	nd	12	0.50	15.0
25-60	23	120	20	nd	17	0.47	18.7
25-63	30	21	24	4	28	1.16	23.0
25-401	52	73	43	6	35	1.17	36.6
25-402	50	210	53	4	55	1.86	53.3
25-404	4150	407	50	nd	83	3.66	58.1
25-406	54	215	42	4	49	1.93	44.7
25-411	39	326	11	3	18	0.89	19.1

Table 6. Mo content (ppm) of Hat Creek coals.

Sample #	Dry coal	Coal ash*
25-1	1.4	10.0
-3	3.1	6.9
-5	2.7	5.1
-7	1.9	6.1
-9	2.8	6.7
-11	2.6	5.8
-13	2.7	5.4
-15	2.6	4.7
-17	2.8	12.3
-19	3.5	8.0
-24	20.0	36.8
-27	2.6	4.3
-30	2.5	11.8
-33	2.6	8.5
-36	3.6	8.2
-39	2.5	4.2
-42	2.4	4.4
-45	2.7	9.8
-48	3.1	12.3
-51	3.2	12.6
-54	2.4	12.0
-57	4.3	28.7
-60	2.3	12.3
-63	2.5	10.9
401	3.3	9.0
402	2.6	4.9
404	21.2	36.5
406	2.8	6.3
411	2.0	10.5

* Calculated from ash contents in Table 5.

Table 7. Summary of trace element content of 24 Hat Creek coal samples from hole 74-25 (all values in ppm unless otherwise indicated).

Element	Average	Range
Cu	39 (4782)*	15 - 62
Mn	245	13 - 680
Ni	36	12 - 53
Pb	6	nd - 12
Zn	40	8 - 77
Mo	2.7 (20.0)	1.4 - 4.3
Fe (%)	1.54	0.22 - 3.51

* Values in parentheses excluded.

Table 8. 'Sulphide' trace elements leached from whole coal with potassium-chlorate + hydrochloric acid (all values in ppm unless otherwise indicated)

Sample #	Cu	Ni	Pb	Zn	Fe (%)
25-1	18	11	-	10	0.11
25-3	40	39	8	34	2.33
25-5	48	26	7	45	1.08
25-7	25	21	-	25	2.81
25-9	41	33	-	29	1.49
25-11	40	37	-	28	2.34
25-13	43	37	6	33	1.77
25-15	54	25	-	36	2.05
25-17	33	31	-	19	0.87
25-19	61	32	-	48	2.01
25-24	5667	42	-	49	3.25
25-27	50	31	-	38	2.05
25-30	25	21	-	13	0.22
25-33	40	21	-	26	1.06
25-36	55	25	-	50	1.97
25-39	50	30	-	42	2.05
25-42	85	37	-	36	1.61
25-45	67	34	-	28	0.72
25-48	38	19	-	15	0.35
25-51	37	19	-	15	0.35
25-54	22	7	-	9	0.41
25-57	13	9	-	8	0.42
25-60	23	13	-	11	0.36
25-63	25	18	-	21	1.08
25-401	52	29	-	19	0.59
25-402	48	37	9	31	1.32
25-404	4583	39	-	55	3.81
25-406	48	34	-	38	1.65
25-411	40	6	-	15	0.92

Determination of Mo in coals

Reagents

1) Fusion mixture: grind and mix 100 g Na_2CO_3 (AR) and 80 g NaCl (AR)
2) Sodium peroxide:
3) 95% ethanol:
4) HCl: concentrated
5) Thiocyanate solution (5%): dissolve 5 g sodium thiocyanate in water
6) Stannous chloride (10%): dissolve 10 g stannous chloride in 100 ml 2M HCl - prepare fresh each day
7) Iron solution: dissolve 1 g hydrated iron ammonium sulphate with 0.5 ml H_2SO_4 in 100 ml water
8) Isopropyl ether:

Method

1) Weigh 1 g powdered coal sample into a Ni-crucible and ash in a muffle furnace at 600°C for 3 hours
2) Mix ash with 2.0 g of fusion mixture: add 0.25 g sodium peroxide (use scoop), mix rapidly and fuse at 900°C for 30 minutes
3) Cool and add 10 ml water and a few drops of ethanol. Leave to stand overnight
4) Break up the residue with a teflon rod, heat on a sandbath and filter into a 100 ml volumetric flask calibrated at 50 ml.
5) Wash the residue with hot water and add washings to filtrate
6) Bring volume up to 50 ml with water: add 10 ml HCl shaking to liberate CO_2
7) Add 1 ml iron solution and mix
8) Add 3 ml thiocyanate solution and mix
9) Add 2 ml stannous chloride solution and mix
10) After 30 seconds add 4 ml isopropyl ether, stopper and shake for 30 seconds
11) Allow the organic phase to separate and then carefully add water to bring the organic phase into the neck of the volumetric flask
12) Compare visually against standards or measure absorbance at 465 nm on a spectrophotometer

Standards Transfer 0, 1, 2, 3, 4, 5, 7.5 and 10 ug Mo to 100 ml volumetric flasks: proceed from 6) above.

K. Fletcher

APPENDIX B

TRACE ELEMENT CONCENTRATIONS IN HAT CREEK RECEPTORS AND NATURALLY OCCURRING LEVELS IN SELECTED ECOSYSTEM COMPONENTS

APPENDIX B

TRACE ELEMENT CONCENTRATIONS IN HAT CREEK RECEPTORS AND NATURALLY OCCURRING LEVELS IN SELECTED ECOSYSTEM COMPONENTS

CONTENTS

Section	Subject	Page
B.1	ANTIMONY	B - 1
B.2	ARSENIC	B - 2
B.3	BERYLLIUM	B - 3
B.4	BORON	B - 4
B.5	CADMIUM	B - 5
B.6	CHROMIUM	B - 6
B.7	COBALT	B - 7
B.8	COPPER	B - 8
B.9	FLUORINE	B - 9
B.10	LEAD	B - 10
B.11	MANGANESE	B - 11
B.12	MERCURY	B - 12
B.13	MOLYBDENUM	B - 13
B.14	NICKEL	B - 14
B.15	SELENIUM	B - 15
B.16	SILVER	B - 16
B.17	THALLIUM	B - 17
B.18	THORIUM	B - 18
B.19	TIN	B - 19
B.20	TUNGSTEN	B - 20
B.21	URANIUM	B - 21
B.22	VANADIUM	B - 22
B.23	ZINC	B - 23

B.1 ANTIMONY (Sb)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0022 mg/l	ERT,Appendix F,1978.	<0.00033 mg/l	Bowen, 1966
Soils	<0.57 mg/kg	ERT,Appendix F,1978.	<0.43 mg/kg	Ecology Consultants 1975.
Vegetation	<0.29-0.57 mg/kg	ERT,appendix F,1978	0.06 mg/kg <0.22 mg/kg	Bowen, 1966 Ecology Consultants,1975.
Aquatic Vegetation (algae)			2.0-6.0 mg/kg	Rehwoldt et al., 1975.
Animals (excluding fish)	<0.33 mg/kg	ERT,Appendix F,1978	0.14 mg/kg	Bowen, 1966.
Fish	<0.10 mg/kg	ERT,Appendix F,1978	0.005-0.10 mg/kg 0.001 mg/kg	Lucas, et al., 1970 Rancitelli et al., 1967
			0.002-0.004 mg/kg	Rancitelli et al., 1968

B.2 ARSENIC (As)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0022-0.05 mg/l <0.005 mg/l	ERT, Appendix F,1979 Beak, Volume 2, 1978	0.001 - 0.05 mg/l, rivers 90% <0.008 mg/l 0.0005-0.02 mg/l, lakes <0.00001-0.0012, Great Lakes 0.0004 mg/l	Demayo et al., 1979 " " Bowen, 1966.
Sediment	6.5-34.5 mg/kg	ERT, Appendix F,1978	0.5-14 mg/kg	Demayo et al., 1979
Soils	4.87-93.4 mg/kg 5.8-8.3 mg/kg 8.92 mg/kg	ERT, Appendix F,1978 B.C.Hydro Env.Studies 1978, 1979.	1.1-16.7 mg/kg 0.2-40 mg/kg	" Walsh and Keeney, 1975
Vegetation	0.6-7.0 mg/kg 0.5-1.57 mg/kg 0.55-8.92 mg/kg	ERT,Appendix F, 1978 B.C.Hydro Env.Studies 1978, 1979.	0.2 mg/kg 0 - 10 mg/kg 0.5 mg/kg 0.1-1.0 mg/kg	Bowen, 1966 Chapman, 1966. Underwood, 1971 Ecology Consultants,1975.
Animals (excluding fish)	1.85-2.66 mg/kg	ERT, Appendix F,1978	<0.2 mg/kg <0.45 mg/kg, deer mice	Bowen, 1966. Ecology Consultants,1975.
Fish	0.43-1.95 mg/kg	ERT, Appendix F,1978.	< 3 mg/kg 0.03-0.12 mg/kg 0.2-0.5 mg/kg	Underwood, 1971 Demayo et al., 1979 Munro, 1976.

B.3 BERYLLIUM (Be)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.0009 mg/l	ERT,AppendixF, 1978	<0.001 mg/l <0.001 mg/l	Bowen, 1966. Drury et al., 1979
Sediment	<0.23 mg/kg	ERT, Appendix F, 1978	2.0-3.0 mg/kg	Drury et al., 1979
Soils	<0.41 mg/kg	ERT, Appendix F, 1978.	0.1-40 mg/kg	Bowen, 1966.
	0.43 - 1.9 mg/kg	B.C. Hydro Env. Studies	6.0 mg/kg	Vinogradov, 1959.
	8.92 mg/kg	1978, 1979.	0.34-3.1 mg/kg	Ecology Consultants, 1975.
Vegetation	0.13-0.21 mg/kg 0.01-0.23 mg/kg 0.02-0.22 mg/kg	ERT, Appendix F, 1978 B.C.Hydro Env. Study 1978, 1979	<0.1 mg/kg	Bowen, 1966.
Animals (excluding fish)	0.19 mg/kg	ERT, Appendix F, 1978.	0.0003-0.002 mg/kg in soft tissues.	Bowen, 1966.
Fish	<0.18 mg/kg	ERT, Appendix F, 1978.		

B.4 BORON (B)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.031 mg/l	ERT,Appendix F,1978	0.013 mg/l 0.01 mg/l	Bowen, 1966. Valkovic, 1975.
Sediment	4.92 mg/kg	ERT,Appendix F,1978		
Soils	8.93 mg/kg 15.0-18.1 mg/kg 5.4 mg/kg 1.8-20.4 mg/kg 6.75-21.95 mg/kg	ERT,Appendix F,1978 B.C. Hydro Env.Study 1978, 1979 B.C.Hydro Env.Studies 1978, 1979	0.5 mg/kg 10 mg/kg, range 2-100 mg/kg highest levels found in saline and alkaline soils 20-35 mg/kg	Temple et al., 1978 Bowen, 1966. Ecology Consultants,1975.
Vegetation	2.01-39.33 mg/kg	ERT, Appendix F,1978	50 mg/kg 120 mg/kg, fruits of different plants 2550 mg/kg, legumes 1.5 mg/kg, cereal and hay	Bowen, 1966. Valkovic, 1975 Underwood, 1971 Underwood, 1971
Animals (excluding (Fish)	0.77 mg/kg	ERT, Appendix F,1978	0.5 mg/kg 0.51-1.0 mg/l cow milk	Bowen, 1966 Underwood, 1971
Fish	1.30 mg/kg	ERT, Appendix F,1978		

B.5 CADMIUM (Cd)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0013-0.005 mg/l <0.005 mg/l	ERT,Appendix F,1978 Beak, Vol. 2, 1978	0.08 mg/l 0.0006 mg/l <0.02 mg/l	Bowen, 1966 Mathis & Cummings 1973 Enk and Mathis, 1977
Sediment	0.38-2.83 mg/kg	ERT,Appendix F,1978.	0.08-0.23 mg/kg 0.1-2.0 mg/kg 2.0 mg/kg	Enk and Mathis, 1977 Peyton and McIntosh 1974 Mathis & Cummings,1973
Soils	0.58-6.18 mg/kg 0.10-0.43 mg/kg	ERT,Appendix F,1978 B.C.Hydro Env. Studies 1978, 1979	0.06 mg/kg 0.15-0.20 mg/kg 1.5 mg/kg 0.55 mg/kg 1.0 mg/kg	Bowen, 1966 Fleischer, et al., 1974 Ecology Consultants,1975 Heit, 1977 Mills & Zwarich,1975.
Vegetation	0.2-0.56 mg/kg	ERT,Appendix F,1978	0.60 mg/kg 0.1-1.0 mg/kg, food plants 0.16-1.9 mg.kg	Bowen, 1966. Gough & Shacklette,1976. Ecology Consultants, 1975.
Invertebrates			0.22-1.98 mg/kg	Mathis & Cummings, 1973
Animals (excluding fish)	0.27-0.46 mg/kg	ERT,Appendix F,1978	0.5 mg/kg 0.04-0.14 mg/kg deer mice	Bowen, 1966 Ecology Consultants,1975.
Fish	0.10 - 0.26 mg/kg	ERT,Appendix F, 1978	0.01-0.142 mg/kg 0.05-0.32 mg/kg 0.6 - 1.1 mg/kg	Lovett et al., 1972 Enk and Mathis, 1977 Mathis and Cummings,1973

B.6 CHROMIUM (Cr)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.002-0.012 mg/l <0.01 mg/l	ERT,Appendix F,1978 Beak, Vol. 2, 1978	0.08 mg/l <0.0002 - 0.34 mg/l 0.001-0.01 mg/l	Bowen, 1966 WQB, 1978 NAS, 1974
Sediment	77.38 - 285.75 mg/l	ERT,Appendix F,1978	18-140 mg/kg	Leland et al., 1978
Soils	46.2-247.07 mg/kg	ERT,Appendix F,1978	12.6-20.3 mg/kg 16-46 mg/kg 250 mg/kg as CrO, higher in igneus rocks, shales and clays and phosphorites	Singh and Steinnes,1976. Ecology Consultants,1975 NAS, 1974.
Vegetation	1.53-5.50 mg/kg 1.0-9.67 mg/kg 0.73-3.95 mg/kg	ERT,Appendix F,1978 B.C. Hydro Env. Studies	0.02-0.08 mg/kg for food consumption 0.59, hay 39-48 mg/kg, lichens and grasses 4.9-7.6 mg/kg, higher plants, trees, shrubs 6.5 - 180 mg/kg 0.03-1.0 mg/lg 0.31-0.65 mg/kg	NAS, 1974. Vinogradov, 1959 " " Ecology Consultants,1975 Pratt, 1966 Singh and Steinnes, 1976.
Animals (excluding fish)	3.6-4.92 mg/kg	ERT,Appendix F,1978	0.075 mg/kg 0.02-0.33 mg/kg	Bowen, 1966. Ecology, Consultants,1975.
Fish	2.10-5.34 mg/kg	ERT,Appendix F,1978	<0.02 mg/kg 0.48-0.50 mg/kg 0.21 mg/kg	Rancitelli et al., 1967 Rehwoldt et al., 1975 Rehwoldt et al., 1976

B.7 COBALT (Co)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.004 mg/l	ERT, Appendix F,1978	0.0009 mg/l 0.0058 mg/l	Bowen, 1966. Valkovic , 1975.
Sediment	12.67 mg/kg	ERT, Appendix F,1978	5.0-35 mg/kg	Leland et al., 1978.
Soils	12.93 mg/kg 12.0 - 18.0 mg/kg 25.67 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978,1979	1-40 mg/kg 13 mg/kg 2.3 mg/kg	Allaway, 1968. Horton et al., 1977 Klein and Russell, 1973.
Vegetation	0.31 - 2.15 mg/kg 0.04 - 3.93 mg/kg 0.08-0.56 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	0.5 mg/kg <1.0 mg/kg 0.26 - 2.6 mg/kg 0.2-1.1 mg/kg	Bowen, 1966. Chapman, 1966 Ecology Consultants, 1975 Horton et al., 1977
Animals (excluding fish)	0.96 mg/kg	ERT, Appendix F, 1978	0.03 mg/kg 0.02-0.22 mg/kg 0.02-0.33 mg/kg, deer mice	Bowen, 1966 Underwood, 1971 Ecology Consultants, 1975.
Fish	0.34 mg/kg	ERT, Appendix F, 1978	0.006-0.014 mg/kg <0.02 mg/kg in salmon liver 0.03 - 0.21 mg/kg	Rancitelli et al., 1968 Rancitelli et al., 1967 Rehwoldt et al., 1976

B.8 COPPER (Cu)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.0008-0.01 mg/l <0.005 mg/l	ERT, APPENDIX F, 1978 Beak, Volume 2, 1978	0.01 mg/l 0.00083-0.00105 mg/l 0.015 mg/l, average	Bowen, 1966. Valkovic, 1975 USEPA, 1976
Sediment	25.20-33.67 mg/kg	ERT, Appendix F,1978	1-476 mg/kg 100-200 mg/kg	Leland et al., 1978 Wisseman and Cook, 1978
Soils	28.20 - 47.13 mg/kg 50-58.3 mg/kg 50.67 mg/kg	ERT, Appendix F, 1978 B.C.Hydro Env. Studies, 1978, 1979	2-100 mg/kg 7-61 mg/kg 2.15 mg/kg 4.0-300 mg/kg 6 33 mg/kg	Allaway, 1968. Mills and Zwarich, 1975. Chapman, 1966. Gough and Shacklette, 1976 Ecology Consultants,1975
Vegetation	7.33-35.53 mg/kg 5.5 - 31.33 mg/kg 5-16.67 mg/kg	ERT,Appendix F,1978 B.C. Hydro Env. Studies, 1978, 1979	5-20 mg/kg 14 mg/kg 1.3-20 mg/kg	Chapman, 1966 Bowen, 1966 Ecology Consultants, 1975.
Animals (excluding fish)	42.54 - 58.20 mg/kg	ERT, Appendix F,1978	2.4 mg/kg 1.9 - 7.5 mg/kg	Bowen, 1966. Ecology Consultants, 1975.
Fish	3.10-4.33 mg/kg	ERT,Appendix F, 1978	0.27-21.84 mg/kg kidney and liver 0.12 - 1.14 mg/kg muscle 0.77-1.56 mg/kg	Brown and Chow 1977. Kelso and Frank, 1974.

B.9 FLUORINE (F)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.10-0.545 mg/l	ERT, Appendix F, 1978	0.01 - 0.02 mg/l 1.0 mg/l 0.14-1.12 mg/l	Carpenter, 1969 Bowen, 1966 Harbo et al., 1974
Sediment	194.5-461.25 mg/kg	ERT, Appendix F, 1978.	540-620 mg/kg, marine environment	Acres, 1978
Soils	186.0-528.4 mg/kg 273-470 mg/kg 287.5 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	0.3-2.25 mg/kg 20 - 500 mg/kg 30-300 mg/kg 200 mg/kg	Temple et al., 1978 Weinstein, 1977 Allaway, 1968 Bowen, 1966
Vegetation	20.47 - 1448.25 mg/kg 10-157 mg/kg 1.77-10.63 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	3-12 mg/kg 0.5-40 mg/kg 20-700 mg/kg	Temple et al., 1978 Bowen, 1966 Ecology Consultants, 1975.
Animals (excluding fish)	51.0-118.0 mg/kg	ERT, Appendix F, 1978	5-70 mg/kg, herbivores 5 mg/kg carnivores 1-16 mg/kg, birds 150 - 500 mg/kg, soft tissues 1500 mg/kg, bone	Kay et al., 1975 " Stewart et al., 1974 Bowen, 1966 "
Fish	17.0 - 94.22 mg/kg	ERT, Appendix F, 1978		

B.10 LEAD (Pb)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.05 - 0.064 mg/l <0.01 mg/l	ERT,Appendix F.1978 Beak, Volume 2,1978	0.001-0.01 mg/l <0.02 mg/l 0.005 mg/l 0.006-0.095 mg/l	USEPA, 1976 Enk and Mathis 1977 Bowen, 1966 Atchison et al., 1977
Sediment	3.0 -4.4 mg/kg	ERT,Appendix F,1978	5-3,423 mg/kg, all sources, range, largely. 5-810 mg/kg 200-900 mg/kg	Leland et al., 1977 Atchison et al., 1977
Soils	2.0 - 7.73 mg/kg 7.7 - 9.5 mg/kg 12.67 mg/kg	ERT,Appendix F,1978 B.C. Hydro Env. Studies, 1978,1979	1-356 mg/kg 2-200 mg/kg 5-50 mg/kg	Wilking, 1978 USEPA, 1976 Van Hook et al., 1977
Vegetation	4.04 - 30.33 mg/kg 3-53.33 mg/kg 1-31.67 mg/kg	ERT,Appendix F,1978 B.C. Hydro Env. Studies, 1978,1979	1-9 mg/kg 10-40 mg/kg 14-160 mg/kg 0.4 mg/kg	Wilkings, 1978 Underwood, 1971 Ecology Consultants, 1975 Waldron and Stofen, 1974
Animals (excluding fish)	3.46-5.2 mg/kg	ERT,Appendix F,1978	2 mg/kg 0.03 mg/kg 0.2-0.4 mg/kg	Bowen, 1966 Weldron and Stofen, 1974 Underwood, 1971
Fish	2.22-3.10 mg/kg	ERT,Appendix F,1978	1.25-4.81 mg/kg 0.1-1.3 mg/kg 1.3-4.2 mg/kg 0.05-6.76 mg/kg	Pagenkopf and Neuman, 1974 Gajan and Larry, 1972 Atchison et al., 1977 Brown and Chow, 1977

B.11 MANGANESE (Mn)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.012 mg/l	ERT,Appendix F, 1978	<1.0 mg/l <1.0 mg/l	McKee and Wolf, 1963 USEPA, 1973
Sediment	847.50 mg/kg	ERT,Appendix F, 1978	20-220 mg/kg	Leland et al., 1978
Soils	945.33 mg/kg	ERT,Appendix F, 1978	100-4000 mg/kg 200-3000 mg/kg	Allaway, 1968 Horton et al., 1977
Vegetation	150.33 - 222.67 mg/kg	ERT,Appendix F, 1978		
Animals (excluding fish)	4.0 mg/kg	ERT, Appendix F,1978	50-100 mg/kg	Prosser, 1973
Fish	17.56 mg/kg	ERT, Appendix F, 1978	0.32 - 1.0 mg/kg 0.02-0.25 mg/kg	Brooks et al., 1976 Koli et al., 1978

B.12 MERCURY (Hg)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.001-0.0001 mg/l	ERT,Appendix F,1978	0.0008 mg/l	Bowen, 1966
	<0.0004 mg/l	Beak, Volume 2, 1978	0.00004 mg/l	Kothny, 1973.
	0.00005-0.00007 mg/l	B.C. Ministry of the Environment (1980)		
Sediment	0.10-0.14 mg/kg	ERT, Appendix F, 1978	0.07-0.10 mg/kg	D'Itri, 1972
			0.001 mg/kg	Reeder et al., 1979
			0.01-1.78 mg/kg	Leland et al., 1978
			0.025-1.0 mg/kg	Norstrom et al., 1973
			9.8 - 288 mg/kg, industrial areas	Batti et al., 1975
Soils	0.09 - 0.18 mg/kg	ERT, Appendix F, 1978	0.02 - 1.0 mg/kg	Kothny, 1973
	0.055-0.07 mg/kg	B.C. Hydro Env.	0.2-5.0 mg/kg	Allaway, 1968
	0.057 mg/kg	Studies, 1978, 1979	0.01-0.06 mg/kg	Warrow and Delavault, 1967
			0.03-0.8 mg/kg	Chapman, 1966
Vegetation	0.07-1.32 mg/kg	ERT, Appendix F, 1978	0.1-0.7 mg/kg	Kothny, 1973
	0.055-0.90 mg/kg	B.C. Hydro Env.	0.09-0.15 mg/kg	Wallin, 1976
	0.039-0.45 mg/kg	Studies, 1978, 1979	0.5-3.5 mg/kg in high Hg areas	U.S. Geological Survey,1970
			0.015 mg/kg	Bowen, 1966
Animals (excluding fish)	0.03 - 0.33 mg/kg	ERT, Appendix F, 1978	0.5 mg/kg	Palmer et al., 1973
			0.045 mg/kg	Bowen, 1966
			0.05 - 0.07 mg/kg, deer mice	Ecology Consultants, 1975.
Fish	0.05-0.39 mg/kg	ERT, Appendix,F, 1978	0.03-0.15 mg/kg muscle	Brown and Chow, 1977
			0.06-0.54 mg/kg, liver kidney	
			0.11-1.13 mg/kg	Summer et al., 1972
			0.02-0.63 mg/kg	Koli et al., 1977
			0.1-0.25 mg/kg	Aronson et al., 1976
			0.02-0.18 mg.kg	Underwood, 1971

B.13 MOLYBDENUM (Mo)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0011 mg/l <0.02	ERT, Appendix F, 1978 Beak, Volume 2, 1978	0.03 - 0.13 mg/l	Dvorak et al., 1978
Sediment	1.64 mg/kg	ERT, Appendix F, 1978		
Soils	2.87 mg/kg 1-3 mg/kg 1.33 mg/kg	ERT Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	0.2-5.0 mg/kg 2.9-141.2 mg/kg 0.6-3.5 mg/kg	Allaway, 1968 Sharma and Shupe, 1977 Horton et al., 1977
Vegetation	0.14 - 6.13 mg/kg 1 - 5.7 mg/kg 1 - 1.67 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	0.2-5.0 mg/kg 2.9 - 141.2 mg/kg 0.6 - 3.5 mg/kg	Allaway, 1968 Sharma and Shupe, 1977 Horton et al., 1977
Animals (excluding fish)	4.27 mg/kg	ERT,Appendix F, 1978	9.9-17.5 mg/kg, bones 3.9-9.6 mg/kg,soft tissues	Sharma and Shupe, 1977
Fish	4.22 mg/kg	ERT, Appendix F, 1978		

B.14 NICKEL (Ni)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0092 mg/l	ERT,Appendix F,1978	0.01 mg/l	Bowen, 1966
Sediment	84.0 mg/kg	ERT,Appendix F, 1978	40 - 200 mg/kg 1 - 135 mg/kg	Wisseman and Cook, 1978 Leland et al., 1978
Soils	45.53 mg/kg	ERT, Appendix F, 1978	10 - 1000 mg/kg 18-145 mg/kg 5 - 500 mg/kg 16 - 5,000 mg/kg	Allaway, 1968 Mills & Zwarich, 1975 Bowen, 1966 Chapman, 1966.
Vegetation	4.02-8.13 mg/kg	ERT,Appendix F, 1978	0.05-5 mg/kg 3 mg/kg 4-134 mg/kg 250 - 6000 mg/kg plants on serpentine soils 0.15 - 0.35 mg/kg, tubers, fruits, grains	NAS,1975 Chapman, 1966 NAS, 1975 Underwood, 1971
Animals (excluding fish	4.8 mg/kg	ERT, Appendix F, 1978	0.8 mg/kg 0.02 - 4.5 mg/kg	Bowen, 1966 Schroeder et al., 1962
Fish	2.87 mg/kg	ERT, Appendix F, 1978	<0.20 mg/kg	Uthe and Bligh, 1971

B.15 SELENIUM (Se)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0023 mg/l <0.003 mg/l	ERT, Appendix F,1978 Beak, Volume 2,1978	0.001 - 0.006 mg/l 0.001 - 0.40 mg/l 0.05 -0.30 mg/l	Adams and Johnson, 1977 Lakin, 1973 USEPA, 1976
Sediment	2.04 mg/kg	ERT, Appendix F, 1978	0.1-1.0 mg/l	Adams and Johnson, 1977
Soils	2.18 mg/kg 1.0 - 2.0 mg/kg <1.0 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	0 - 2.3 mg/kg 0.2 mg/kg 0.01 - 80 mg/l 0.1 - 1200 mg/l	Sharma and Shupe, 1973 Chapman, 1966 Trelease, 1945 Lakin, 1973
Vegetation	0.39 - 3.09 mg/kg 0.2 - 2.3 mg/kg 0.23-0.37 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	1.4 - 3.3 mg/kg	Sharma and Shupe, 1977
Animals (excluding fish)	0.69 mg/kg	ERT, Appendix F, 1978	8.9 - 53.0 mg/kg	Sharma and Shupe, 1977
Fish	0.69 mg/kg	ERT, Appendix F, 1978	0.33 - 2.66 mg/kg 0.04 - 2.0 mg/kg 0.95 - 4.6 mg/kg, fish meat 0.32 - 1.85 mg/kg, wet weight 1.52 - 9.95 mg/kg, dry weight	Pratt et al., 1972 Beal, 1974 Lakin, 1973 Adams and Johnson, 1977

B.16 SILVER (Ag)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0011 mg/l	ERT, Appendix F, 1978	rarely detected above 1 µg/l	USEPA, 1973
Sediment	4.28 mg/kg	ERT, Appendix F, 1978	<0.5 mg/kg	Leland et al., 1978
Soils	<0.60 mg/kg	ERT, Appendix F, 1978	2.8-31 mg/kg	Ragaini et al., 1977
Vegetation	0.19 - 0.21 mg/kg	ERT, Appendix F, 1978	0.8 - 1.02 mg/kg in uncontaminated areas 0.9 - 18 mg/kg in contaminated areas	Ragaini et al., 1977
Animals (excluding fish)	<0.25 mg/kg	ERT, Appendix F, 1978		
Fish	1.96 mg/kg	ERT, Appendix F, 1978	<0.001 mg/kg	Rancitelli et al., 1968

B.17 THALLIUM (Tl)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	< 0.0011 mg/l	ERT, Appendix F,1978	0.00001 mg/l	Bowen, 1966
Sediment	< 0.27 mg/kg	ERT, Appendix F, 1978		
Soils	0.31 mg/kg	ERT, Appendix F, 1978	0.1 mg/kg	Bowen, 1966
Vegetation	0.13 - 0.21 mg/kg	ERT, Appendix F, 1978	2 - 100 mg/kg, trees and shrubs 1 mg/kg spinach and rye	Gough and Shacklette, 1976
Animals (excluding fish)	0.19 mg/kg	ERT, Appendix F, 1978	20.4 mg/kg	Bowen, 1966
Fish	0.18 mg/kg	ERT, Appendix F, 1978		

B.18 THORIM (Th)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0065 mg/l	ERT, Appendix F, 1978	usually not detected	Russell and Smith, 1966
Sediment	<0.27 mg/kg	ERT, Appendix F, 1978		
Soils	<0.31 mg/kg	ERT, Appendix F, 1978		
Vegetation	0.13 - 0.21 mg/kg	ERT, Appendix F, 1978		
Animals (excluding fish)	<0.19 mg/kg	ERT, Appendix F, 1978		
Fish	<0.18 mg/kg	ERT, Appendix F, 1978	<0.2 µg/kg	Lucas et al., 1970

B.19 TIN (Sn)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0616 mg/l	ERT, Appendix F, 1978	0.001 - 0.017 mg/l 0.04 mg/l	Peterson et al., 1976 Bowen, 1966
Sediement	data not reliable	B.C. Hydro Trace Element Report 1979		
Soils	data not reliable	B.C. Hydro Trace Element Report 1979	2-200 mg/kg, strongly absorbed by humus	Bowen, 1966
	<1.0 mg/kg 1.0 mg/kg	B.C. Hydro Env. Studies, 1978, 1979	0.4 - 1.5 mg/kg	Ecology Consultants,1975
Vegetation	data not reliable	B.C. Hydro Trace Element Report, 1979	0.3 mg/kg, higher in lichens	Bowen, 1966
	<1.0 mg/kg <1.0 mg/kg	B.C. Hydro Env. Studies, 1978, 1979	1.4 - 2.4 mg/kg, mangroves (uncontaminated) 9.4 - 15.0 mg/kg, mangroves contaminated 32 mg/kg, lichen	Peterson et al., 1976
Animals (excluding fish)	data not reliable	B.C. Hydro Trace Element Report, 1979	0.15 mg/kg 0.16 mg/kg	Bowen, 1966 Ecology Consultants, 1975
Fish	data not reliable	B.C. Hydro Trace Element Report, 1979	0.55 - 5.43 mg/kg wet weight (industrialized area)	Uthe and Blight, 1971

B.20 TUNGSTEN (W)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0014 mg/l	ERT, Appendix F, 1978		
Sediment	<0.27 mg/kg	ERT, Appendix F, 1978		
Soils	<0.27 mg/kg	ERT, Appendix F, 1978	9.0 mg/kg, enriched soils 1.3 mg/kg, crustal rock	Ragaini et al., 1977 Wedepohl, 1968
Vegetation	<0.13 - 0.21 mg/kg	ERT, Appendix F, 1978	not detectable	Ragaini et al., 1977
Animals (excluding fish)	<0.19 mg/kg	ERT, Appendix F, 1978		
Aquatic invertebrates			<0.005 mg/kg ash	Fukai and Meinke, 1959
Fish	<0.18 mg/kg	ERT, Appendix F, 1978	<0.008 mg/kg ash 0.029 - 0.042 mg/kg	Fukai and Meinke, 1959 Fukai and Meinke, 1962

B.21 URANIUM (U)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	<0.0055 mg/l	ERT, Appendix F, 1978		
Sediment	<3.50 mg/kg	ERT, Appendix F, 1978		
Soils	<3.60 mg/kg <0.50 mg/kg 0.83 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979		
Vegetation	0.73 - 1.20 mg/kg <0.10 mg/kg <1.0 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	100 mg/kg	Cannon, 1960
Animals (excluding fish)	<0.30 mg/kg	ERT, Appendix F, 1978		
Fish	<0.18 mg/kg	ERT, Appendix F, 1978	1.0 - 3.0 mg/kg, wet weight industrialized area 3.0 µg/kg 0.021 mg/kg	Uthe and Blight, 1971 Lucas et al., 1970 Aten et al., 1961

B.22 VANADIUM (V)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.0002 - 0.0059 mg/l <0.005 mg/l	ERT, Appendix F, 1978 Beak, Volume 2, 1978		
Sediment	61.75-154.0 mg/kg	ERT, Appendix F, 1978		
Soils	59.20-297.60 mg/kg 173-195 mg/kg 195.8 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978, 1979	100 mg/kg, in humus alkaline soils 16 - 59 mg/kg 20 - 500 mg/kg 62 mg/kg	Bowen, 1966 Ecology Consultants, 1975. Allaway, 1968 Horton et al., 1977
Vegetation	0.30 - 3.47 mg/kg 0.40 - 6.8 mg/kg 0.80 - 38.5 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies 1978, 1979	0.18-8.90 mg/kg 1.60 mg/kg 0.27 - 4.2 mg/kg <1.0 mg/kg 2.4 mg/kg	Ecology Consultants, 1975 Bowen, 1966 Chapman, 1966 Ruhling and Tyler, 1973 Horton et al., 1977
Animals (excluding fish)	<0.25 mg/kg	ERT, Appendix F, 1978	0.1 mg/kg 0.15 mg/kg 0.01-0.59 mg/kg	Prosser, 1973 Bowen, 1966 Ecology Consultants, 1975
Fish	0.35 - 0.82 mg/kg	ERT, Appendix F, 1978	<0.5 mg/kg ash	Fukai and Meinko, 1959

B.23 ZINC (Zn)

RECEPTOR CONCENTRATIONS

Receptor	Hat Creek	References	Natural Components	References
Water	0.0162 - 0.05 mg/l <0.007 mg/l	ERT, Appendix F, 1978 Beak, Volume 2, 1978	0.0009 - 0.293 mg/l 0.01 mg/l	Atchison et al., 1977 Bowen, 1966
Sediment	29.08 - 94.75 mg/kg	ERT, Appendix F, 1978	10 - 3500 mg/kg 300 - 102 mg/kg	Leland et al., 1978 Wisseman and Cook, 1978
Soils	99.20 - 147.13 mg/kg 139-148 mg/kg 139.67 mg/kg	ERT, Appendix F, 1978 B.C. Hydro Env. Studies, 1978,1979	54.4 - 666.7 mg/kg 10 - 300 mg/kg 31 - 350 mg/kg 260 mg/kg	Sharma and Shupe, 1977 Allaway, 1968 Mills and Zwarich, 1975 Strojan, 1978
Vegetation	22.07-223.21 mg/kg 18 - 60 mg/kg 24.83 - 38.5 mg/kg	ERT, Appendix,F,1978 B.C. Hydro Env. Studies 1978, 1979	20.2 - 141.4 mg/kg 0.2 - 36 mg/kg 53.1 - 66.7 mg/kg 30 - 102 mg/kg	Sharma and Shupe, 1977 VanHook et al., 1977 Barclay-Estrup and Rinne, 1978 Jackson et al., 1978
Animals (excluding fish)	81.84 - 124.67 mg/kg	ERT, Appendix F, 1978	106.8 - 384.3 mg/kg, soft tissues 134-364.5 mg/kg, bone 95.8 - 191.6 mg/kg	Sharma and Shupe, 1977 Johnson et al., 1978
Fish	69.50 - 81.11 mg/kg	ERT, Appendix F, 1978	86-480 mg/kg 2.85 - 9.20 mg/kg, wet weight (muscle) 6.51 - 54.46 mg/kg, liver, kidney 0.02 - 0.59 mg/kg	Atchison et al., 1977 Brown and Chow, 1977 Koli et al., 1978

APPENDIX C

LITERATURE REVIEW OF THE ENVIRONMENTAL CONSEQUENCES OF TRACE ELEMENT REDISTRIBUTION

APPENDIX C

LITERATURE REVIEW OF THE ENVIRONMENTAL CONSEQUENCES OF TRACE ELEMENT REDISTRIBUTION

CONTENTS

Section	Subject	Page
C.1	ANTIMONY	C - 1
C.2	ARSENIC	C - 2
C.3	BERYLLIUM	C - 7
C.4	BORON	C - 11
C.5	CADMIUM	C - 14
C.6	CHROMIUM	C - 21
C.7	COBALT	C - 27
C.8	COPPER	C - 30
C.9	FLUORINE	C - 38
C.10	LEAD	C - 50
C.11	MANGANESE	C - 58
C.12	MERCURY	C - 61
C.13	MOLYBDENUM	C - 79
C.14	NICKEL	C - 80
C.15	SELENIUM	C - 86
C.16	SILVER	C - 93
C.17	THALLIUM	C - 95
C.18	THORIUM	C - 97
C.19	TIN	C - 99

CONTENTS - (Cont'd)

Section	Subject	Page
C.20	TUNGSTEN	C - 101
C.21	URANIUM	C - 102
C.22	VANADIUM	C - 105
C.23	ZINC	C - 108

TABLES

Table No.		
C-1	The Tolerance of Crop Species to Arsenic	C - 5
C-2	Toxic Boron Concentrations of Saturation Extracts for Sensitive, Semitolerant and Tolerant Crop Species	C - 13
C-3	96-hour LC_{50} of Copper for Various Fish Species	C - 35
C-4	Relationship between Fluorine Content of the Diet and the Development of Various Symptoms in Cattle	C - 43
C-5	Dietary Fluoride Tolerance for Domestic Animals	C - 44
C-6	96-hour LC_{50} of Lead for Various Fish Species	C - 55
C-7	Distribution of Mercury in Mammals	C - 64
C-8	96-hour LC_{50} of Nickel for Various Fish Species	C - 85
C-9	96-hour LC_{50} of Zinc for Various Fish Species	C - 115

APPENDIX C

LITERATURE REVIEW OF THE ENVIRONMENTAL CONSEQUENCES OF TRACE ELEMENT REDISTRIBUTION

A general introduction to the consequences of trace elements entering the environment has been given in Section 4.2. This Appendix is intended to provide the most recent assessment of trace element toxicity in the environment based upon an extensive literature survey as well as the reports previously prepared by ERT.

Each of the 23 elements selected for detailed study is addressed in this Appendix. Cited articles may be located in Section 4.8, References.

C.1 ANTIMONY (Sb)

There is little known of the ecological effects of Sb. Antimony has been shown to be enriched in soils near industrial smelting operations (Ragaini et al., 1977). Antimony in these soils was not evenly distributed as concentrations of the element showed a sharp decrease with depth (Ragaini et al., 1977). This suggests that Sb movement in soils is limited. The consequences of soil enriched in antimony are unknown although quantities of it may be found in various species of vegetation (Ecology Consultants, Inc., 1975). Concentrations of Sb in mammals, deer, mice and others, are reported to be in the range of 0.03 to 0.14 mg/kg (Ecology Consultants Inc., 1975; Bowen, 1966).

Bowen (1966) reports that the lethal dose of various chemical forms of Sb to kill 20 percent of the test population (LD_{20}) of a variety of mammalian species ranges from about 20 to 4000 mg/kg. In mammals, Antimony is slowly absorbed from the gastrointestinal tract,

C.1 ANTIMONY - (Cont'd)

trivalent forms concentrate in the red blood cells and the liver, and are slowly excreted in the feces. Pentavalent forms accumulate mainly in the blood plasma, liver and spleen, and are primarily released through the urine (Belilles, 1975). In man, the chronic effects of Sb uptake are unknown but it has been suggested that a relationship between antimony and pulmonary carcinogenisis based on a possible antimony-containing abnormal enzyme system may exist (Belilles, 1975). This may be consistent with Bowen's (1966) view that Sb exerts its toxicity by acting as an antimetabolite. It is also generally considered as moderately toxic to all organisms.

In marine environments Sb can be concentrated by various marine organisms to over 300 times the amount present in sea water (Goldberg, 1957). Background concentrations of Sb in fresh water are quite low (Bowen, 1966).

Few studies of Sb toxicity in aquatic organisms have been conducted. Tarzwell and Henderson (1956, 1960), however, observed that the 96-hour LC50 (concentration that kills 50 percent of the test animals within 96 hours) of Sb for fathead minnows (Pimephales promelas) in soft water was 9 mg/L and 17 mg/L in hardwater. Cellular division of green algae was hindered at 3.5 mg/L and 9 mg/L retarded the movement of Daphnia (Bringmann and Kuhn, 1959). Concentrations of 5 mg/L $SbCl_3$ or $SbCl_5$ in soft water, however, did not affect rainbow trout (Salmo gairdneri), Bluegill (Lepomis macrochirus) or sea lamprey (Petromyzon marinus) (Applegate et al., 1957). Projectile vomiting in large mouth bass (Micropterus salmoides) was caused by 1.0 mg/L Sb in the form of tartar emetic (Jernejcic, 1969).

C.2 ARSENIC (As)

Arsenic is one of the more volatile trace elements and is distributed from coal combustion in the vapour phase as well as

C.2 ARSENIC - (Cont'd)

absorbed onto particulates of submicron size. Such particles are inhaled to the alveolar portions of the lung where the As may enter the bloodstream (Natusch and Wallace et al., 1974). Arsenic dust inhalation or As ingestion may induce gastrointestinal and respiratory tract inflammation, skin lesions, degeneration of body organs, hemorrhage and lung congestion (Masek and Hais, 1965).

Arsenic is ubiquitous in the environment ocurring in various forms. Generally, trivalent arsenic compounds (arsenite) are more toxic than the pentavalent compounds (arsenate). The latter compounds, in nature, are more common than the former (Heit, 1977).

Water appears to be the most common transfer route of As to wildlife (ERT, Appendix F, 1978). Some may be transmitted from soils into certain species of plants that are known to accumulate the element (Porter and Peterson, 1975). The lethal dose for animals is believed to be approximately 44 mg/kg body weight (Luh et al., 1973). The following arsenic doses have been listed for farm animals: poultry, 0.05 to 0.1 g per bird; dogs, 0.1 to 0.2 g per animal; pigs, 0.5 to 1.0 g per animal; sheep, goats and horses, 10 to 15 g per animal; and cattle, 15 to 30 g per animal (Wadsworth, 1952). Calvert (1975) found that accumulation of As in various organs was proportional to the amount ingested.

Arsenic has been shown to have a teratogenic effect in chick embryos at an As concentration in the egg yolk of 0.001 mg/kg, as arsenite (Birge and Roberts, 1976). Rabbits with an As intake of 2.5 mg/kg showed disturbance in their muscular co-ordination, morphological changes in the red blood cells, and kidney impairment (Akulou et al., 1959). In a study by Peoples (1964) it was found that very little or no As fed as arsenic acid was stored in the tissue of cows or in their milk, although reductions of milk production has been reportad due to As poisoning (Lillie, 1970). Most of the ingested As was eliminated in the urine. The chemical signs of As poisoning are

C.2 ARSENIC - (Cont'd)

vomiting, diarrhea, thirst, emaciation and unco-ordination (Dickinson, 1972; Lillie, 1970). Toxic doses for a variety of As compounds to selected mammals under laboratory conditions range from an LD_{10} of 4 mg/kg for oral doses of arsenic trioxide (As_2O_3) to an LD_{50} of 1100 mg/kg for oral doses of lead orthoarsenate (Pb As O_4) Christensen and Luginbyhl, 1975).

Where As compounds have been used for pesticide control the concentration of As in both surface and subsurface soils increased exponentially with the age of the orchard or with the period of time arsenic pesticides had been applied to the soil (Frank et al., 1976a, 1976b). Herbivorous insects (katydids) have demonstrated an increase in mortality rates and tissue accumulations where the insects had fed on dosed crop areas (Watson et al., 1976).

The amount of As accumulated in soils varies with soil type and depth (Johnson and Hiltbold, 1969; Frank et al., 1976B). Concentrations decreased with depth, the majority being in the upper 30 cm of soil. An approximate calculation using the formula of Deuel and Swoboda (1972) showed that roughly one percent or less of the applied As could be recovered as the water soluble form and the remainder was probably tied down by the soil, the element usually occurs as a divalent anion in soils (Berry and Wallace, 1974).

The signs of As toxicity in plants is wilting of new cycle leaves followed by retardation of root and top growth of the plant (Liebig, 1966). As concentrates in or on the roots, the tips of new, fine roots being affected first. Seed germination can also be arrested by toxic amounts of As. Liebig (1966) has summarized the toxicity of As to various crop species (Table C-1). Very little or no As was found in the edible parts of plants such as snap beans, sweet corn, peas or potatoes.

C.2 ARSENIC - (Cont'd)

TABLE C-1

THE TOLERANCE OF CROP SPECIES TO ARSENIC

Very Tolerant	Fairly Tolerant	Low or No Tolerance
Asparagus	Strawberry } on heavy and medium soils	Snap bean
Potato	Sweet corn } on heavy and medium soils	Lima bean
Tomato	Beet	Onion
Carrot	Squash	Pea
Tobacco		Cucumber
Strawberry		Alfalfa
Grape		Sweet corn } on light and sandy soils
Red raspberry		Strawberry } on light and sandy soils

Note: Some of the tolerant crops - potatoes, corn, rye, wheat, lemon plants - exhibit small yield increases at low levels of arsenic.

Source: Liebig, 1966.

Arsenic can occur in a number of forms in the aquatic environment (Penrose, 1974). In water, arsenite is far more poisonous than arsenate, under aerobic conditions arsenite is quickly converted to arsenate (Dabrowski, 1976). Arsenic compounds are reduced and methylated by anaerobes to form highly toxic methylarsenic or dimethylarsenic but these forms are readily oxidized to give products which are less toxic like cacodylic acid (Wood, 1974; Braman and Foreback, 1973).

As is accumulated by fish from both water and food. Fats contain more As compared with other tissues as the element has a lipid affinity (lipophilic) (Phillips and Russo, 1978). The half-life of As in the muscle of green sunfish (Lepomis cyanellus) was only seven days

(Sorenson, 1976). As uptake by liver, gut and muscle of green sunfish increased with As concentration in water, temperature and exposure interval (Sorenson, 1976).

Gilderhus (1966) investigated the effects of As on bluegills (Lepomis macrochirus) and other aquatic organisms in concrete ponds which received doses of As. Fish survival was reduced at concentrations as low as 0.69 to 2.76 mg/L. Only 18 percent of immature fish survived in the pool receiving 11.07 mg/L As (in doses of 0.69 mg/L once weekly for 16 weeks) compared with 90 percent survival in the controls. Of the adult bluegills, 31 percent of those receiving As survived whereas 60 percent survived in the control group. Tissue residues of 1.3 and 5.0 mg/g As were associated with reduced growth rates and increased mortality in immature and adult bluegills respectively. Macroinvertebrate densities and diversities were also reduced when the As treatment over a year equalled or exceeded 4.0 mg/L (Gilderhus, 1966).

The 96-h LC_{50} of sodium arsenite varies between species. The values for brook trout, Salvelinus fontinalis and bluegills, for example, were 25.8 mg/L and 72 mg/L respectively (Cardwell et al., 1976). The eyed stage of rainbow trout eggs could withstand 50 mg/L of either arsenate or arsenite while the same concentrations were reported lethal to the swimming stages (Dabrowski, 1976).

Temperature also affects As toxicity. The LT_{50} (lethal temperature at which 50 percent of the test organisms die) decreased from 678 h at 10°C to 124 h at 30°C when the fish were exposed to 60 mg/L arsenic as sodium arsenate. The LT_{50} at 30°C for 30 mg/L arsenic was 209 h (Sorenson, 1976).

Daphnia were immobilized after exposure to As concentrations ranging from 18 to 31 mg/L sodium arsenate, or 4.3 to 7.5 mg/L as arsenic in Lake Erie water (Anderson, 1944, 1946). A 16 percent

C.2 ARSENIC - (Cont'd)

reduction in Daphnia magna reproduction occurred at 0.52 mg/L As (as Na_2HAsO_4) over a period of three weeks (Biesinger and Christensen, 1972).

Although As is accumulated from water by aquatic organisms there does not appear to be biomagnification through the food web (Lunde, 1970; Seydel, 1972; Isensee et al., 1973). Bioaccumulation ratios for As in selected fish and invertebrates ranged from 110 to 14 500, the emergent parts containing less than the submerged parts. The levels of As in algae ranged from three to 7000 times the concentration in water (Demayo et al., 1979).

In summary, Arsenic is a cumulative poison and is potentially toxic to plants and animals. Its toxicity depends on the chemical form and mode of intake.

C.3 BERYLLIUM (Be)

Beryllium ranks 44th in abundance among the elements, constituting about 0.0006 percent of the earth's crust. Beryllium enters the environment principally from coal combustion (Drury et al., 1978). The chemical species of Be emitted through coal combustion are not known although investigators recognize that the element is partially volatilized and occurs in airborne particulate form as well as in the vapour phase (Klein et al., 1975; Lindberg et al., 1975).

Beryllium compounds in airborne particulate form are of toxicological interest. Inhalation is the chief form of entry into animals as little accumulation or toxicity results from oral exposures because ingested forms of Be are poorly absorbed through the intestinal wall (Stokinger, 1972). Inhaled soluble salts of Be hydrolyze to a colloidal form on the mucous surfaces of the bronchopulmonary tract.

C.3 BERYLLIUM - (Cont'd)

Some Be is retained in the lung for long periods but portions are transported to and stored in the major tissues of the body. The manner of this redistribution seems to depend more on the extent of exposure and the physicochemical state of the Be than on metabolic differences of animal species (Browning, 1969; Stokinger, 1972).

The adverse health effects caused by Be are well known and have been described quite thoroughly from data on occupational exposures. The purpose of this discussion is to address the impacts of Be on the natural environment (exclusive of man). Consequently, the reader is referred to the review by Drury et al., 1978, for information pertaining to the effects of Be on human health.

Beryllium sulphate has been shown to inhibit the embryonic development of chicks, Gallus gallus (Palmer, 1972). Beryllium administered as a profusion was lethal to pigeons and chickens; it was found (Chanh and Maciotte - Lapoujade, 1966) that chickens were about three times as sensitive as pigeons, with the lethal dose averaging 0.56 ± 0.15 g/kg and 1.49 ± 0.16 g/kg respectively.

There are few data which describe the effects of Be toxicity to mammals. In a review of Be toxicity presented by Drury et al. (1978), it would appear that many of the biochemical and physiological mechanisms that are affected by Be in humans are also influenced by the element in similar fashion in other mammals. For example, experimental findings show that some beryllium compounds are carcinogenic in test animals (Vorwald et al., 1966). Pulmonary cancer has been produced in rats and monkeys by inhalation exposure (Vorwald et al., 1966). Sarcomas have also been induced in rabbits by injection (Tapp, 1966). No data were uncovered concerning the teratogenic or mutagenic effects or lack of these effects by Be in mammals. Lethal oral doses in several laboratory animals range from 80 to 146 mg/kg for different Be compounds (Christensen and Luginbyhl, 1975).

C.3 BERYLLIUM - (Cont'd)

Beryllium chemistry in the soil has not been thoroughly investigated but it is thought to be similar to that of aluminum or zinc (Bohn, 1972; Romney and Childress, 1965). The Be ion participates in cation exhange reactions and undergoes isomorphic substitution in secondary clay minerals. It is fixed in many soils and will displace divalent cations which share common sorption sites.

Uptake of Be by plants from both soils and nutrient solutions does occur (Romney and Childress, 1965). Increasing the Be concentration in the nutrient solution increases the Be content of the plant material. High concentrations of insoluble $BeCO_3$ and BeO did not influence bean growth but $Be(NO_3)_2$ and $BeSO_4$ at 10 mg/L inhibited plant growth (Romney and Childress, 1965). The binding of Be by soils also affects uptake by plants. Beryllium (40 mg/L added in soluble form) is more available in acid soils, pH = 5.8, than in slightly alkaline soils, pH = 7.5 to 8.0 (Williams and LeRiche, 1968). Beryllium is not readily translocated from roots to shoots. Some plants, however, as in the case of maize, concentrated Be in the reproductive apparatus (Oustrin et al., 1967). Bingham and Steucek (1972) reported that roughly 46 percent of radioactive Be applied to plants was absorbed while four percent of that was transported out of the leaves.

Generally, Be inhibits plant growth, but in some cases may be stimulatory. Growth inhibition is more frequently observed in experiments with Be. Amounts of Be greater than 4 percent of the cation exchange capacity of soil reduced the yield of beans, wheat, and clover (Romney and Childress, 1965). In nutrient solutions Be toxicity occurs at about one mg/L.

In fresh water Be is primarily in dissolved form averaging less than 0.001 mg/L. Sediments generally contain about 2 to 3 mg/L Be (Drury et al., 1978). The small amounts of Be in natural waters is due to the low solubility of its oxide and hydroxide at the common pH of such waters (Kopp and Kroner, 1968).

C.3 BERYLLIUM - (Cont'd)

Guppies (Poecilia reticulata) accumulated radioactive Be and uptake was directly related to the Be concentration in the water (Slonim and Slonim, 1973). Levels were highest in the viscera and intestinal tract followed by the kidney and ovary.

The development of eggs and tadpoles of the common frog (Rana temporaria) was retarded by treatment with Be (Needham, 1941). Beryllium sulphate acts as a mitotic suppressor in snails (Lymnaea sp.) (Bose, 1973).

The toxicity of Be compounds to fish has been studied. According to Tarzwell and Henderson (1960) Be was the most toxic of the less common metals tested. They reported a 96-h LC_{50} of 11 mg/L Be for fathead minnows (Pimephales promelas) in a water hardness of 400 mg/L and 0.2 mg/L (as $CaCO_3$) in soft water. They suggested a safe concentration of 1.1 mg/L for fathead minnows in a water of hardness 400 mg/L but indicated the corresponding safe level for soft water would be lower. Slonim and Slonim (1973), for example, report the safe concentration of Be to be between 0.011 mg/L (100 mg/L hardness) and 1.1 mg/L (400 mg/L hardness) for the common guppy.

The protective effect of water hardness on Be toxicity to fish is believed to be due to the antagonism between calcium and Be (Slonim and Slonim, 1973). Beryllium may penetrate vital organs more readily in soft water of low Ca content and its toxicity may be 100 times greater in soft water compared with hardwater (Slonim and Slonim, 1973).

Beryllium does not magnify in food chains as Be ingested by higher animals is not absorbed through the digestive tract but is readily excreted. The results of laboratory experimentation have generally shown that Be is toxic to plants and animals but under normal circumstances should present no environmental health hazard.

C.4 BORON (B)

Boron occurs enriched in solid chemical species in the particles of fly ash upon the combustion of coal. Much of the B remains in the ash within the plant, but a few percent are released into the environment (Ruch et al., 1974; Klein et al., 1975).

Data describing the effects of inhalation of B and its compounds by animals are limited. In experiments where animals inhaled borax and boron oxide particles for varying lengths of time no damage to lungs was reported. The most serious damage incurred was a mild nasal irritation at concentrations 47 times the occupational threshold limit value (Lavinskas, 1964; Durocher, 1969). On the basis of experimental evidence B is not recognized as a problematic air pollutant (Schroeder, 1971; Weir and Fischer, 1972).

Boron would appear to have a relatively low toxicity to mammals since cattle have consumed nearly 20 g of borax per day and humans 3 g boric acid per day with no adverse symptoms (McKee and Wolf, 1963). Boron apparently does not accumulate in mammalian tissues (USEPA Water Quality Criteria, 1972). Gastrointestinal and pulmonary disorders have been reported in lambs however, due to grazing on vegetation growing in areas of high boron soil content (Belilles, 1975).

Boron levels of 0.2 to 2.2 mg/L in drinking water or 5300 mg/kg of B per day dry weight of diet are also reported toxic to lambs (Gough and Shacklette, 1976). The LD_{50} for B in mice is reported to be 2000 mg/kg and an oral dose of 0.15 mg/day is toxic to rats (Bowen, 1966).

Boron is an essential nutrient element for higher green plants (Bingham, 1973). In relatively low substrate concentrations, however, B is phytotoxic to many plants. The range between beneficial and toxic concentrations is narrow with levels from 0.05 to 0.10 mg/mL B being safe while concentrations from 0.5 - 1.0 mg/mL B being excessively high for B - sensitive plants. Toxic boron concentrations of

C.4 BORON - (Cont'd)

saturation extracts for a number of plant species are given in Table C-2. Boron plays an important role in organic translocation in plants and plant growth regulator responses, it also influences enzymatic responses, cell division, cell maturation, nucleic acid metabolism, phenolic acid biosynthesis and lignification as well as carbohydrate metabolism (Kothny, 1973).

Boron toxicity to vegetation is generally associated with B levels in acid soils and soils weathered from marine sediments or high B levels in irrigation waters and over-application of B containing fertilizers (Temple et al., 1978). Much of the B in soils is associated with minerals resistant to weathering, although B is also contained in the organic fraction of soils (Bingham, 1973). It appears that this B is small in quantity and primarily restricted to the surface horizon of soils. As this fraction mineralizes the B redistributes in the soil-water system becoming available in part for plants. A large portion of B added to soils is absorbed by certain soil materials, the balance remaining in solution. This solution is important to plant nutrition because of B availability.

Increases in pH result in increased soil adsorption of B with maximum adsorption occurring at pH 9.0. Boron adsorption takes place independently of other anions. Although B leaches it does not ordinarily leach out of the profile as readily as chloride, nitrate and sulphate salts. Variations in soil properties such as pH, organic matter content and clay content may influence the availability of a given amount of B.

Early stages of B excess in vegetation are characterized by leaf-tip yellowing. In the later more acute stages, a progressive necrosis of the leaf occurs, beginning at the tip and/or margins as a chloratic yellowing eventually spreading between the lateral veins between the midrib (Underwood, 1975). Foliar concentrations in excess of 300 mg/kg accumulated by plants exposed to atmospheric emissions

TABLE C-2

TOXIC BORON CONCENTRATIONS OF SATURATION EXTRACTS FOR SENSITIVE, SEMITOLERANT AND TOLERANT CROP SPECIES

Saturation-Extract Boron (µg of B/mL)		
0.5-1.0 Sensitive	1.0 -5.0 Semitolerant	5.0-10.0 Tolerant
Citrus	Lima bean	Carrot
Avocado	Sweet potota	Lettuce
Apricot	Bell pepper	Cabbage
Peach	Oat	Turnip
Cherry	Milo	Onion
Persimmon	Corn	Broad bean
Fig	Wheat	Alfalfa
Grape	Barley	Garden beet
Apply	Olive	Mangel
Pear	Field pea	Sugar beet
Plum	Radish	Palm
Navy bean	Tomato	Asparagus
Jerusalem artichoke	Cotton	
Walnut	Potato	

Note: Listed in each category according to susceptibility to boron injury (viz., citrus is more sensitive than walnut, lima beam more than potato, etc.).

Source: Bingham, 1973.

C.4 BORON - (Cont'd)

have been shown to produce injury (Temple et al., 1978). The symptoms of injury were similar to those produced by toxic concentrations of B absorbed through the roots. There is some evidence to suggest that an interaction may exist between F and B in plants (Temple et al., 1978).

There are limited data on the toxicity of B to aquatic organisms. It occurs regularly, however, in natural water supplies (Heit, 1977). The minimum lethal dose for minnows exposed to boric acid at 20°C for 6 hours was reported to be 18,000 to 19,000 mg/L in distilled water and 19,000 to 19,500 mg/L in hard water (LeClerc and Devlaminck, 1955; LeClerc, 1960). At a concentration of 2000 mg/L boric acid showed no effect on trout and rudd (Scardinius erythrophthalmus); at 5000 mg/L it caused discoloration of the trout's skin and at 80 000 mg/L the trout became immobile (Wurtz, 1945). The 96-h LC_{50}'s for mosquito fish (Gambusia affinis) at 20 to 26°C and a pH range of 5.4 to 9.1 were 5600 mg/L for boric acid and 3,600 mg/L for sodium borate (Wallen et al., 1957). The above data clearly indicate that B is relatively non-toxic to fresh water fish.

Generally, B has a low order of toxicity to both plants and animals in the biota.

C.5 CADMIUM (Cd)

Cadmium ranks 64th in order of elemental abundance in the earth's crust (Taylor, 1964). It is not an essential trace element for either plants or animals.

The amount of Cd entering the environment from coal combustion is significant (Friberg, 1974) although it is not the major source (Bertine and Goldberg, 1971). Cadmium is partially concentrated on smaller particulates and is also volatilized and emitted in the

C.5 CADMIUM - (Cont'd)

vapour phase upon coal combustion (Lim, 1979). Consequently, airborne Cd is available via the inhalation route to air breathing animals.

In humans approximately 60 to 65 percent of the Cd deposited in the lungs is absorbed but only 1 to 7 percent from the normal daily diet is retained. The remainder is excreted via the urine and feces (Friberg et al., 1975). In mammals, approximately 6 to 10 percent of ingested Cd is absorbed and transported through the body by red blood cells. Few data are available which describe the effects of inhaled Cd on wildlife. Inhaled Cd caused pulmonary damage especially emphysema in both humans and other mammals (Dugdale, 1978; Miller, 1971). Once absorbed from the lungs the transport of Cd basically follows that of ingested Cd. Once ingested and absorbed, Cd is stored largely in the kidneys and liver and is excreted at an extremely slow rate (USEPA, 1976; Reeder et al., 1979). The biological half-life has been estimated at 10 to 30 years (Friberg et al., 1974).

The symptoms of acute Cd toxicity following a high dosage are nausea, salivation, vomiting, diarrhea, abdominal pains, myalgia and weakness (Reeder et al., 1979). The lethal dose for man has been estimated to be between 5 and 50 mg/kg body weight for a single ingestion. The 14 day LD_{50} values for rats ranged between 130 and 180 mg/kg of body weight. An intake of 1600 mg/kg for rats is lethal (Bowen, 1966).

The chronic toxicity associated with long-term effects of low levels of Cd intake results in a total or partial loss of smell, coughing, difficulty in breathing, weight loss, yellowing of teeth, caries, irritability, gastrointestinal upset and proteinuria. There is evidence to suggest that Cd also has carcinogenic, genetic, teratogenic, testicular and cardiovascular effects (Reeder et al., 1979). Chronic Cd concentrations may impair the reproductive potential of

C.5 CADMIUM - (Cont'd)

mammalian populations through an increase in embryonic mortality and/or decrease in sperm viability (Birge et al., 1974a and 1974b).

Teratogenic effects were observed in mice after long-term exposure to 10 mg/L Cd in water (Friberg, 1978). A level of 5 mg/L Cd in the drinking water of rats given over a period of 180 to 240 days produced systolic hypertension (Gough and Shacklette, 1976). Only slight toxic effects were observed in a 2-year study with rats fed a diet containing 50 mg/kg Cd (Lorke, 1978). A dose level of 6 mg/kg Cd over 10 days reduced weight gain and changed the behaviour of pregnant rats. Cadmium also inhibits hemoglobin production, the symptoms are the same as iron deficient anemia (Wagner, 1972). The element may also produce hemolysis, abnormal liver, kidney damage and osteomalasia in rats similar to Cd - induced Itai-Itai disease (Friberg, 1976).

The uptake of Cd by plants varied over a wide range, depending on the plant species, type of soil, acidity of the soil, cation exchange capacity, organic matter and zinc content of the soil (Reeder et al., 1979). In sandy soils uptake is greater than in soils high in clay or organic matter (Friberg et al., 1974). Soil pH is the greatest single factor affecting Co uptake. Generally, Cd uptake by plants increases with an increase in soil acidity which is probably related to the greater fraction of soluble Cd in the soils due to increased leaching from a decreased pH.

Cadmium can affect several plant processes such as CO_2 fixation, gas transpiration through stomata mitochondiral respiration and coupling in addition to interfering with normal metabolism of zinc and iron (Chaney, 1978).

Visual symptoms of Cd toxicity in wheat were observed at 2.5 mg/kg Cd in soil while red maple grown on soils containing 1.0 mg/kg Cd showed symptoms of Cd poisoning (Mitchell and Fretz, 1977;

C.5 CADMIUM - (Cont'd)

Haghiri, 1973). The primary symptoms of Cd toxicity on vegetation include foliar necrosis and chlorosis. Food crops have displayed reduced yields at soil Cd concentrations in the range of 4 to 20 mg/kg although rice was not affected by soil containing 640 mg/kg Cd (Reeder et al., 1979). The general toxicity of Cd is moderate to vegetation being normally toxic at 1 mg/kg to plants in soils. The average background soil concentration of Cd is reported to be about 0.55 mg/kg with plants growing in this soil containing 0.12 mg/kg Cd (Heit, 1977). Similar soils present around a coal-fired powerplant were found to have 1.46 mg/kg Cd and the plants growing on this soil had an average of 0.35 mg/kg Cd (Klein and Russell, 1973).

Herbivorous animals may be affected with Cd through ingestion of contaminated vegetation. Cadmium, for example, is suspected in the death of a horse which contained 410 mg/kg Cd in its kidney and 80 mg/kg in the liver (Allaway, 1968).

Certain plants display such a tolerance to Cd that they are used as indicators of Cd contamination (Simola, 1977). Species of moss and lichens are known, for example, to accumulate Cd to 10 times background concentrations (Fleischer et al., 1974).

Cadmium in natural waters and sediments is found in relatively low concentrations (Enk and Mathis, 1977). Airborne Cd as a result of emissions from coal combustion may ultimately find its way to aquatic sediments. Peyton and McIntosh (1974) have observed that airborne Cd may be contributing significantly to the Cd concantration of stream sediments. The distribution of the metal in the system was a function of basin depth and slope, point sources and water currents. The element is taken up in large amounts by aquatic organisms and causes progressive chronic poisoning in fish similar to mammals because the metal is excreted at an extremely slow rate (USEPA, Water Quality Criteria, 1973). Macrophytic vegetation takes up large amounts of Cd

C.5 CADMIUM - (Cont'd)

from both sediments and water, concentration factors for the roots of shoots of pondweed (Elodea), for example, were 20 000 and 21 000 respectively (Ravera et al., 1973). Concentration factors for other species of aquatic vegetation range from 100 to 9500 times. (Ladner and Jernelov, 1969; Hutchinson and Czryska, 1972). Some of these plants are ingested by waterfowl and may represent a significant route of uptake for these birds. Benthic macroinvertebrates have been shown to accumulate Cd by concentration factors ranging from 300 to 30 000 times the level of Cd in the water (Whitton and Say, 1975; Spehar, et al., 1978).

Cadmium is taken up and accumulated by fresh water fish. A good review of these phenomena is provided by Phillips and Russo (1978). The Cd present in fish appears to be associated with a Cd - binding protein metallothionein (Marafante, 1976). In bluegills exposed to Cd for 30, 60 and 90 days, Mount and Stephan (1967) showed that substantial Cd accumulation had occurred in the kidney, liver, gill and gut but there was no significant accumulation in the muscle and bone. The same authors were able to correlate Cd mortalities in bluegill to the amount of Cd accumulated in the gill tissue. In shorter more acute studies it was observed that very little Cd had accumulated in the liver. Cadmium-contaminated fish placed in fresh water lost Cd from the gills but not from the liver and kidney where the element was bound (Kumada et al., 1973).

Very little evidence of accumulation through the food web was found. Concentrations of Cd in bottom sediments, worms, clams omnivorous fish, carnivorous fish, and water were about 2.0, 1.1, 0.6, 0.003, 0.03 mg/kg and 0.0006 mg/L respectively (Mathis and Cummings, 1973).

Cadmium is toxic to aquatic organisms at low concentrations. Phytoplankton has displayed reductions in photosynthetic activity and

regenerative changes at concentrations as low as 0.03 to 0.05 mg/L Cd (Burnison et al., 1975). Growth inhibition of algae was observed at similar concentrations (Burnison et al., 1975). Chlorophyll levels were reduced in macrophytes and turgor pressure as well as stolon development were affected by 0.007 mg/L Cd (Cearley and Colemman, 1973).

Acutely toxic concentrations for various species of zooplankton (48-h LC_{50}) ranged from 0.065 to 3.8 mg/L Cd (Biesinger and Christansen, 1972; Bandouin and Scoppa, 1974). Aquatic insects are less sensitive than zooplankton, the LC_{50}'s ranging from 1.2 to 28.0 mg/L (Warnick and Bell, 1969; Rehwoldt et al., 1972).

Sediments contaminated with Cd have been observed to retard the development of midge larvae (Wentsel et al., 1977). Concentrations of Cd in the control sediment was 0.6 mg/kg (dry weight) and in the contaminated sediments, 1030 mg/kg (dry weight).

Fish vary in their sensitivity to Cd, the most sensitive being the salmonid. Some of the more tolerant species include goldfish, catfish (Ictalurus sp.) and fathead minnows. Acute toxicity varies with the fish species tested, time exposure, temperature and water chemistry. The 96-h LC_{50} for fathead minnows in water hardness of 200 mg/L as Ca CO_3 was 7.2 mg/L Cd (Pickering and Gast, 1972). The 7-day LC_{50} for rainbow trout was 0.008 to 0.01 mg/L Cd and the 10-day LC_{50} was 0.005 to 0.007 mg/L (Ball, 1967). Coho salmon (Oncorhynchus kisutch) exposed to 0.008 and 0.012 mg/L Cd for 6 days exhibited a 14.3 percent and 53.1 percent mortality respectively (Kumada et al., 1972).

The toxicity of Cd decreases with increasing water hardness. The differences are thought to be due to an antagonistic effect of calcium and maybe magnesium (Hutchinson and Csyrska, 1972; Davies, 1976). A temperature increase from 5°C to 20°C increased the 96-h LC_{50}

of Cd for Fundulus heteroclitus in sea water by two to three times (Eisler, 1971). Dissolved oxygen also protects against the toxic effects of Cd on fish.

The chronic or sublethal effects of Cd on fish affect growth, reproduction, behaviour, survival and osmoregulation (Reeder et al., 1979). Growth of brook trout was reduced at a Cd concentration of 0.0038 mg/L at a hardness of 45 mg/L as $CaCO_3$ (Eaton et al., 1978). In waters of greater hardness (200 mg/L as $CaCO_3$), at similar concentrations of Cd there were no adverse effects on the survival, growth or reproduction of fathead minnows (Pickering and Gast, 1972). The MATC (maximum acceptable toxicant concentration) for brook trout in soft water (37 mg/L as $CaCO_3$) was between 0.001 and 0.003 mg/L Cd and in hard water (188 mg/L as $CaCO_3$) between 0.007 and 0.012 mg/L Cd (Sauter et al., 1976). This is similar to the MATC of between 0.0017 and 0.0034 mg/L Cd suggested for brook trout in Lake Superior water (hardness 44 mg/L as $CaCO_3$) by Benoit et al. (1976).

Histopathological changes have resulted in mature male brook trout exposed for 24 hours to 0.025 mg/L Cd (Sangalang and O'Halloran, 1972). Similar observations have been made for brook trout exposed to water containing 0.01 and 0.025 mg/L Cd for 24 h. If Cd is present under natural conditions for a short time at a critical period in the life cycle, breeding may be affected.

Cadmium has also caused teratogenic effects in trout embryos, 28 percent of exposed fish had abnormalities after exposure to 0.5 mg/L Cd, 9 percent after exposure to 0.05 mg/L Cd and 7 percent after exposure to 0.005 mg/L Cd (Birge et al., 1974a and 1974b).

Other metals, lead, zinc and selenium also influence the toxicity of Cd to aquatic organisms. These range from Zn enhancement of Cd toxicity, antagonism of Cd toxicity by Se and both synergism and antagonism of Cd effects by lead (Reeder et al., 1979).

C.5 CADMIUM - (Cont'd)

In summary Cd is a highly toxic trace element to all levels of the biota. It is also a cumulative poison although direct evidence of biomagnification through the food chain is lacking.

C.6 CHROMIUM (Cr)

Chromium is the 21st most abundant element in the earth's crust (Taylor, 1964; Bowen, 1966). A small portion of the Cr present in coal is released, concentrated on small particulates, while the majority is collected on ash particles and retained within the plant (Ruch et al., 1973; Klein et al., 1975; Lim, 1979).

Chromium is an essential element for humans and animals; some different opinions exist, however, whether it is essential to vegetation (Chapman, 1966; NRC, NAS, 1974). Chromium is essential for maintenance of glucose tolerance in mammals. As part of an organic complex it is probably active during the first steps of glucose metabolism (Vokal et al., 1975). It has also been shown that Cr is essential to the metabolism of cholesterol (Schroeder, 1968). Deficiency impairs glucose and cholesterol metabolism leading to higher blood levels of both substances. Its deficiency has also been implicated to be a basic factor in atherosclerosis (Schroeder, 1974).

There are few data which address the toxicity of Cr taken into animals via inhalation. The major route of entry appears to be through ingestion although adverse effects to human health have been observed due to inhalation of excessive amounts of Cr under occupational settings (Cassarett and Doull, 1975). Harmful effects have not been noted from ambient exposure (NRC, NAS, 1974).

Chromium can enter the body of an animal via the repiratory and digestive systems and the skin with the latter two being the most significant routes. The different valence states of Cr exhibit varying toxicities. Hexavalent Cr (chromate ion) is the most toxic form being

C.6 CHROMIUM - (Cont'd)

a potent oxidizing agent and penetrating biological membranes. Trivalent Cr (chromic ion) forms complexes with biological macromolecules restricting its movement across biological membranes. It binds strongly to proteins and in sufficient concentration forms cross linkages between carboxyl groups of different protein molecules. Chromates and dichromates can readily penetrate cell membranes to a greater extent than trivalent Cr compounds accounting for one of the reasons why hexavalent Cr is more toxic than the trivalent species (Taylor et al., 1979).

The Cr content in the diet ranges from 10 to 400 mg/d. Of this amount about 95 percent originates in the food, the rest from drinking water and a negligible amount from air (NRC, NAS, 1974; Clemente, 1976). The element is poorly absorbed by the gastrointestinal tract of mammals. Only 2 to 6 percent of an oral dose was absorbed by rats (National Research Council, 1976).

Trivalent Cr has a low toxicity to animals if ingested as it readily adsorbs to food fibres and precipitates as an insoluble form in the intestine. Hexavalent Cr can cross biological membranes and participates in the non-specific binding of biological molecules. Low levels of Cr (III) can inhibit respiratory chain activity and energy production from food by inactivating certain enzymes.

According to the National Research Council and National Academy of Science (1974) concentrations of Cr in drinking water that elicit sublethal toxic effects appear to be greater than 25 mg/L. Chronic toxicity, however, has been observed in several mammalian species at concentrations of Cr (VI) greater than 5 mg/L. At a level of 5 mg/L of Cr (VI) in drinking water the element was found to accumulate in rats but did not affect growth rate, food intake or blood chemistry (NRC, NAS, 1974). The same study also reported that mixed dust containing 7 mg/m^3 of CrO_3 was fatal to laboratory mice over a 10-day exposure period and was poorly tolerated by rats.

C.6 CHROMIUM - (Cont'd)

The symptoms of Cr poisoning in animals include neoplasms, irritation of the gastrointestinal tract, vomiting, diarrhea, gastric and intestinal hemorrhage and kidney lesions (NRC, NAS 1974; Christensen and Luginbyhl, 1975). Different types of cancer have been produced by implantation of various Cr (VI) compounds in test aminals (National Research Council, 1976). An increased cancer risk in the respiratory tract has been linked to Cr (VI) compounds (Smith, 1972). Lead chromate was shown to be carcinogenic when administered intramuscularly to rats (Furst et al., 1976). Hexavalent Cr compounds also produced mutagenesis in the bacterium Escherichia coli whereas Cr (III) compounds had no effect (Venitt and Levy, 1974).

The concentration of Cr in soils varies greatly but its soil chemistry is relatively unknown (Berry and Wallace, 1974). Chromium (VI) is anionic in nature and is not strongly absorbed by soil or particulate matter. It is more mobile than Cr (III) and hence is not subject to sedimentation. Chromium (VI) reacts strongly with oxidizable substances, generally organic molecules forming Cr (III). If the water contains little organic material, however, Cr (VI) can remain in the hexavalent form for long periods. When Cr (VI) contacts soil it is converted to Cr (III) which is rapidly immobilized by the formation of insoluble hydroxides and oxides, sorption phenomena or by complexing thus becoming less available for plant uptake (National Research Council, 1976; CAST, 1976). The concentration of Cr shows a positive correlation with the clay and aluminum content of soils (Mills and Zwarich, 1975; Whitby et al., 1978). Liang and Tabatabai (1977) have shown that Cr (III) applications to soils can inhibit nitrogen mineralization. The degree of inhibition varied among the four soils studied. Chromium (III) inhibition was evident in the two acid soils (pH, 5.8 and 6.6) studied but not in the calcareous types that had pH values of 7.4 and 7.8.

C.6 CHROMIUM - (Cont'd)

The toxicity of Cr to vegetation depends on its chemical form, solubility, concentration and type of soil. The element may act synergistically with Ni, Co, and Mg in soil in exerting its toxicity. Chromium (VI) is more toxic than the trivalent form due to its greater mobility in soils (Taylor et al., 1979). Chromium is considered to interfere with the root uptake of some essential elements namely calcium, potassium, phosphorus and their subsequent transport to the aerial portions of plants (National Research Council, 1976). Water-culture yields of soybeans were reduced by 0.5 mg/L Cr in the solution (Turner and Rust, 1971). Chapman (1966) has reported that 8 to 16 mg/L Cr as chromic or chromate ion produces chlorosis on sugar beets in sand culture. In some agricultural crops, high levels of Cr can cause reduced growth or death, whereas adverse effects of low concentrations of Cr on corn, tobacco and sugar beets have also been reported (Krickenbeyer, 1974). Additions of Cr to Cr deficient soils on the other hand, stimulate the growth of lettuce and corn seedlings at concentrations of 0.1 and 0.5 mg/L Cr (Chapman, 1966).

Chromium occurs in natural waters at average concentrations less than 0.0002 and 0.34 mg/L (WQB, 1978). Chromium (III) is a positively charged ion that has a tendency to form stable complexes with negatively charged inorganic and organic species (Taylor et al., 1979).

In the absence of anionic species, Cr (III) in neutral solutions can react with water to form colloidal hydrous oxides. It is unlikely, therefore, that much Cr will be present in aqueous solution. In fact, Cr (III) is least soluble in the pH range covered by natural waters (National Research Council, 1976). There is some evidence to suggest that enrichment of the hypolimnion in lakes with Cr is a result of interactions with bottom sediments (Funk et al., 1969).

C.6 CHROMIUM - (Cont'd)

Chromium is moderately accumulated by aquatic organisms (Phillips and Russo, 1978). The Cr content in lake trout (Salvelinus namaycush) increased with age collected in a New York State lake (Tong et al., 1974). Rainbow trout exposed to 2.5 mg/L Cr (VI) for 24 days showed the highest accumulation in pyloric caeca followed by gut, kidney and liver. Transference to fresh water resulted in a rapid loss of Cr from the tissues with the exception of the spleen and kidney (Knoll and Fromm, 1960). The gill was indicated as the major route of Cr accumulation with little accumulating in edible tissues. In another study, trout exposed to 2.5 mg/L Cr (VI) accumulated Cr rapidly during the first day but after this the fish did not accumulate appreciable amounts of Cr up to 22 days (Buhler et al., 1977). Accumulations were greatest in the spleen, kidney, gastrointestinal tract, gall bladder and opercular bone. Fish should not experience a cumulative Cr uptake from intermittent exposures due to the fact that Cr is rapidly lost upon return to freshwater.

Hexavalent chromium is the principal toxic form to fish and other aquatic organisms (Taylor et al., 1979). Invertebrates and phytoplankton have been reported to be more sensitive than fish (Strik et al., 1975). Macroinvertebrates display a wide range of sensitivities, 96-h LC_{50} ranges in soft water for various species of macroinvertebrates ranged from 2.0 to 64 mg/L. Similar values were reported by Rehwoldt et al. (1972).

Chromium (VI) in relatively low concentration can inhibit photosynthesis. Wium-Anderson (1974) found that photosynthesis in some species of diatoms (Bacillariophyceae) was inhibited by as much as 50 percent upon exposure of 0.65 mg/L Cr (VI).

The acute toxicity of Cr to aquatic organism varies among species and chemical form of the element. A higher mortality rate has been observed for chinook salmon fingerlings (Oncorhynchus tshawytscha)

in 0.2 mg/L Cr (VI) after 12 weeks exposure than in 0.3 mg/L Cr (III) (Olson, 1958). Trivalent and hexavalent Cr were more toxic in soft water (20 mg/L as $CaCO_3$) for fathead minnows; the 96-h LC_{50} in soft water for Cr (III) was 5.07 mg/L compared with 67.4 mg/L Cr (III) in hard water, and for Cr (VI) in soft water the LC_{50} was 17.6 mg/L compared with 27.3 mg/L in hard water (Pickering and Henderson, 1966). Tabata (1969) showed that hardness affected the toxicity of Cr (VI) for Daphnia sp. but not for carp (Cyprinius carpio) which is a fairly tolerant species. Pickering and Henderson (1966), on the other hand, conducted bioassay tests with four species of fish and found that hardness had little effect on Cr toxicity. Reported 96-h LC_{50}'s ranged from 17 to 118 mg/L.

It is obvious that the sensitivity to Cr of various species of aquatic organisms is wide. Those lethal levels reported are 5.07 to 118 mg/L for fish, 0.05 mg/L for invertebrates and 0.032 to 6.4 mg/L for algae, the highest value being 3200 times the lowest one (USEPA, Water Quality Criteria, 1973).

At low concentrations Cr exhibits sublethal toxicity to fish. Growth was retarded in rainbow trout exposed to 0.35 mg/L in soft water for 12 months (Benoit, 1976). The MATC was determined to be between 0.2 and 0.35 mg/L Cr. The lower value corresponds to the results reported by Olson and Foster, (1956). The survival, egg production and hatchability of fathead minnows, however, was not affected by 1.0 mg/L Cr (VI) in hard water (209 mg/L as $CaCO_3$); although early growth was affected, the final lengths and weight did not differ from controls (Taylor et al., 1979). The activities of gill and kidney adenosive triphosphatase enzymes in rainbow trout exposed to a sublethal level of 2.5 mg/L Cr (VI) were altered (Kuhnert et al., 1976). The biochemical mechanism of the alterations is not known. Some implications of chromium's toxic mechanism may be derived from the observation that these enzymes are involved in ion and osmoregulation.

C.6 CHROMIUM - (Cont'd)

Based on the information in the literature, Cr appears to be moderately toxic to both plants and animals. It is accumulated by various plant and animal species but its biological half life is short and it is rapidly eliminated. There are no data to suggest it is biomagnified through the food chain.

C.7 COBALT (Co)

Cobalt is emitted from coal-fired power plants partially in fly ash while the rest remains in the plant as slag (Heit, 1978; Lim, 1979).

Colbalt is an essential element for both plants and animals. In animals it is a constituent of vitamin B_{12} and micro-organisms use Co in the synthesis of this vitamin (Prosser, 1973; Belilles, 1975). Ruminants require Co for the rumen organisms; in sheep this requirement is about 0.05 mg/d (Prosser, 1973). The daily intake for sheep and cattle (as distinct from that required for ruminants) is about 200 mg/d (Underwood, 1971). Cobalt is essential to blue green algae and some bacteria seed plants. Green algae use it to catalyze enzyme activation for nitrogen (Bowen, 1966). According to Valkovic (1975) and Horton et al (1977) no evidence has been presented that indicates it is essential to higher plants.

Few data are available which address the toxicity of airborne Co to animals. Human poisoning, however, has been reported from the inhalation of Co dust from refinery and alloy plants. The symptoms of the poisoning were; dermatitis, gastrointestinal pain, vomiting and low blood pressure (Berry et al., 1974).

In laboratory organisms it has been shown that the slow accumulation of Co at a concentration of 1 µg/g over a period of a

C.7 COBALT - (Cont'd)

month caused cardiomyopathy (Belilles, 1975). The symptoms were similar to congestive heart failure. Cobalt salts are readily absorbed by the small intestine but significant retention of Co in the human does not occur. Approximately 80 percent of the ingested Co is excreted in the urine and 15 percent is removed in the feces (Belilles, 1975). The element may be accumulated in the liver, kidney and bones of animals (Bowen, 1966; Underwood, 1971; Valkovic, 1975; Gough and Shacklette, 1976).

The concentrations of Co in body tissues that are non-toxic are 2.4 mg/kg for rats, 10 mg/kg for dogs, and 3 mg/kg for sheep (Gough and Shacklette, 1976). Underwood (1971) indicated that sheep could tolerate an intake of 150 mg/kg/d up to 8 weeks while Gough and Shacklette (1976) found they could tolerate 350 mg/kg/d in their diet with no ill effects.

The symptoms of Co poisoning in animals includes loss of appetite, weight loss and anemia in sheep. It has also resulted in polythemia, reticulocytosis and increased blood volume in mice, rabbits, guinea pigs, dogs, pigs, ducks and chickens (Underwood, 1971). Becker and Smith (1951) also observed petechial and ecchymotic hemorrhage in the small intestine, fatty infiltration of the liver, slight pulmonary edema and congestion in sheep.

Cobalt in soils apears most often as a cation, the availability being controlled in part by the cation exchange capacity (CEC) of the soil (Romney and Childress, 1965; Pratt, 1966; Brady, 1974). Being a cation, it will be bound tightly in neutral or alkaline soils but may become more available in acidic soils. The content of Co in most soils is between 1 and 40 mg/kg (Allaway, 1968; Horton et al., 1977). Cobalt has been reported to increase in concentration in the soil around a coal-fired powerplant from 2.3 mg/kg in background soil to 4.6 mg/kg in enriched soils near the plant (Klein and Russell, 1973).

C.7 COBALT - (Cont'd)

Cobalt is not accumulated in plants to any great extent. The ability of plants to accumulate Co was approximated using Hodgson's (1970) methodolgy. The calculated concentration factor was 0.11. According to Wallace and Romney (1977) Co is distributed more in roots than in shoots but is often found in moderate to large quantities in shoots.

Bowen (1966) reports that Co is toxic to plants. Concentrations as low as 0.1 mg/L in solution cultures produced toxic effects in many crop species (Chapman, 1966). According to Kubota et al., (1963) a concentration of 0.1 mg/L Co in nutrient solutions is near the threshold toxicity of most plants, whereas a concentration of 0.05 mg/L appears to be satisfactory for continuous application on all soils. Corn has exhibited the symptoms of Co toxicity at concentrations between 4 and 8 mg/kg in the leaves (Vanselow, 1977). Horton et al. (1977) indicate that a concentration of one to 8 mg/kg in the leaves of dox fennel was non-toxic. The symptoms of Co toxicity include depressed growth, chlorosis, necrosis and even death of plants (Chapman, 1966).

Cobalt is found in natural waters at relatively low concentrations of 0.009 to 0.0058 mg/L (Bowen, 1966; Valkovic, 1975). In sediments the concentration range is from 5 to 35 mg/kg (Leland et at., 1978). Upon entering water, Co apparently tends to associate quickly with particulate matter and sediments becoming unavailable for accumulation by most organisms (Phillips and Russo, 1978).

Little information is available on the toxicity of Co to aquatic organisms. Thomas (1915) found that 16 mg/L of cobalt chloride was lethal to Fundulus heteroclitus within 5 days. The 96-h LC_{50} for rotifers exposed to Co cobalt sulphate was found to be 59 mg/L (Buikema et al., 1974). Enlarged livers were reported in rainbow trout inhabiting waters with high Co concentrations (Oguri, 1976).

C.7 COBALT - (Cont'd)

The introduction of radioactive Co to a pond containing warm water fauna resulted in Co accumulations in the soft tissues of organisms (Brungs, 1967). The eggs of pike (Esox lucius) when exposed to radioactive Co accumulated the element but rapidly eliminated it upon transfer to fresh water (Kulikov and Ozhegov, 1975). Rainbow trout eggs accumulated Co to levels directly proportional to the Co level in the water. Cobalt uptake decreased with increasing calcium in concentration in the water suggesting that Co may be antagonistic to Co (Kunze et al., 1978).

Cobalt appears to be moderately toxic to plants and animals. The concentration factor for Co in plants is low and herbivorous animals do not concentrate the element as it is readily excreted. Cobalt is accumulated by fish but is eliminated upon transfer to fresh water. Intermittent increases in the Co concentration of water should not adversely affect aquatic organisms.

C.8 COPPER (Cu)

Copper is emitted in the vapour phase but is also found in the mechanically collected fly ash or bottom ash from coal-fired power-plants (Klein et al., 1975; Horton et al., 1977; Lim, 1979). The chemical species of copper emitted through coal combustion are postulated as being elemental copper and copper II oxide (CuO) (Davidson et al., 1974)

Copper is essential to the physiological functioning of man as well as plants and animals. In plants it is a constituent of many essential enzymes and proteins one of which is cytochrome oxidase (Bowen, 1966; Valkovic, 1975; Gough and Shacklette, 1976). In animals copper is necessary for the manufacture of some of the ferroproteins. Ceruloplasmin, for example, is a copper containing protein in blood plasma that has ferroxidative capacity and is essential to the transfer

C.8 COPPER - (Cont'd)

of iron between plasma and cells (Roeser et al., 1970). Various molluscs and arthropods concantrate copper to 1 mg/100 mL of blood when it functions in the oxygen-carrying pigment, hemocyanin (Prosser, 1973). Coppper is also a constituent of cytochrome oxidase in animals, the terminal enzyme in the energy transport system of animals (Maniloff et al., 1970). Copper is also essential for polyphenol oxidase, cytochrome oxidase, uricase, laccase, ascorbic acid oxidase and tyrosinase (Prosser, 1973). The element is integral for the biosynthesis of proteins involved in the structure of the connective, dermal and elastic tissues (Maniloff et al., 1970). Underwood (1975) indicates that Cu is also required for red blood cell formation as well as normal growth and reproduction.

Plants grown on soils deficient in Cu may become chlorotic characterized by leaf-tip yellowing. It can be added to Cu-deficient soils as a trace nutrient supplement to other fertilizers. The minimum reported concentration of Cu that begins to exhibit toxicity to some agricultural plants is 0.10 mg/L (USEPA, 1976). Chickens with Cu deficiency die from rupture of the aortic blood vessel associated with increased mucopolysaccharides in the aorta and reduced cytochrome oxidase in the liver and heart (Hunt et al., 1970). Man requires about 2 mg Cu/d, more while growing with blood concentrations ranging from 0.05 to 1.0 mg/L (Prosser, 1973). Sheep require 1 mg Cu/d, pigs about 6 mg/L and most laboratory animals require about 50 mg/L/d (Underwood, 1971). Copper concentrations found in natural waters are not known to have any adverse effect on humans. Concentrations greater than 1 mg/L may impart an undesirable taste to drinking water.

In most mammals Cu is poorly absorbed from the small intestine. A small fraction, roughly 5 percent, is bound to albumin but the majority is associated with ceruloplasmin. Copper has the capacity to readily penetrate red blood cells and in the liver it is released for incorporation into various enzymes requiring copper. Accumulations of the metal have also been noted in the brain, adrenal gland, heart,

intestine, kidney and stomach (Bowen, 1966; Underwood, 1971; Valkovic, 1975).

Some information is available on the toxicity of airborne Cu to animals. Bischoff and Haun (1939) reported that animals were affected as far away as 5 km from a Cu smelter with flydust containing 25 mg/kg Cu. Sheep grazing within 20 m of high tension copper tower lines became ill and died after ingesting forage that had grown on soil cotaining Cu excesses (Hemkes and Hartman, 1973). Molybdenum antagonizes the toxic effects of Cu as sheep that grazed on pastures of normal Cu content but low in Mo resulted in liver accumulations (Gough and Shacklette, 1976). This accumulation can often result in Cu poisoning followed by death. The symptoms of Cu poisoning include conjunctivitis, stomach and intestinal catarrh, salivary secretion, miscarriage, emphysematose facti, afterbirth retention and reduction or complete stoppage of milk production (Maniloff et al., 1970).

Copper occurs most often as a cation in soils, its availability depending partially on the CEC of the soil and relevant interphase equilibria (Brady, 1974; Payne and Pickering, 1975). Leeper (1952) indicates that Cu is held more strongly than most cations by the cation exchange complex and are, therefore, less mobile in soil solution. Copper will be more available in acid soils than those that are neutral or slightly alkaline. The concentration of copper in soils generally ranges from 2 to 100 mg/kg although this range is narrower (1 to 30 mg/kg) in sandy soils (Horton et al., 1977).

The uptake of Cu by plants is dependent upon its availability in soils. Availability is influenced, partially, by pH as more acidic soils will leach Cu from bound sites placing it in solution. Although Cu is held more strongly in soils than many cations, plants possess the ability to take up sufficient quantities of Cu even in very low concentration. Increases in soil concentrations of Cu will result in a further accumulation of plants perhaps to the point that toxic

concentrations to the plant or its consumer may be reached (Dvorak and Lewis et al., 1978). There appears to be more Cu in the roots than shoots, but often moderate with sometimes large quantities being observed in shoots (Wallace and Romney, 1977).

Concentrations of 20 mg/kg in plant tissues have elicited symptoms of Cu toxicity (Chapman, 1966, Valkovic, 1975). Grain, on the other hand, can apparently accumulate Cu to 15 mg/kg without ill effects but these levels may be harmful to sheep (Hemkes and Hartman, 1973). Grass seedlings (Agrostis sp.) have been shown to develop a tolerance to Cu over a 10-week period (Wu and Bradshaw, 1972). Spinach and gladiolus also exhibit some apparent tolerance as neither species was affected by Cu at relatively high soil concentrations (93 to 130 mg/kg) at acidic pH values, 4.5 to 4.7 (Chapman, 1966).

Snapbeans were adversely affected by tissue concentrations of 40 mg/kg or greater and reduced yields were observed at Cu tissue levels of between 20 and 30 mg/kg (Walsh et al., 1972) Concentrations of 0.5 to 50 mg/kg of copper acetate in the tissues of cauliflower, lettuce, potato and carrot inhibited growth (Bell and Rickard, 1974). Excessive Cu can interfere with iron metabolism in plants, the symptoms usually appear as necrosis in foliar regions (Gough and Shacklette, 1976). Another mechanism of Cu toxicity may be related to effects of Cu on nitrogen mineralisation in soils. Liang and Tabatabai (1977) observed that the Cu divalent cation inhibited the nitrogen metabolism in various soils.

Copper is found in most natural waters at an average concentration of 0.015 mg/L (USEPA, 1976). The concentration of Cu in sediments ranges from 1 to 476 mg/kg with the majority being between 1 and 110 mg/kg (Leland et al., 1978). Copper enrichment in the sediments of an aquatic ecosystem has been reported from urban-industrial sources of air pollution. Aerial fallout increased Cu sediment levels above a control system, the distribution of the metal in the ecosystem was a

C.8 COPPER - (Cont'd)

function of basin depth and slope, point sources and water currents (Peyton et al., 1974). The chemistry of Cu in water is quite complex. When solutions of inorganic copper salts are added to natural fresh waters, particularly alkaline ones, basic copper carbonate ($Cu_2(OH)_2CO_3$) is precipitated. In the presence of organic substances copper can be complexed and held in solution in hard waters (Brown et al., 1974). At pH and bicarbonate (CO_3) levels typical of most surface fresh waters and at Cu concentrations of 1 mg/L or less most of the Cu in a soluble state is present as $CuCO_3$ and only a small fraction as Cu^{2+}. In natural surface waters, Cu can occur in a number of other soluble forms such as complexes with humic or amino acids or associated with suspended materials (Stiff, 1971).

Many studies have been conducted which have investigated the acute and chronic toxicity of copper to aquatic organisms. The principal test organisms in these experiments were fish. Copper toxicity is dependent on alkalinity, pH, organic compounds and hardness. At lower alkalinity copper is generally more toxic so there are fewer unions with which to complex (USEPA, 1976). Decreases in pH and hardness increase the toxicity of Cu to aquatic organism. In most natural fresh waters alkalinity parallels hardness. The salmonids appear to be the most sensitive fish species to Cu and, hence, are commonly employed in bioassays to determine Cu toxicity under variable conditions.

Copper is known to be particularly toxic to algae and molluscs. Solutions of Cu, for example, are commonly emmployed as algicides. The acute toxicity of Cu to fish varies with species and water quality. Reported 96-h acute toxicity studies with Cu are summarized in Table C-3. Perusal of the table indicates that toxicity also varied with temperature, increasing as the thermal regime increased and with hardness.

TABLE C-3

96-HOUR LC_{50} OF COPPER FOR VARIOUS FISH SPECIES

Species	Temp °C	DO mg/L	pH	Hardness mg/L-$CaCO_3$	96-hour LC_{50}	References
Bluegill	20	-	-	-	0.74	Trama, 1954
Atlantic salmon	15	-	7.3 to 7.6	20	0.048	Sprague, 1964
Atlantic salmon	17	-	7.0 to 7.4	14	0.032	Sprague and Ramsey, 1965
Fathead minnow	25	7.8	7.5	20	0.022 to 0.025	Pickering and Henderson, 1966
Fathead minnow	25	7.8	8.4 to 7.4	360	1.14, 1.76	Pickering and Henderson, 1966
Bluegill	25	7.8	7.5	20	0.66	Pickering and Henderson, 1966
Goldfish	25	7.8	7.5	20	0.036	Pickering and Henderson, 1966
Fathead minnow	23	7.0	7.5	198	0.47	Mount, 1968
Fathead minnow	23	7.0	7.5	198	0.43	Mount, 1968
Fathead minnow	25	7.2 to 7.9	6.9 to 7.2	30	0.075	Mount and Stephan, 1969
Fathead minnow	25	7.2 to 7.9	6.9 to 7.2	30	0.084	Mount and Stephan, 1969
Brook trout	12	10	7.5	42	0.09	McKim and Benoit, 1971
Brown bullhead	23	7.0	7.5	202	0.17, 0.19	Brungs et al., 1973
Bluglll	27	7+1.2	7.0 to 8.0	45+0.9	1.100	Benoit, 1975
Rainbow trout	12	a	8	360	0.33	Waiwood, 1977
Rainbow trout	12	a	7.75	100	0.066	Waiwood, 1977
Rainbow trout	12	a	7.75	30	0.034	Waiwood, 1977
Rainbow trout	12	a	6	360	0.125	Waiwood, 1977
Rainbow trout	12	a	6	100	0.042	Waiwood, 1977
Rainbow trout	12	a	30	30	0.032	Waiwood, 1977
Guppy	25	7.8	7.5	20	0.036	Pickering and Henderson 1966

Note: a - above 90 percent air saturation.

C.8 COPPER - (Cont'd)

The 96-h LC_{50} concentrations for Cu have been found to range from 0.022 to 0.66 µg/L in soft water and 0.066 to 1.76 µg/L in hard water. Of the species tested, Atlantic salmon (Salmo salar) were the most sensitive to copper. At similar test temperatures the warm water species can be expected to display a greater tolerance. At a pH of 6 the 96-h LC_{50} concentrations of Cu for rainbow trout were 0.042 and 0.125 µg/L at hardnesses of 100 and 360 mg/L (as $CaCO_3$) respectively. At comparable levels of hardness and a pH range of 7.75 to 8.0 the 96-h LC_{50} range increased to 0.066 to 0.33 µg/L in the same species.

In chronic or sublethal tests, 33 µg/L Cu did not affect the survival or physical appearance of fathead minnows in hardwater (200 mg/L as $CaCO_3$); in soft water the no-effect concentration was about 10.6 µg/L Cu. The concentrations of Cu having no effect on catfish (Ictalurus nebulosus) exposed for 600 days to the metal were from 16 to 27 µg/L in hard water (202 mg/L as $CaCO_3$) (Brungs et al., 1973). Similarly, the level for bluegills in soft water over a 22-month exposure was 21 µg/L Cu (Benoit, 1975).

A copper concentration of 17.5 µg/L did not adversely affect the survival, growth or spawning of adult brook trout or the hatchability of eggs when chronically exposed to Cu in water with a mean alkalinity of 41.6 mg/L as $CaCO_3$ (McKim and Benoit, 1971). For young brook trout the no effect level is roughly 9.5 µg/L Cu. The authors found that in a second generation experiment exposure to sublethal concentrations of Cu for yearling through spawning to 3-month juveniles was sufficient to establish no-effect concentrations which were factors (application factor) of 0.17 and 0.10 of the 96-h LC_{50} value. Davies and Goettl (1976) report that Cu concentrations of 0.012 to 0.019 and 0.0095 to 0.0175 mg/L have no effect on rainbow trout and brook trout respectively. These concentrations are similar to those derived from the use of the application factors listed above. The maximum acceptable copper concentrations, based on a conservative application factor of 0.05 x, range from 0.003 to 0.088 mg/L in hard water and from

C.8 COPPER - (Cont'd)

0.001 to 0.033 mg/L in soft water, over a pH range of 7.0 to 8.4. At a pH of 6, the range for hard water is decreased to 0.002 to 0.006 mg/L for rainbow trout.

For zooplankton (Daphnia magna) a 16 percent reproductive impairment was noted at a Cu concentration of 22 µg/L in a chronic 3-week exposure to soft water (45.3 mg/L as $CaCO_3$). The 3-week LC_{50} was 44 µg/L Cu (Biesinger and Christensen, 1972). The total Cu concentration having no effect on Campeloma decisim, Physa integra and Gammarus pseudolimnaeus in chronic studies was between 8.0 and 14.8 µg/L Cu with a total hardness of 45.3 mg/L as $CaCO_3$ (Arthur and Leonard, 1970).

The concentrations of Cu that have been associated experimentally with no harmful effect for serveral water species are approximately from 5 to 15 µg/L (USEPA, 1976). Water with high alkalinity and hardness may be able to tolerate higher ambient levels. Generally, the concentration of Cu should not exceed 0.10 times the 96-h LC_{50} for continuous exposure as determined with the most sensitive resident species.

Copper is accumulated by freshwater fishes and aquatic insects. There appears to be a good correlation between the onset of Cu accumulation above background levels and the development of chronic symptoms in fish (Phillips and Russo, 1978). Benoit (1975) found that bluegill exposed for up to 22 months accumulated Cu at all concentrations 40 µg/L and above. This level was the lowest concentration having an adverse effect on the fish suggesting that fish may be adversely affected by Cu if they are accumulating Cu tissue levels above natural backgound levels. Measured Cu concentrations in the gills of catfish accurately reflected the Cu exposure conditions. Equilibrium concentrations were reached in these tissues after 30 days exposure (Brungs et al., 1973). Rainbow trout, on the other hand,

C.8 COPPER - (Cont'd)

continued to accumulate Cu in the liver up to 107 weeks and accumulated Cu in this organ after exposure to only 3 µg/L Cu (Goettl et al.,1974).

Mayflies (Ephemerella grandis) and stoneflies (Pteronarcys californica) accumulate Cu in their tissues to levels that reflect the insects' copper exposure history. Nehring (1976) has suggested that such forms may be possibly used to detect instances of intermittently acute copper pollution in streams by monitoring Cu levels in aquatic insects. The isopod, Asellus meridianus, accumulated Cu from both the food and water, particularly in the hepatopancreas (Brown 1977). The histopathological and physiological effects of Cu poisoning in aquatic organisms include: renal and lateral bone lesions, increased corrticosteroid levels, increased red blood cell production and hematacrit, reduced natality and increased blood pH (Grande, 1967; McKim et al., 1970; Eisler and Gardner, 1973; Donaldson and Dye, 1975; Sellers et al., 1975).

Copper is concentrated by duckweed (Lemna minor) by a factor of roughly 1000 times the water concentration (Hutchinson and Czyrska, 1972). Aquatic insects accumulate the metal by roughly the same factor (Vaughan et al., 1975). Bryophytes concentrated Cu almost 4000 times that of background levels (Dietz, 1973).

In conclusion, Cu is an essential trace element to both plants and animals. It may be accumulated by these organisms to levels that are toxic to a consumer or the organism itself. It does not, however, tend to accumulate in the edible tissues of fish.

C.9 FLUORINE (F)

The element fluorine in coal is usually chemically bound in the fluoride form. Upon the combustion of coal the majority (in excess of 60 percent) of this F is released in the vapour phase of the stack

emissions (Heit, 1977; Lim, 1979). There is some discussion as to what a reasonable percentage F emitted in this fashion is. Most investigators do agree, however, that F is volatilised when coal is burned and that the smaller percentage of it is collected and retained within the powerplant. The chemical species of F emitted are believed to be gaseous hydrogen fluoride (HF), silicon tetrafluoride (SiF_4) and solid inorganic fluoride compounds (NRC, NAS, 1971).

Fluorine is an essential trace element to animals but not plants (Muhler, 1959; Bowen, 1966; Prosser, 1973; Underwood, 1975). Fluorine is found in traces of vertebrate bone and aids in the hardening of dental enamel. It is also known to partially prevent osteoporosis (Chapman, 1966; Prosser, 1973; Underwood, 1975). Goodman and Gilman (1970) state, however, that it has been difficult to determine whether F serves a specific physiological role. The problem is complicated by the universality of F which makes it difficult to produce F-free diets with which to study the element's essentiality. Messer et al., (1972) reported, however, that mice with low fluoride intake demonstrated fertility impairment.

There are not many studies which address the toxicity of F to wildlife via inhalation relative to those conducted for humans and livestock. Extrapolations of F effects in man and livestock can intuitively be made on the basis of similarities in biochemical and physiological mechanisms among the three mammalian groups. The effects of airborne fluorides in man will be discussed elsewhere. The reader is, however, referred to the reviews by Hodge and Smith, (1977) and Rose and Marier, (1977) for specific information concerning the subject.

It is usually assumed that the direct inhalation of F from the atmosphere constitutes a small amount of the total F intake of animals in an area of industrial pollution (Suttie, 1977). The major source is that ingested, primarily in the vegetation. There are few

data in the available literature, even for domestic animals let alone wildlife, that deal with the question of the F hazard due to inhalation. Fluorine is emitted on particles of submicron in size. These particles can deposit in the alveolar regions of the lung providing access to the bloodstream and subsequent transport to internal organs (Natusch et al., 1974). The well-being of wildlife surrounding fluoride-emitting facilities is of concern. A few studies have reported increases in the skeletal fluoride concentrations of deer and elk in these areas (Kay, 1975; Kay et al., 1975). According to Rose and Marier (1977) wild animals are more susceptible to the effects of F than domestic cattle. Their nutritional status (especially in winter) and physical exertion may be particularly significant factors which under conditions of stress can make the wild animal more susceptible to the effects of F (Rose and Marier, 1977). In a predator-prey situation even a minor loss of mobility can lead to rapid elimination of the individual affected. Kay (1975) has also reported an apparent age shift due to fluorosis that was so extreme that older deer and more susceptible deer were removed from the herd. Suttie's (1977) suggestion that wildlife may be protected by employing similar F guideline values as for the most sensitive domestic species, cattle, therefore, does not apply. In certain instances wildlife could be conceivably less susceptible to F as they are more mobile than the cattle which would be contained near the F source. The current information available, however, is not adequate to produce separate guidelines for wildlife nor to indicate the environmental significance of fluoride pollution for these species.

The metabolism of F in animals follows typical patterns regardless of whether the F entered the organism via inhalation or ingestion through food and water. Fluorine is rapidly and almost completely absorbed from the gastro-intestinal tract; it is distributed throughout the body and the F ion is retained by the bones or teeth where it accumulates. Many of the studies have been done with domestic

C.9 FLUORINE - (Cont'd)

rumens. There is no reason to believe they would metabolize the element differently than other mammals. Direct comparisons to ruminant wildlife species can certainly be made. In rumens F is rapidly absorbed through the rumen wall (Bell et al., 1961). A single oral dose of F in sheep is rapidly absorbed into the bloodstream and the plasma. F concantration reaches a maximum after about 3 hours (Simon and Suttie, 1968). About three quarters of the F in blood is contained in the plasma, the remainder in the red blood cells. The plasma F level responds rapidly and systematically to varying F ingestion and various physiological factors (Taves, 1970). Rats given a single dose of F (50 mg/kg, body weight) raised plasma F levels about 2.0 mg/L in 1 hour. (Suketa, et al., 1976).

The content of F in urine has been suggested as an index of animal exposure (Burns, 1970). Some relation has been reported between urinary F and the F concentration in samples from pasture vegetation. The main fate of ingested F in animals is the bone. Accumulation of F in the mammalian skeleton begins during gestation. The F content in the offspring of mice and piglets appears to be a function of the F fed to the mothers (Forsyth et al., 1972; Messer et al., 1974). The accumulation of F in the skeleton is controlled by three factors: the amount of F absorbed via the digestive system and lungs; the receptivity of the skeletal surfaces; and the efficiency of F excretion by the kidneys. On the basis of background levels, bone fluoride concantrations ranging up to and above 5000 mg/kg, dry fat-free basis, are indicative of environmental contamination by F and its ingestion by wild animals (Rose and Marier, 1977).

The inhalation and ingestion of F by animals may lead to fluorosis. Symptoms of this disorder are characterized by dental lesions and mottling of the teeth, skeletal lesions and deformities, lameness and stiffness, appetite impairment, cachexia and diminished milk yield (Suttie, 1977). Fluorine toxicity mechanisms also include

C.9 FLUORINE - (Cont'd)

interference with calcium metabolism, enzymatic processes, normal cellular respiration and reduction of the immune biological response of the animal to certain diseases (Lillie, 1970).

Fluoride has caused chromosomal bridges, fragments and gaps to develop during mitosis of cells in barley (Bale and Hart, 1973). Concentrations of 1.3 and 2.6 mg/L of airborne F and HF caused genetic damage in fruit flies (Gerdes et al., 1971). Chromosomal aberations have been observed (Jagrillo and Lin, 1974) in mammalian oocytes during meiosis in the following concentrations in:

Mouse oocytes: 91 and 181 mg/L;
Ewe oocytes: 11, 23 and 91 mg/L;
Cow oocytes: 4, 5, 11, 23 and 91 mg/L.

The major source of F contributing to fluorosis in animals is through the ingestion of contaminated vegetation and other foods. There is a diversity of opinion as to the levels of F than can be permitted in animal forages and feeds. Suttie (1969) has proposed that standards for the fluoride content of forage should be set at:

Not over 40 mg/kg dry weight basis, as a yearly average;
Not over 60 mg/kg for more than two consecutive months;
Not over 80 mg/kg for more than one month.

The relationship between F content in the diet of cattle and the development of fluorosis is summarized in Table C-4. The table shows that if the F level is maintained under 40 mg/kg only a slight periosteal hypertosis and some incisor mottling will occur. Histological changes in bone and tooth structure which have no known effect on the well being of the animal may also be seen at ingestion levels below 40 mg/kg. The relative tolerance of other domestic animals to F in their diets is presented in Table C-5. The stated tolerance levels

TABLE C-4

RELATIONSHIP BETWEEN FLUORINE CONTENT OF THE DIET AND THE DEVELOPMENT OF VARIOUS SYMPTOMS IN CATTLE

Symptom	Total Fluorine in Diet (ppm)			
	20-30	30-40	40-50	>50
Discernible dental mottling[1]	yes	yes	yes	yes
Enamel hypoplasia (score number (4))[1]	no	no	no	no
Slight gross periosteal hyperostosis	no	yes	yes	yes
Moderate gross periosteal hyperostosis	no	no	yes	yes
Significant incidence of lameness	no	no	no	yes
Decreased milk production	no	no	no	yes
Skeletal F equivalent to 5000 ppm at 5 year[2]	no	no	no	yes
Urine F of 25 ppm[3]	no	no	yes	yes

Note: Based upon data discussed in detail in references (11, 41), the statements "yes" or "no" indicate if the symptom would be reproducibly seen at this level.

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1 Only if fluoride is present during formative period of the tooth.

2 Metacarpal or metatarsal bone, dry, fat-free basis.

3 Based on values taken after 2 to 3 years of exposure; specific gravity = 1.04.

Source: Suttie, 1977.

TABLE C-5

DIETARY FLUORIDE TOLERANCE FOR DOMESTIC ANIMALS

Animal	Performance (ppm F)
Beef or dairy heifers	40
Mature beef or diary cattle	50
Finishing cattle	100
Feeder lambs	150
Breeding ewes	60
Horses	60
Finishing pigs	150
Breeding sows	150
Growing or broiler chickens	300
Laying or breeding hens	400
Turkeys	400
Growing dogs	100

Note: The values are presented as ppm F in dietary dry matter and assume the ingestion of a soluble fluoride, such as NaF. These tolerances are levels that, on the basis of published data for that species, could be fed without clinical interference with normal performance. At lower levels of intake, some pathological changes may occur, but these changes have not been shown to influence performance.

Source: Suttie, 1977.

indicate a level of F ingestion that on the basis of published data for that species could be fed without clinical interference with its normal performances. The table indicates that cattle are the most sensitive domestic species.

Fluorine may be taken up by plants from the air, the soil or water. The F accumulated in plants enters the food chain through herbivores and passes into the soil in animal wastes. The uptake of F in the soil by plant roots is dependent upon the element's availability. Plants in acid soils for example, tend to have a higher F content.

Fluorides are bound to soils in different ways; they may be chemically combined inside the clay lattice, absorbed on colloidal surfaces or mechanically retained in the soil solution within soil micropores (Ares, 1978). Under relatively stable environmental conditions, adsorbed or loosely retained F can be exchanged in aqueous solution. Soil organic colloid may be important in F adsorption increasing the capacity of the soil clays. The amount of F normally accumulated by plants from the soil is, however, small and there is little relationship between the concentration of F in the soil and that of the plant (Weinstein, 1977).

The major mode of entry of F into plants is via uptake from airborne gases. The mechanisms and ultimate fate and effects of gaseous fluorides entering plants have been the topic of review articles (Rose and Marier, 1977; Weinstein, 1977). The effects and impacts of fluorine compounds on vegetation arising from F emissions associated with the Hat Creek project have been previously discussed (Tera, 1978). The purpose of the following discussion is to briefly review the effects of F on terrestrial vegetation as taken from the reviews listed above.

C.3 FLUORINE - (Cont'd)

Fluorine compounds, notably HF are three orders of magnitude more lethally toxic than SO_2. Fluoride affects cellular metabolism which in turn influences CO_2 assimilation or oxygen uptake. The visible symptoms of F damage in plants include folian necrosis and chlorosis. Effects at the organism level can include altered growth, reduced reproduction, increased susceptibility and decreased resistance to environmental stresses and perhaps death (Tera, 1978).

Gaseous HF enters the plant through the leaf stomata and the plant cuticle. Fluoride salts will also be absorbed but in proportion to their solubility (NAS, 1971). Due to the high solubility of the HF gas in water it is readily taken into the transpirational stream and transported to the leaf tips and margins where it is known to accumulate (Woltz, 1964; Ziegler, 1973). It appears that little or no movement occurs between leaves and other organs.

Studies performed *in vitro* with F salts have revealed that many enzymes are F sensitive (Slater and Bonner, 1952; Melchior and Melchior, 1956; Miller, 1958). The effect of F on plant enzymes has ranged from stimulation to inhibition (Weinstein, 1977).

There are likely many different possibilities as to the locus of F action. Respiratory activity and CO_2 assimilation are likely the primary sites but the steps *in vitro* are not well understood (Weinstein, 1977). Bush beans fumigated for 20 days at a HF concentration of 1.8 µg/L increased their rate of respiration (Applegate and Adams, 1960).

If a threshold of HF is exceeded by acute fumigation, carbon dioxide assimilation is decreased in a number of plants (Thomas, 1958). Below threshold levels the rates of CO_2 assimilation are normal. The threshold for gladiolus was observed to be about 6 to 7 µg/L following exposure at the rate of 35 hours a week for several weeks (Thomas,

1958). Photosynthetic rates were reduced in oats, barley and alfalfa when fumigated with 10 mg/L HF (Bennett and Hill, 1974).

Plants exposed to F may display reduced chlorophyll content of the foliage and F accumulation in chloroplasts (Neuman and McNulty, 1959; Chang and Thompson, 1966). Other effects include the occurence of visible symptoms at the organ level, foliar chlorosis or a manifestation of altered structure and function of chloroplasts.

Ponderosa pine needles injured by F display histopathological alterations including hypertrophy of resin duct epithelial cells and hypertrophy of transfusion parenchysma and phloem and xylem parenchyma (Solberg and Adams, 1956). Changes in broad-leaved plants are characterized by collapse of mesophyll and distortion and collapse of epidermal leaf cells (Solberg and Adams, 1956; Treshow, 1957).

Fluoride effects on growth, yield and reproduction in plants depend on deficiencies in species and varieties, fluoride concentration, length of exposure and climatic factors. Fluoride caused a 25 percent net growth reduction in Douglas fir without visible needle necrosis (Treshow et al., 1967). An accumulated concentration of 100 mg/kg in the needles was suggested as the threshold for growth reduction in the species. It appears that the threshold for injury of plants classified as susceptible is less than 150 mg/kg and for most plants may be less than 100 mg/kg. Plants classified as intermediate or resistant can probably tolerate concentrations in excess of 200 mg/kg without expressing foliar symptoms.

Exposure of bean seedlings to 2.1 $\mu g/m^3$ F caused the development of less vigorous second-generation seedlings (Pack, 1971a and 1971b). A 30 to 70 percent reduction in diameter growth of pine trees was reported at F - pollution levels that otherwise caused no visible injury. The growth of pollen tubes in the styles of cherry blossoms

C.9 FLUORINE - (Cont'd)

was decreased by fumigation with HF either before or after pollination (Facteau et al., 1973). Fluoride-induced reduction in pollen germination and tube growth has also been observed in tomato and cucumber plants (Pack and Sulzbach, 1976) while inhibited seed production of fruiting has been reported, with soybean, bell-pepper, sweet corn, and cucumber being more susceptible than peas, grain sorghum, or wheat (Pack and Sulzbach, 1976). Beans and oranges experienced decreased crop yields with increasing F levels, i.e. approximately 19 percent per 0.1 $\mu g/m^3$ for oranges, and 3 percent per $\mu g/m^3$ (approximately 1.2 $\mu g/L$) for beans (Leonard and Graves, 1970; Pack, 1972). A 5 percent loss in the weight of individual strawberries occurred per $\mu g/m^3$ increase in airborne F, fruit quality also declined (Pack, 1972); McCune et al., (1974) established acceptable limits of F in the air as 0.005 to 0.01 mg/L for a two to four hour peak concentration and 0.003 to 0.006 mg/L for 30 to 60 day periods.

Forage species grown with irrigation water containing F had an elevated F content. (Rand and Schmidt, 1952). Fluoride in solution is readily absorbed by plants (Adams and Sulzbach, 1961). Baby doll, a horticultural foliage plant, suffered serious (50 percent) leaf necrosis when set for rooting in water containing 0.5 mg/L F (Canover and Poole, 1971). As fluoride salts can be directly absorbed through the leaves, F in irrigation water sprayed directly on crops could also result in higher F content (Weinstein, 1977). In culture media deficient in calcium and magnesium, added fluoride markedly reduced oxygen absorption in the tissues of Rubus hispidus (Pilet and Bejaoui, 1975). Increased levels of Ca and Mg had a protective action.

The site of F accumulation in plants is the leaf. Although it is assumed little translocation to other plant tissues takes place, Benedict et al., (1964) reported translocation of F from leaves to the roots. Keller (1974) has suggested a similar movement of the element. Other plant tissues may contain measurable amounts of F, especially the

C.9 FLUORINE - (Cont'd)

roots (Leone et al., 1956). Fruits are usually low in F but large amounts can accumulate after F exposure (Weinstein, 1977). Plants become the vehicle for the concentration and transfer of F to herbivores and the potential problems associated with F ingestion. Three types of processes appear to mediate the concentration of F in plants: accumulation, distribution and elimination.

Fluoride is a natural constituent of water and sediments. The average concentration in water is about 0.01 to 0.02 mg/L (Carpenter, 1969). Almost no data are available on the toxicity of F to aquatic organisms. A number of fish species have exhibited injury from F exposure, the response being influenced by a number of factors such as species and strain, concentration of Ca and chloride in the water, temperature and fish size (Sigler and Neuhold, 1972; Groth, 1975). Concentrations as low as 1.5 mg/L of F have affected the hatching of fish eggs (Ellis et al., 1946) and 2.3 mg/L introduced as sodium fluoride was lethal to rainbow trout at 18 °C (Angelovic et al., 1961).

Aquatic animals tend to accumulate environmental F, primarily in the skeleton as well as in the gills and exoskeleton. Brown trout (Salmo trutta) exposed to 5.0 mg/L F for 200 hours in tap water displayed a whole-body fluoride concentration of 10 mg/kg net weight (Wright, 1977).

Groth (1975) has reviewed the data on the effects of F to aquatic vegetation. The data indicated that levels as low as 2 mg/L can decrease the growth of one species of Chlorella, an algae. In addition, many aquatic plants accumulate F to concentrations that may be many times that of background levels. The accumulation of F by aquatic plants is of interest because of the element's potential impact on animals that consume this vegetation. Stewart et al.,(1975) report that the apparent food-chain concentration factor in an unpolluted marine ecosystem is 10.

C.9 FLUORINE - (Cont'd)

There is virtually no information available on the long-term chronic effects of F in the aquatic biota. The potential accumulation of F in the aquatic environment is, however, more ecologically important.

Fluorine in the gaseous form, particularly as HF is very toxic to vegetation. Plants have the capacity to accumulate F from the ambient environment where herbivorous animals may be potentially affected through the consumption of contaminated forage. Fluorine is an essential element for animals but is also toxic in high concentrations causing fluorosis. Some evidence is available that suggests F is concentrated in aquatic food chains.

C.10 LEAD (Pb)

When coal is combusted, some lead is absorbed onto fly ash particles of the order of 1 μm or less in size and a portion is emitted in the vapour phase (Natusch et al., 1974; Klein et al., 1975; Lim, 1979).

Lead is present in all soils and plants but it is not known to be an essential for vegetation nor is it required for animals. As a result of coal combustion, airborne Pb in the form of particulates and gas can enter organisms respiring air. The major routes of Pb uptake in man and presumably animals are through the lungs and gastrointestinal tract. Particulates of less than 1 μm in size bearing adsorbed lead can be deposited in the alveolar regions of the lung where the element has access to the bloodstream and ultimate transport to internal organs (Natusch et al., 1974). As particle size decreases, the solubility of Pb adsorbed onto them will increase. (Underwood, 1971). These particles upon entering the lungs are usually absorbed or transported to the base of the ciliated bronchiolar epithelium (Piperno, 1975). Lead that is absorbed enters the blood bound to

C.10 LEAD - (Cont'd)

erythrocytes and plasma proteins and reaches the bones and soft tissues. Some elimination occurs via bile excreted into the small intestine. Approximately 32 percent of the Pb that is inhaled is absorbed from the lungs (Waldron and Stofen, 1974). Lead taken in via inhalation produces higher blood and tissue concentrations more rapidly than higher amounts obtained by ingestion (Egan and O'Cuill, 1970). The attendant amount of Pb absorbed from the amount ingested is about 5 to 10 percent. Lead accumulates primarily in the bones, with lesser amounts in the liver, kidney, muscle and hair (Bowen, 1966; Belilles, 1975; Underwood, 1975). Once taken in and absorbed, Pb may accumulate to toxic proportions. The symptoms of lead poisoning include: derangement of the central nervous system, gastrointestinal tract, musculature and the hematopoietic system (Aronson, 1971).

Lead has been shown to be teratogenic in laboratory animals but no such effects have been observed in cattle or sheep (National Academy of Sciences, 1972; Christensen and Luginbyhl, 1975). It has also been found to be a renal carcinogen and a poison in animals and is correlated with mortality from kidney cancer, leukemia, lymphomas and stomach as well as intestinal and ovarian cancers (Valkovic, 1975). Lead has also been implicated in the reduction of resistance to bacterial infections in mice, rats and chicks by decreasing the numbers of antibody forming cells (Hemphill et al., 1971; Killer and Kovaeic, 1974; Waldron and Stofen, 1974).

Lead occurs most often as a cation in soil, its availability being controlled by the CEC of the soil (Romney and Childress, 1965). Lead markedly accumulates in soils but it is not easily leached out by rainfall. In neutral or slightly alkaline soils Pb is bound relatively tight while in acidic soils the element is more mobile. The general range of Pb concentrations is between 2 and 200 mg/kg (USEPA, 1976).

C.10 LEAD - (Cont'd)

The uptake of Pb by plants depends on the metal's availability in soils and a number of other factors including soil fertility and the general nutritional status of the plant. An increase in the soil cation exchange capacity and organic matter decreases the uptake of Pb by plants (Haghiri, 1973). Corn plants grown with insufficient amounts of phosphate, for example, accumulated 5 to 10 times more added lead than plants provided with sufficient phosphate (Miller and Koeppe, 1971). Lead taken up by corn plants in solution culture is concentrated in dyctosome vesicles (normally involved in compound secretion and cell wall deposition). Eventually, Pb deposits were concentrated in the cell wall outside the plasmalemma (Malone et al., 1974). Lead is accumulated by the roots of plants and is not readily accumulated to the above ground parts of plants. This occurs even when the soil lead is soluble and available in the soil (John, 1972). In radishes, a ten-fold increase in soil Pb content increases the Pb concentration by a factor of less than two (Ratsch, 1974). It would appear then, that soil lead may not be readily incorporated into the food chain via the soil plant pathway.

The major route of Pb entry into plants is through leaf surfaces (Holl and Hampp, 1975; Ward et al., 1977; Belal and Saleh, 1978). Leaf surfaces that are rougher or more hairy apparently accumulate more Pb (Holl and Hampp, 1975). There is little translocation of Pb in plants, most of the metal appears to be bound to poly-manic acids of the cell wall (Waldron and Stofen, 1974). Those plant organs which exhibit a gas exchange capacity with the atmosphere contain the largest amount of lead (Holl and Hampp, 1975). This observation is indicative of the metal's uptake behaviour in plants.

There are few data which describe the toxicity of Pb taken up from culture solutions or soils. This is primarily due to the fact that Pb is poorly translocated in plant tissues. Many plants, however, will tolerate high Pb levels but some show retarded growth of 10 mg/L

C.10 LEAD - (Cont'd)

insolution cultures (Valkovic, 1975). The growth of grape, apple or orange seedlings was not affected by soil concentrations of 150 to 200 mg/kg (Chapman, 1966). A few plants can accumulate Pb with no visible effects. Certain shrubs, for example, have accumulated Pb to 350 mg/kg and leaves of corn 75 yards from a smelter contained 3200 mg/kg (Waldron and Stofen, 1974; Gough and Shacklette, 1976). A concentration of 30 mg/kg in French beans, however, damaged the plants (Gough and Shacklette, 1976). Lead can also inhibit nitrogen mineralization in soils which may adversely affect the nutritional status of plants (Liang and Tabatabai, 1977).

The primary effect of Pb on plants is the metal's phytotoxicity arising from interactions of airborne lead and the aerial portions of plants. Transpiration and photosynthesis was decreased in sunflowers exposed to Pb (Bazzaz et al., 1974). Lead ions also affect photosynthesis by reducing CO_2 fixation of isolated chloraplasts and inhibit the election transport of photosystem II between the site of the primary electron donor and water oxidation. The metal can also apparently block the sulfhydryl groups of plant enzyme proteins effecting an alteration in phosphate levels (Holl and Hampp, 1975).

Lead may enter animals through the ingestion of contaminated forage or prey. Horses grazing on contaminated hay were affected by a consumption rate of 214 mg/kg per day while cattle were affected by 6 to 7 mg/kg per day (Aronson, 1971). Lead at an intake rate of 1 mg/kg per day in cattle will produce effects in fetuses prior to the recognition of physiological effects in adults. Lead has been shown to be fatal to domestic animals at the following blood levels: horse, 0.38 mg/L; cattle, 0.4 mg/L; dogs, 0.8 mg/L; and, pigs, 1.2 mg/L (Egan and O'Cuill, 1970). Diagnosis of lead poisoning in sandhill cranes has been confirmed over a blood concentration of 1.46 - 3.78 mg/L (Kennedy, et al., 1977). Accumulation to 42 mg/kg in the breast tissue of pheasant and 168 mg/kg in the liver was reported as fatal to pheasants

C.10 LEAD - (Cont'd)

(Hunter and Merton, 1965). Blood Pb levels in excess of 6 mg/L in wild ducks were shown to be fatal (DelBono and Buggiani, 1971). Lead induced renal inclusions and renal edema occurred in rodents collected at abandoned metalliferous mine sites in Wales; field voles (Microtus agnestis) with both abnormalities contained body burdens of Pb that averaged 42.8 to 45.3 mg/kg; renal edema occurred in field mice (Apodemus sylvaticus) that averaged 8.60 mg/kg (Roberts et al., 1978). Clark (1979) found that the average lead concentrations in bats and shrews near a major highway equalled or exceeded those reported by Roberts et al., (1978) for small rodents. Clark (1979) however, did not report any attendant pathological observations with these concentrations.

Lead is found in natural waters at a concentration from 0.001 to 0.010 mg/L and in sediments generally ranging from 5 to 810 mg/kg (USEPA, 1976; Leland et al., 1978). Animals ingesting less than 0.005 mg/L Pb in water showed not to be adversely affected by the metal. Lead has a low solubility of 0.5 mg/L in soft water and only 0.003 mg/L in hard water, although higher concentrations of suspended and colloidal Pb may remain in the water (USEPA, 1972). The pH and hardness of water are important factors which govern the toxicity of Pb to aquatic organisms. Upon entry into water most Pb is precipitated as carbonates or hydroxides but decreasing pH increases the availability of divalent lead, the principal toxic form. A number of studies have been conducted which address both the chronic and acute effects of Pb to aquatic organisms. The principal test species has been the fish with those of the salmonid family being the most sensitive.

Wide variations exist in the reported 96-hour LC50's for lead. These may be due to differences in water quality, fish species tested and the type of bioassay (static versus flow through). Some 96-hour LC50 data for Pb in fish are summarized in Table C-6. The data indicate that Pb is more toxic to fish in soft water than hard water.

TABLE C-6

96-HOUR LC_{50} OF LEAD FOR VARIOUS FISH SPECIES

Species	Temp °C	DO mg/L	pH	Hardness mg/L-$CaCO_3$	96-hour LC_{50} mg/L	References
Mosquito fish	-	-	-	a	240	Wallen, et al., 1957
Fathead minnow	-	-	-	Soft	2.4	Tarzwell & Henderson, 1960
Fathead minnow	-	-	-	Hard	75	Tarzwell & Henderson, 1960
Fathead minnow	-	-	-	20 to 45	5 to 7	Pickering & Henderson, 1966
Brook trout	-	-	-	20 to 45	4 to 5	Pickering & Henderson, 1966
Rainbow trout	-	-	-	50	1.0	Brown & Dalton, 1970
Rainbow trout	15	-	-	25	0.14	Goettl et al., 1972
Rainbow trout	15	-	-	366	0.14	Goettl et al., 1972
Rainbow trout	11.1	-	-	27.7	1.17	Davies et al., 1976
Brook trout	9 to 15	-	6.8 to 7.6	44	4.1	Holcombe et al., 1979

Note: a - highly turbid water, hardness unknown

C.10 LEAD - (Cont'd)

Exceptions to this are the data for trout which are comparable in both hard and soft waters. Salmonids appear to be the most sensitive species to Pb while the warmer water types exhibit a higher degree of tolerance. The 96-hour LC50 for Pb in highly turbid water is 240 mg/L. In natural waters, Pb is absorbed by clays or complexed with dissolved or suspended organics. This would effectively reduce the toxicity while not affecting the total amount of lead. The mechanism of acute lethal toxicity of Pb to fish is related to the destruction of gill tissue followed by impairment of respiration and death caused by anoxia.

Chronic Pb exposure may result in perturbances of behavioural patterns, reproduction, survival and growth. Exposures of 2 to 3 months of rainbow and brook trout indicated that Pb had determined effects at concentrations as low as 0.10 mg/L in soft water (20-45 mg/L as $CaCO_3$) (NRC, NAS, 1974). Guppy growth was affected by 1.24 mg/L Pb while concentrations of 0.1 and 0.3 mg/L elicited sublethal effects in threespine sticklebacks, Gasterosteus aculeatus (Crandall and Goodnight, 1962; Hawksley, 1967). The conditional behaviour of gold fish was adversely affected by 0.07 mg/L in soft water (50 mg/L as $CaCO_3$) (Weir and Hine, 1970). The highest mean continuous-flow concentrations for total Pb that did not have an adverse affect on survival, growth and reproduction were 0.12 and 0.36 mg/L; for dissolved Pb the concentrations were 18 and 32 µg/L (Davies and Everhart, 1973).

The divalent ion of Pb is the form most readily accumulated by aquatic organisms. Fish accumulate very little lead in edible tissues but marine benthic invertebrates can attain unacceptably high levels of the metal in edible portions after exposure to low Pb levels in the water (Phillips and Russo, 1978). Calcium decreases the Pb accumulation by fishes while Pb can inhibit Ca accumulation and deposition.

C.10 LEAD - (Cont'd)

Fish maintained at a pH of 6.0 accumulated three times more lead than those held at pH 7.5 (Merlini and Pozzi, 1977a). In another study, the same authors (Merlini and Pozzi, 1977b) found a direct correlation between Pb accumulation and the concentration of ionic Pb at various concentrations of total Pb. Their data indicate that under the conditions existing in most natural waters, most of the Pb in the water would be rendered available for uptake by aquatic animals. Brook trout accumulated Pb in the kidney and gill over three generations, the no effect concentrations were found to be between 58 and 119 µg/L Pb (Holcombe et al., 1979). Upon transfer to a Pb-free environment for 12 weeks the gills and kidney lost about 75 percent of the accumulated Pb. Lead has recently been shown to be methylated by micro-organisms in sediments (Wong et al., 1975). This methylated lead may have some significance in the uptake and accumulation of the metal similar to methylated forms of arsenic and mercury in the aquatic environment.

The isopod, Asellus meridianus accumulated lead from both the food and water (Brown, 1977). Individuals from the most tolerant population accumulated the most lead. Concentration factors for Pb in the fresh water environment for various aquatic organisms are as follows:

847 for duckweed, Lemna minor (Hutchinson and Czyrska, 1975);
5300 for bryophytes (Dietz, 1973);
100 for invertebrates; and,
300 for fish (Vaughan et al., 1975).

Lead is moderately toxic to both plants and animals. In plants the primary route of toxicity is via airborne Pb, the amounts absorbed from the soil are small in comparison and little translocation takes place with the plant. Herbivores may become affected through the ingestion of contaminated foliage. Lead is not biomagnified in the aquatic food chain although it is toxic to fish and invertebrates in relatively small concentrations.

C.11 MANGANESE (Mn)

Manganese does not occur naturally as a metal but is found in various salts and minerals frequently in association with iron compounds (USEPA, 1976). Upon the combustion of coal a portion of the Mn is released into the environment but the majority of it is concentrated and collected in the ash (Ruch et al., 1973; Klein et al., 1975; Lim, 1979). The forms emitted are either elemental or solid inorganic oxide compounds (Davidson et al., 1974; Sullivan, 1975).

Manganese is an essential trace element for mammals and other animals as well as plants. Manganese occurs at levels of 50 to 100 mg/kg ash weight in many animals, it is absorbed from food via the gastrointestinal tract. In mammals it is essential and is stored in the liver. Manganese functions as a cofactor in oxidative phosphorylation, in isocitric dehydrogenase, L-malic dehydrogenase and in liver arginase (Prosser, 1973). When Mn is not present in sufficient quantities, plants exhibit chlorosis and failure of the leaves to develop properly (USEPA, 1976). In animals, Mn deficiency can lead to reduced reproductive capabilities and deformed or poorly maturing young.

There are very few data on the toxicity of Mn to animals from inhalation. Generally, Mn is not toxic to mammals in abnormally large amounts and acute Mn poisoning is rare (NRC, NAS, 1973; USEPA, 1975). The majority of the data concerning Mn toxicity via inhalation come from observations of humans under occupational exposure. Inhalation of Mn dusts and fumes has been known to cause subacute chronic adverse health effects under such conditions. Manganic pneumonia, a pneumonia with sudden onset and affecting only one lung is characteristically caused by exposure to high concentrations of Mn dust. The more chronic Mn poisoning results by exposure to high concentrations of Mn for a few months or more (Belliles, 1975). Symptoms of the disease are: sleepiness, muscular twitching, leg cramps, increased tendon reflexes, spastic gait, emotional irregularity and a fixed mask-like facial

C.11 MANGANESE - (Cont'd)

expression. Cirrhosis of the liver is also observed with chronic Mn poisoning. Manganese has not proven to be carcinogenic although some laboratory culture studies have produced a delayed in vitro mutation with Mn exposure (Markaryan et al., 1966).

In soils Mn occurs usually as a divalent cation, its availability determined, in part, by the CEC of the soil. Manganese is more tightly bound in neutral or slightly alkaline soils but is more available in acidic soils due to its increased solubility under such conditions.

The uptake of Mn by plants depends on a number of factors including plant species, fertility of the soil, nutritional status of the plant, soil pH and CEC (Dvorak and Lewis et al., 1978). Wallace and Romney (1977) on the basis of a literature search, have found that manganese is readily absorbed by plants and appears to be uniformly distributed between the roots and shoots of plants. This generalization may not always be true for all species under all conditions, particularly when very high levels of the element are present in the soil.

At concentrations of slightly less than 1 mg/L to a few milligrams per litre, Mn may be toxic to plants from irrigation water applied to soils with pH values lower than 6.0. Problems may develop with long-term (20 year) continuous irrigation on other soils with water containing about 10 mg/L Mn (NRC, NAS, 1974).

Manganese is often found with iron in groundwaters and can be leached from the soil and can occur in drainage in high concentrations. The carbonates, oxides and hydroxides are slightly soluble, so that manganous (Mn^{2+}) and manganic (Mn^{3+}) ions are rarely present in surface water in excess of 1 mg/L (USEPA, 1972).

C.11 MANGANESE - (Cont'd)

The growth of phytoplankton in sea water was stimulated by 0.5 µg/L Mn (Harvey, 1947) while 5 µg/L had a toxic effect on certain algae types in reservoirs (Guseva, 1939). The threshold for immobilization of Daphnia was reported to be 0.63 mg/L of $KMnO_4$ and for the same species in Lake Erie water 50 mg/L of $MnCl_2$ (Anderson, 1944; 1948). Bringmann and Kuhn (1959) reported the threshold effect for Daphnia magna as 50 mg/L of $MnCl_3$ as manganese at 23°C. Crayfish were observed to tolerate 1 mg/L Mn (USEPA, 1972).

The tolerance values for Mn by fish range from 1.5 mg/L to over 1000 mg/L (McKee and Wolf, 1963). The toxicity of Mn to fish depends on a number of factors. Manganese for example, apparently antagonizes the toxicity of Ni toward fish (Blebaum and Nichols, 1956). Sticklebacks survived 50 mg/L manganese as manganese sulphate for 3 days and eels withstood 2700 mg/L for 50 hours (Doudoroff and Katz, 1953). Jones (1939) gave the lethal concentration as 40 mg/L for sticklebacks and noted that the toxic action was slow.

Average survival times of sticklebacks in manganous nitrate solution were 1 week at 50 mg/L, 4 days at 100 mg/L, 2 days at 150 mg/L and 1 day at 300 mg/L as manganese (Murdock, 1953). Manganous chloride was lethal to minnows in fresh water in 6 days at 12 mg/L $MuCl_2$ (Doudoroff and Katz, 1953). Groups of rainbow trout eggs exposed to 0, 1, 5 and 10 mg/L of manganous sulphate for 29 days exhibited 7, 12, 22 and 30 percent mortality respectively (Lewis, 1976). Fry were unable to detect high (10 mg/L) levels of manganous sulphate.

Manganese is accumulated via the food chain by fresh water invertebrates, the concentration factor being roughly 40 000 (Vaughan et al., 1975; Phillips and Russo, 1978). The concentration factor is only 100 for fish but for duckweed and bryophytes the factors are 10 923 and 28 900 respectively (Hutchinson and Czyrska, 1972; Dietz, 1973).

C.11 MANGANESE - (Cont'd)

Manganese is a relatively non-hazardous element in most waters due to its low toxicity to aquatic organisms and wildlife and the insolubility of Mn under most natural conditions.

C.12 MERCURY (Hg)

Mercury is a unique element due to its wide distribution and mobility throughout the environment. It is extremely volatile and is in natural equilibrium between the biosphere and geosphere. Mercury is known to be emitted from the combustion of coal primarily as elemental mercury in the vapour phase (Ruch et al., 1973; Klein et al., 1975; Lim, 1979).

Mercury is not essential to plants or animals but is toxic to both types of organisms. Mercury is unique in its power to form stable compounds with organic radicals. In fact, it has been suggested (Peakall and Lovitt, 1972) that the number of compounds which can be formed is so large, mercury can be said to have an organic chemistry of its own. Mercury is transformed in both the aquatic and terrestrial environments to methylmercury which is generally 10 times more toxic than inorganic Hg and is the form which is bioaccumulated (Peakall and Lovitt, 1972). Coal combustion emissions of mercury are not considered hazardous by the USEPA (1973b) even under restrictive dispersion conditions since Hg is not likely to be brought to ground level except under fumigation conditions. Mercury vapours, however, can be toxic to mammals in poorly ventilated areas. Exposure to mercury vapour results in absorption by the lungs with some secondary amounts taken in by the skin (Belilles, 1975). Inhaled mercury vapours rapidly leave the lungs and gradually concentrate in other tissues probably as mercaptides (Goodman and Gilman, 1970). Mercury accumulates in the liver, hair, skin, nails and lungs in mammals and feathers for birds (Underwood, 1975; Johnels et al., 1979). In humans concentrations from 50 to 350 $\mu g/m^3$ are 75 to 85 percent absorbed by the lungs and an even higher

C.12 MERCURY - (Cont'd)

percentage of lower concentrations is absorbed (Babu, 1973). Inhalation of acute doses of Hg, from 1.2 to 8.5 $\mu g/m^3$, causes adverse health effects to the respiratory tract (Cassarett and Doull, 1975). The symptoms of these effects include pneumonitis, bronchitis, chest pains, dyspnia (shortness of breath) and coughing (Babu, 1973). Chronic exposure to low doses causes the disease "mercurialism" characterized by gingivitis, stomatitis, renal toxicity, tremor and disturbances of the gastrointestinal system (Goodman and Gilman, 1970).

Elimination of inorganic mercury begins immediately after absorption, mainly by way of the kidney and colon and to a lesser extent via the bile and saliva. In experimental animals, several percent are excreted in the volatile elemental form through both the lungs and the skin (Clarkson and Rothstein, 1964).

The metallic and elemental Hg as well as the inorganic mercurial forms generally have a lower toxicity than organic Hg compounds (Valkovic, 1975). All of the organic forms of mercury (alkoxy, alkyl, and aryl) are toxic but the alkyl form is one of the most toxic. Typical examples would be methylmercuric hydroxide, methoxyethylemercuric hydroxide and phenylmercuric acetate. The accumulation and retention of these mercurials in the nervous system, the ease with which they penetrate the blood barrier and their effect on developing tissues, make them particularly insidious (Aulerich et al., 1974). Organic Hg fed to developing mammalian fetuses resulted in a reduced litter size and/or weight, morphological lesions and damage to the fetus's central nervous system (Skerfving, 1972). Similar effects may be produced by the inhalation of Hg. Mercury can cause C - mitosis leading to variable chromosome numbers which may be reflected in the reduced productive potential of mercury exposed mammals (Rand and Schmidt, 1952).

The distribution of mercury following administration of the various classes of mercurials to mammals is of importance in understanding Hg toxicity. The distribution of these compounds is shown in

Table C-7. Inorganic and alkoxyalkyl compounds cause kidney damage usually leading to death. Alkyl Hg compounds usually display a period of latency without symptoms then signs of damage to the central nervous system appear similar to those observed in chronic poisoning. Chronic alkyl mercury poisoning has been called Minamata Disease after the district in Japan where 46 fatal cases occurred following the ingestion of methylmercury contained in marine organisms (Irukayama, 1966). Symptoms of the disease include cerebellar ataxia, tremors, constriction of visual fields and lack of co-ordination.

Airborne mercury can be introduced into biological cycles through the soil component. Although the properties and transport dynamics of airborne Hg are not completely understood, it appears there is a global circulation of the element (Kothny, 1973a; Wallin, 1976). In the vapour phase, Hg is released from the transpiration of soils, there also seems to be an equilibrium between gaseous uptake and release from soils (Lockaretz, 1974). Mercury may also enter soils through scavenging from precipitation. Anderson (1967) has indicated that precipitation may be a significant source of soil mercury. In the gaseous phase, Hg is readily taken up by water being soluble over the range of 20 to 47 µg/L (Kothny, 1973a and 1973b). Gaseous Hg will also absorb to fine particles (submicron) in the atmosphere. These dust particles can deposit on soils where the Hg will be incorporated. Mercury in soils is, therefore, the result of equilibrium between the Hg in the atmosphere, particulate matter, water and rocks.

Mercury is generally not very soluble in soil and as such is not readily leached or available to plants (Geological Survey, 1970; Lorenz, 1979). Mercury tends to be retained in the surface layers of the soil due to adsorption by organic and inorganic materials and the low solubilities of mercury salts (phosphates, carbonates, sulphides) (Berry and Wallace, 1974). There is a good correlation between the mercury concentration in soil and its organic matter content and an

TABLE C-7

DISTRIBUTION OF MERCURY IN MAMMALS

	Inorganic	Aryl	Alkoxyalkyl	Alkyl
Blood levels (single or repeated administration)	Disappears rapidly	Some increase after repeated administration	Disappears rapidly	Marked increase bound to erythrocytes
Kidneys	100-1000 times blood levels	20-100 times blood levels	100-1000 times blood levels	1-1.5 times blood levels
Liver	5-20 times blood levels	Twice blood levels	2-10 times blood levels	0.2-0.4 times blood levels
Brain	Equal to blood	1-3% of blood levels	30% of blood levels	4-6% of[1] blood levels
Relative amount of single i.v. dose excreted within 4 hours (inorganic 1)	1	2	-	0.1
Half-life of single injected dose (in days)	3-4	3-4	3-4	15

[1] Due to high blood levels, the total amount retained in the brain is higher than for other compounds. (After Swensson, 1967).

C.12 MERCURY - (Cont'd)

inverse correlation with depth (Whitby et al., 1978; Reeder et al., 1979). Groundwater also affects mercury distribution in the soil profile as does pH, the lower the pH, the more sorption of Hg by organic material (Krenkel et al., 1973). Mercury is strongly bonded to humic acids. An increase in the sodium chloride concentration decreased the fixation of Hg by humic acids (Strohal and Huljev, 1971).

Mercuric ion is methylated under a variety of conditions in alkaline agricultural soils (Rogers, 1975). Similarly, Beckert et al., (1974) found methylmercury in desert soils which had been amended with mercuric nitrate. Recent evidence indicates that there is a constituent in soil which can methylate mercuric ion biologically. It appears it is associated with the lower molecular weight fraction of the soil organic matter (Rogers, 1977). Only a small part, 1×10^{-5} of the mercuric ion applied to the soil is found in the form of methylmercury (Rogers, 1976). A good review of the interaction of Hg with soils of varying type can be found in Krenkel et al., (Vol. 1, 1973).

Plants may accumulate mercury from soils, water and the atmosphere (Dvorak and Lewis et al., 1978). At the mercury concentrations prevailing in soils, however, plants retain mercury almost exclusively within the root, where it seems to be relatively tightly bound to acidic groups of cell walls (Beauford, 1977). Only at exceptionally high soils contents of Hg is there a significant translocation to the shoot. The relatively stable binding of inorganic mercury to organic matter in soils and the plants' capacity of binding inorganic Hg are the general reasons why Hg is not accumulated by higher plants.

Mercury in the gaseous and particulate phases can be absorbed by the aerial portions of plants in the same manner as other gaseous pollutants like fluorine and sulphur dioxide (Treshow, 1970; Dvorak et al., 1978; Siegel et al., 1978). There are few data on the toxicity of airborne Hg to plants. Wallin (1976), however, has observed higher

levels of Hg in the moss, Hypnum cupressiforme for plants in close proximity to the effluents of chlor-alkali plants. The mosses probably accumulated the Hg by intercepting suspended air particulate-containing Hg by the physical processes of sedimentation, impaction and diffusion (dry deposition) or via air particulates scavenged onto the surfaces of the plants. The levels accumulated by the Hg - exposed plants was about an order of magnitude greater than those levels in control plants. Fumigation of tobacco plants with metallic mercury vapour increased the amino acid content of the exposed plants compared with control plants (Anelli et al., 1973). Grapevines sprayed with mercuric sulphate increased the weight of berries compared with controls (Dobrolyubskii, 1959).

Foliar application appears to move in the foliage of apple trees by translocation, the movement being due principally to growing fruit and foliage (Ross and Stewart, 1962). Residues have also been reported from foliar application of mercury to tomatoes, pears, rice and grain (Krenkel et al., 1973). Potato plants sprayed with phenylmercury had concentrations of 0.021 to 0.032 mg/kg Hg compared with 0.005 mg/kg in unsprayed controls (Smart, 1968). Peas sprayed with a solution of mercuric nitrate over an 8 hour period with a total of 90 mL of 10 µg/g exhibited reduced growth and weight and an accumulation of mercuric nitrate (Gay, 1976a). Spraying of phenylmercuric acetate onto the leaves of Coffea analsica reduced the zinc content of the leaves at the distal ends of the shoots (Bock et al., 1958). The growth of cucumber was inhibited and disorientation of the root and shoot was induced by mercuric chloride (Puerner and Siegel, 1972).

Little information is available with respect to the uptake of Hg by vegetation from soils. Plants would appear to have a low tendency to accumulate mercury from soils. Increasing the Hg concentration of test soils by 6400 percent resulted in changes of Hg levels in the plants from a loss of 6 percent to an increase of only 109 percent (MacLean, 1974). In another study, a 250 fold soil amendment in

C.12 MERCURY - (Cont'd)

Hg content resulted in only an increase from four to six times higher than the plants grown in control soil (Stewart et al., 1975). Carrots and mushrooms, however, have the ability to concentrate mercury from soil (Stijve and Besson, 1976; Reeder et al., 1979). Translocation from treated seed does not produce serious contamination in harvested grain (Krenkel et al., 1973, Vol. 1). In most plants, mercury concentrations range from 0.010 to 0.200 mg/kg but plants growing near Hg deposits can contain 0.5 to 3.5 mg/kg Hg. Translocation occurs in most plant tissues, including leaves, fruit and tubers (Ratsch, 1954). Mercury in the ionic form taken up by roots can be translocated, reduced and returned in gaseous form to the atmosphere (Siegel et al., 1978).

Plants have the capacity to methylate mercury in their tissues. Gay (1976b) has reported that peas Pisum sativum methylated organic mercury in vitro. The mechanism of this methylation is accomplished by an enzyme system in the plants. The methylation of the mercury could apparently take place whether the mercury entered the plant via foliar application, in soils with mercuric nitrate or phenylmercury, or when sections of pea plants were surface sterilized followed by incubation with phenylmercury acetate (Gay, 1976a). Cytological studies on onion roots (Allium sp.) have shown that alkyl, alkoxyalkyl and aryl mercurials induce chromosomal changes. Ramel (1967) found that a concentration of 50 µg/kg caused disturbances of the mitotic spinale.

Generally, most higher vascular plants are resistant to Hg poisoning even though they can accumulate relatively high concentrations in their tissues. Labrado tea plants, for example, display no adverse effects from Hg at a tissue concentration of 3.5 mg/kg (Gough and Shacklette, 1976). Methylmercury in terrestrial plants may have some significance to grazing wildlife species as this form of mercury is the most toxic and displays the greatest cumulative potential.

C.12 MERCURY - (Cont'd)

Mercury also enters animals via the ingestion of contaminated water, vegetation and prey. The latter route appears to be the most important, especially for those wildlife species preying upon mercury contaminated fish.

There is no direct experimental evidence using species of wildlife such as ungulates and carnivores with which an adequate drinking water objective can be derived (Reeder et al., 1979). These authors have suggested the limit recommended for livestock (0.003 mg/L) be used as the physiological mechanisms are likely quite similar between various livestock and wildlife species. A similar argument may be advanced in considering the ingestion of mercury from food sources of wildlife. Information collected from experimentation with other domestic animals and laboratory species could also be extrapolated to wildlife. Minute amounts of Hg ingested on a regular basis can lead to relatively high Hg concentrations in the kidney or liver. Cattle ingesting 0.48 mg/day/kg resulted in kidney concentrations of 100 mg/kg after 27 days. In sheep an equal dose led to kidney concentrations of 120 to 210 mg/kg. The background concentration of Hg in the kidney is roughly 0.5 mg/kg (Palmer et al., 1973).

A dosage of 800 mg/kg Hg^{2+} in rats is lethal (Bowen 1966). A cumulative consumption of 24.7 mg of methylmercury is fatal to ring-necked pheasants, symptoms of poisoning occurred between 13 and 17 mg (Stoewsand, et al., 1971). These latter levels also impaired egg production in pheasant hens. Phenylmercury and methylmercury at cumulative doses of 4 and 16 mg can adversely affect egg hatchability. The smaller dose decreases it while the larger results in complete cessation (Adams and Prince, 1972). Japanese quail fed 1 to 3 mg/kg $HgCl_2$ resulted in the production of eggs with thinned shells (Stoewsand et al., 1971).

C.12 MERCURY - (Cont'd)

Young chickens fed in excess of 250 mg/kg $HgCl_2$ showed a suppression of immunological responsiveness, decreased nutritional uptake, high mortality rates, and increase in heart and adrenal gland weight with a decrease in lever, spleen and bursa weight (Parkhurst and Thaxton, 1973). The toxic oral doses for laboratory animals range from an LD50 of 18 mg/kg for HgO to an LD50 of 388 of $HgNO_3$. In the environment, similar effects have been observed in birds which have fed on seeds with mercurial dressings (Fimreite et al., 1970; Johnels et al., 1979).

Dead birds observed in Sweden contained levels of Hg which peaked during June and November, with subsequent rapid decline. The seasonal changes were correlated to the spring and autumn sowing periods. Curnow et al., (1977) found a similar correlation where pheasants feeding on grain dressed with mercurials showed the highest tissue concentrations in those agricultural areas producing the most grain.

Mercury levels were found in the kidney and livers of predatory birds which apparently feed on these seed-eating birds - sparrow hawk (Accipetu nisus), goshawk (A. gentilis), peregrine falcon (Falco peregrinus), eagle owl (Bubo bubo) and whitetailed eagle (Halieatus albicilla and in mammalian species such as red fox (Vulpes vulpes) and mink (Mustela vison) (Johnels et al., 1979).

The mercury in the bird populations was found to be largely methylmercury, tests indicated that 12 to 20 mg/kg resulted in acute toxicity (Krenkel et al., 1973). Mercury residues in liver-kidney composites of birds experimentally killed by seed, ranged from 30 to 130 mg/kg for pheasants, 70 to 115 mg/kg for jackdaws and 50 to 200 mg/kg for magpies (Krenkel et al., 1973). In cases of intoxication with neurological symptoms or death, mercury concentrations in the brains of mammals ranged from 0.01 mg/kg (rat) to 61 mg/kg (cat). The

C.12 MERCURY - (Cont'd)

brain concentrations of alkylmercury in some farm animals with signs of poisoning were approximately 2 mg/kg in turkey, 8 mg/kg in cattle, and 10 mg/kg in sheep (Palmer et al., 1973). In farm animals, the organ that showed the greatest accumulation of Hg was the kidney (Palmer et al., 1973).

Mercury is deposited in large amounts in feathers and other keratinous tissue. Using museum specimens, it is possible to follow the progression of mercury contamination over many past decades. Such analyses, for example, for a number of predatory bird species have shown that the levels of Hg were low in the Swedish environment during the 19th and early 20th centuries but rose considerably during the 1940's, 1950's and 1960's. This correlated with the introduction of methylmercury as a seed-dressing agent in the 1940's (Johnels et al., 1979). Accumulations in birds of Hg due to the ingestion of alkoxy-alkyl compounds do not occur to the same magnitude as methylmercury. It appears there is little biomagnification of the former compounds in predatory birds. Methylmercury is, however, biomagnified in these birds as it is very stable and its excretion in birds and mammals is very slow. It was evident that additional sources of methylmercury were contributing to the total body-burden of Hg in these animals.

In Sweden, grazing and browsing animals like moose (Alces alces) and roe deer (Capreolus capreolus) as well as cattle and horses had low mercury levels during the critical 1940s to 1960s when methyl-mercury was used as a seed dressing. A similar observation was made for vegetarian birds who did not feed on dressed seeds.

The environmental implications of mercury toxicity are quite significant in the aquatic environment. Mercury displays both chronic and acute toxicity and is also methylated in bottom sediments from where it is readily biomagnified in the food chain, perhaps to levels that are not only toxic to the accumulator but also to the browser and predator.

C.12 MERCURY - (Cont'd)

The concentration of mercury in unpolluted waters is less than 0.1 µg/L (USEPA, 1976) and in sediments about 1 µg/kg (Reeder et al., 1979). The current detection limit for the analytical method usually employed to measure mercury in water is 0.05 µg/L. Mercury is present in water in many different forms but calculation of the exact amount of Hg species is difficult due to the complexity of natural waters and the low concentrations of Hg (Shin and Krenkel, 1976).

According to Reeder et al., (1979) the two probable most important reactions of mercury in water are: 1) the exchange of mercuric ions (Hg^{2+}) for other cations in insoluble sulphidic minerals (because mercuric sulphide has the lowest solubility of all sulphides); and 2) the reaction of mercuric ions with bioproducad hydrogen sulphide (H_2S). Both of these reactions occur mainly in sediments and lead to the formation of insoluble mercuric sulphide (HgS).

In aquatic environments, Hg may be precipated or methylated. Inorganic mercury in natural waters was shown to be rapidly and efficiently transferred to the sediment, almost 100 percent in 5 minutes, and was affected little by changing pH (Ramamoorthy and Bust, 1976). Kudo and Hart (1974) showed that the uptake rates of inorganic Hg by Ottawa River sediments was relatively rapid and no significant difference was observed between aerobic and anaerobic conditions. The uptake rate for methylmercury ions was higher than the value for inorganic Hg by about 10 percent (Mortimer and Kaslo, 1975). Mercury is present in sediments in different forms occurring as: 1) particles of mercuric sulphide; 2) droplets of metallic mercury; or 3) chemisorbed or adsorbed in either organic or inorganic materials as mercuric ion and methylmercuric ion (Krenkel, 1974).

It has been demonstrated that microorganisms living in the sediments ingest inorganic mercury and transorm it into dimethyl - or methylmercury (Wood et al., 1968; Jensen and Jernelov, 1969). At low concentrations, the formation of dimethylmercury is favoured in the

C.12 MERCURY - (Cont'd)

methyl transfer reaction but at higher concentrations of mercury, the major product appears to be monomethylmercury. In a particular system, the amounts of mono and dimethylmercury compounds are determined by the presence of microbial species, Hg concentration, temperature and pH (Wood et al., 1969). Spangler et al., (1973) have demonstrated reactions by microbes resulting in possibly zero net methylmercury release to the water.

The corresponding release of mercury from sediments is slow (Jacobs and Keeney, 1974). The desorption rate from Ottawa River sediments, for example, ranged from 0.1 to 1.0 $\mu g/cm^2$ per day and was colume dependent (Kudo et al., 1975).

World attention focussed on the environmental mercury problem when humans were poisoned by eating fish and shell fish contaminated with methylmercury during the middle of the 1950s in Minamata, Japan. The implications of mercury contamination and subsequent methylmercury formation in aquatic sediments were clearly demonstrated. This form of methylmercury is readily taken up by aquatic organisms and is biomagnified through the food chain affecting both aquatic and terrestrial tropic levels.

Inorganic and organic forms of Hg display acute and chronic toxicity effects to aquatic organisms. Methylmercury, the most toxic of all mercurials to the environment, severely retarded the growth of an alga, Chlamydomonas sp. by as low a concentration as 0.02 µg/L. Holderness et al., (1975) reported similar findings in the alga, Coelastrum microporum at a concentration of 0.80 µg/L methylmercury. The presence of mercury affected both the accumulation of starch and cell buoyancy as well as photosynthetic rates. Chlorophyll and galactolipid synthesis were inhibited by 98 percent and 50 percent respectively with alga Ankistrodesmus braumii by 3.5 mg/L $HgCl_2$. A concentration of 2.0 mg/L of methylmercuric chloride inhibits

galactolipid synthesis, the compound also inhibits the galactosyl transferase activity in Euglena chloroplasts (Matson et al., 1972). D'Itri (1972) reports that 0.027 mg/L Hg (as $HgCL_2$ is toxic to Phaeodactylum tricoinutum and Chlorella sp., Chlamydomonas sp. were affected at levels greater than 0.9 mg/L Hg. The same species were affected by phenylmercury acetate at concentrations as low as 0.06 µg/L. Other studies have shown that 0.1 mg/L reduces the growth of algae and photosynthetic rates. (Harriss et al., 1970; Hannan and Patouillet, 1972).

MacLeod and Pessah (1973) found the 96-h LC50 values for mercuric chloride at 5, 10 and 20°C for rainbow trout to be 0.40, 0.28 and 0.22 mg/L respectively. Matida (1971) found that the LC50 for phenylmercuric acetate, methlymercury chloride and mercuric chloride with rainbow trout fingerlings were 8.5, 30 and 310 µg/L respectively. Wobeser (1973) reported the 96-h LC50 for methylmercuric chloride in newly hatched sac fry and fingerlings of the same species to be 24 and 42 µg/L respectively. These data compare favourably with those of Matida (1971). The average 96-h LC50 for yearling and juvenile brook trout was shown to be 0.075 mg/L Hg (McKim et al., 1976). The MATC determined from the long term effects on three generations of the species was from 0.29 µg/L as $CaCO_3$, pH = 7.5. These figures were used to determine the application factor (AF = MATC/96-h LC50) which was between 0.013 and 0.004. Fathead minnows exposed to methylmercuric chloride all died after 3 months exposure to 0.80 and 0.41 µg/L mercury. 92 percent of the fish exposed to 0.23 µg/L also died within the 3-month period (Mount, 1974). Spawning was completely inhibited at 0.12 µg/L mercury with males not developing sexuality. A concentration of 0.07 µg/L did not produce any toxic effects.

Short term 96-hour bioassay studies with Hg in the form of mercuric ions showed that 1 mg/L was fatal to fish (USEPA, 1972).

C.12 MERCURY - (Cont'd)

Panigrahi and Misra (1978) report that the fish Anabas scandens exposed to 5 mg/L or greater of mercuric nitrate all died. At 3 mg/L these fish developed inappetence and ataxia after 5 days and, after 3 weeks exposure, blindness was noted in 29 percent of animals.

Rainbow trout and sockeye salmon (Onchorhynchus nerka) were able to survive in 10 mg/L of pyridyl mercuric acetate for 1 hour with no toxic effects (Rucker and Whipple, 1951). The LC50 of pyridyl mercuric acetate for some fresh water fish ranges from 0.30 to 26 mg/L for exposures between 24 and 72 hours (USEPA, 1972). Van Horn and Balch (1955) reported that the minimum lethal concentrations of pyridyl mercuric acetate, pyridyl mercuric chloride, phenyl mercuric acetate and ethylmercuric phosphate for minnows in 120-hour bioassays were 0.15, 0.04, 0.2 and 0.8 mg/L respectively.

Concentrations of methylmercuric chloride greater than or equal to 1 mg/L reduced sperm viability in rainbow trout. Inorganic or methyl Hg produced 100 percent mortality in rainbow trout embryos exposed to 0.01 mg/L (Birge et al., 1974b). O'Connor and Fromm (1975) reported that rainbow trout exposed to 10 µg/L of methylmercuric chloride for up to 12 weeks did not affect the in vitro metabolism of the gill or the concentration of plasma electrolytes.

Mercury also affects gill structure. Catfish exposed to levels of 0.67 and 15 mg/L Hg displayed changes in gill morphology. The acute toxic mechanism of Hg seems to result from damage to the gill tissues from the "abrasive" effect of the ions and the formation of a mucous film that fills the interlamellar spaces which prevents the normal movement of the gill filaments. Consequently, gas exchange between the animal's blood and the ambient environment cannot take place and the fish dies from asphyxiation. Mercuric ion inhibits the active uptake of sodium by the gills of goldfish resulting in increased Na loss from the fish. The toxicity of Hg could therefore be related to its effects on osmoregulation (D'Itri, 1972).

C.12 MERCURY - (Cont'd)

Mercury as mercuric chloride and methylmercuric chloride caused significant reproductive impairment at concentrations of 2.7 and 0.04 µg/L respectively in Daphnia magna (USEPA, 1976).

Some important factors affecting Hg toxicity are temperature, dissolved oxygen concentration, presence of other metals and water hardness. MacLeod and Pessah (1973) for example, showed that an increase in water temperature decreased the time of death for rainbow trout exposed to Hg. A 10°C rise in temperature increased the toxicity of the mercuric ion three fold (Rehwoldt et al., 1972). Low levels of dissolved oxygen increased the toxicity of heavy metals due to an increase in the rate of respiratory flow (Lloyd, 1961).

Copper seemed to protect against the toxic effects of mercury in a similar fashion to zinc's protective action against mercury in mammalian embryos (Roales and Perlmutter, 1974). The metal most affecting mercury toxicity is selenium. The mercury body-burden in fish exposed to mercury was less in individuals pretreated with selenium (Kim et al., 1977). A study by Huckabee and Griffith (1974), however, using the percentage hatch of carp eggs, indicated a synergistic action between Hg and Se.

Hard water had an antagonistic effect on the toxicity of mercury chloride to the protozoan Tetrahymena pyriformis (Carter and Cameron, 1973). This factor did not appear to alter Hg's toxicity to Daphnia, rainbow trout, carp or killfish (Tabata, 1969).

Regardless of the mercury form present, the major portion of the mercury will ultimately reside in the bottom sediments where, through microbial action, mono - and dimethylmercury can be formed. Therefore, virtually any mercury compound entering water may become a bioaccumulation hazard if the environmental conditions are favourable for methylation (Phillips and Russo, 1978). These are forms biomagnified by fish and other aquatic organisms due to the rapid uptake and

C.12 MERCURY - (Cont'd)

the relative low rates of excretion of methylmercury. The concentration of mercury in the aquatic food chain is much more marked than that for terrestrial systems.

Bacteria accumulate mercury more rapidly than sediment, taking up almost 20 times as much Hg after 72 hours (Ramamoorthy et al., 1977). Mercury loss from the system was attributed to bacteria converting divalent mercury to volatile Hg^{o}.

Mercury released to water from Hg^{203} - enriched sediments was taken up by guppies. Uptake from the water by the guppies was compensated for by increased mobilization of Hg from sediment to water (Kudo, 1976). Mercury uptake increased in fish exposed to a decrease in pH, increasing sharply below pH = 7.0 (Tsai et al., 1975).

Ruohtula and Mieltinen (1975) found that the biological half-life of methylmercury in rainbow trout ranged from about 200 to 500 days. Elimination time was inversely related to temperature. Orally administered methylmercury was retained longer than methylmercury accumulated from the water suggesting the importance of the diet (Miettinen, 1975). Uptake studies with the fresh water clam (Anodonta grandis) showed that only methylmercury was retained by the clams upon transfer to clean water (Smith et al., 1975). A similar observation was reported for rainbow trout. (Fromm, 1977).

The gill of fish appears to be the major site of mercury accumulation from water as opposed to the gastrointestinal tract (ingested water) or the skin (Fromm, 1977). Uptake of Hg by fathead minnows was not proportional to concentration but increased with concentration (Olson et al., 1975). Brook trout exposed to methylmercury concentrations as low as 0.03 µg/L over three generations attained mercury concentrations in edible tissues exceeding the Federal Drug and Administration guideline (McKim et al., 1976).

C.12 MERCURY - (Cont'd)

Most of the reports in the literature recognize food as the major source of Hg to fish. Norstrom et al., (1976) have shown that 80 percent of the methylmercury present in food and 12 percent of that passing over the gills was accumulated by fish. Elimination was described as a function of body weight and methylmercury body burden. The particular properties of methylmercury cause its accumulation in fish tissues especially in brain and muscle tissue. This is in contrast to inorganic mercury and the more easily biodegradable organomercurials. Benthic animals contain little methylmercury in relation to total Hg content, hence the transport of mercury from benthic fauna as food to fish is comparatively small (Jernelov and Lann, 1971). The same would seem to apply for plankton. For fish preying on other piscivorous forms, however, food as a way of methylmercury transport is much more important.

Gardner et al., (1978) have demonstrated the significance of mercury in the environment. They measured the concentration of various forms of mercury in a Hg-polluted marsh ecosystem as a result of industrial discharge. The levels of Hg were elevated in receptor organisms reflective of the pollution source. The predominant form of the metal varied in different components, most of the Hg in sediments and plants, for example, was not methylated but in the higher trophic level organisms (mammals, birds and fish), Hg existed principally as methylmercury. The tissues of animals which fed on plants and detrital material in the sediments tended to contain lower, but measurable, concentrations of methylmercury. The transfer of methylmercury up the food chain explained the high levels of the compound in the tissues of birds and mammals. These animals fed on Littorina and/or Uca, fresh water plants that contained methylmercury, and might explain, in part, the source of methylmercury observed in the birds and mammals investigated in the study. Some general concentration factors for mercury by various trophic levels of the aquatic biota are: > 930 for bryophytes (Dietz, 1973); 100 000 for fresh water invertebrates; and 1000 for fresh water fish (Vaughan et al., 1975).

C.12 MERCURY - (Cont'd)

Mercury is a non-essential element for plants and animals but can be very toxic to both forms of organisms. Mercury, especially methylmercury, is accumulated by fish in the aquatic environment from both their food and water. The slow elimination of the compound from the animals permits its general biomagnification through the aquatic biota. Methylmercury can enter terrestrial food chain via organisms in the terrestrial/aquatic environment interface. Methylmercury at any trophic level is cause for concern because of its bioaccumulatory potential and high toxicity.

C.13 MOLYBDENUM (Mo)

Upon the combustion of coal, Molybdenum is partially volatilized and enriched on fly ash particles (Ruch et al., 1973; Klein et al., 1975).

Molybdenum is required by bacteria, higher plants, and animals for a number of biological processes. In mammals a trace of Mo is needed, but an excess is toxic; it is required for the proper utilization of copper (Prosser, 1973). Molybdenum may be important for several flavoproteins such as xanthine oxidase. Synthesis of the latter compound is induced by Mo in rats (Prosser, 1973). It is also a component of enzymes involved in purine metabolism and sulphite oxidation (Underwood, 1975). Plants require Mo for normal growth (Johnson, 1966).

There are few data which describe the toxicity of Mo via inhalation or by ingestion. Molybdenum exists in various valence forms; the soluble hexavalent compounds are well absorbed from the gastrointestinal tract and transported to the liver. Ruminants are sensitive to Mo which they may ingest while grazing (Kubota et al., 1967). A molybdenum concentration of 5 to 10 mg/kg is considered to be toxic in cattle, sheep and horses while swine are more tolerant to Mo.

C.13 MOLYBDENUM (Mo)

Excess Mo in cattle causes diarrhea and leads to copper accumulation in the kidneys. High levels of Mo also reduce copper utilization in mammals (Prosser, 1973). Molybdenum has also been associated with degenerative changes in liver cells (Dvorak et al., 1978).

In humans Mo accumulates in the kidneys and adrenals, excretion is rapid occurring primarily in the urine. Excess Mo may also be excreted in the bile.

Molybdenum usually occurs as divalent unions in soil solutions. They react somewhat similarly to phosphate and are more soluble in neutral to alkaline soils (Berry and Wallace, 1974). The mobility of Mo has been shown to increase in poorly drained or flooded soils, probably because of the reduction of the element to lower valence states in the absence of good aeration (Johnson, 1966). Molybdenum has been shown to inhibit nitrogen mineralization in soils (Liang and Tabatabai, 1977).

Plants accumulate Mo proportionately to the amount added to the soil. In fact, natural background concentrations of Mo are not toxic to plants (USEPA, 1972). The concentration required to be toxic to plants is not well defined, but hundreds or thousands of mg/kg appear to be needed (Horton et al., 1977). The distribution of Mo in plants appears to be higher in the roots than the shoots (Wallace and Romney, 1977).

Molybdenum can enter herbivorous species through ingestion. Not much information, however, is available on the toxicity of Mo to animals via this route.

Molybdenum occurs in fresh water from 0.03 to 0.13 mg/L (Dvorak et al., 1978). It has not been considered a serious pollutant but it is a biologically active metal. It may be an important element

C.13 MOLYBDENUM - (Cont'd)

for protection of the aquatic ecosystem due to its role in algal physiology. Molybdenum is essential for the fixation of elemental nitrogen by blue - green algae (Hardy and Burns, 1968).

The 96-hour LC50 for fathead minnows exposed to molybdic anhydride (MoO_3) was 70 mg/L in soft water and 370 mg/L in hard water. Although Mo is essential for the growth of the alga Scenedesmus sp. the threshold concentration for a deleterious effect is 54 mg/L (Bringmann and Kuhn, 1959).

Molybdenum does not tend to accumulate in the edible portions of tissues and has a relatively low toxicity to animals. The concentration factor for Mo in the edible portions of fresh water fish is only 10, this corresponds to the value observed for fresh water invertebrates (Vaughan et al., 1975). Molybdenum in the biota would appear to be of little concern although its influence on copper toxicity may be significant.

C.14 NICKEL (Ni)

Coal combustion is a major source of airborne nickel. During the combustion process, hot carbon monoxide is passed over finely divided nickel in fly ash particles and gaseous nickel carbonyl is released. In the atmosphere, nickel carbonyl is transformed into nickel oxide in dry air and nickel carbonate in moist air (IARC, 1973).

Nickel is not essential to plants, but it has been suggested that it is required for animals although the precise role is unknown (Underwood, 1975). Nickel occurs in keratinous tissues, especially feathers, it is also present in the liver and thymus gland (Prosser, 1973). Nickel activates several enzyme systems but these activities are not specific to Ni. It is always present in ribonucleic acid (RNA) and may help maintain the configuration of the molecule. Nickel is essential to hepatic metabolism in chickens and may also be involved in melanin pigmentation. (Underwood, 1975).

C.14 NICKEL - (Cont'd)

Some of the Ni emitted from a coal-fired powerplant is absorbed onto particulates of submicron size (Davidson et al., 1974; Klein et al., 1975). These particles can deposit in the deep alveolar regions of the lung (Natusch et al., 1974). In this fashion, Ni can enter an organism's bloodstream and be subsequently transported to the internal organs. Some pulmonary accumulation may take place. According to Natusch et al., (1974) the alveolar absorption efficiencies for most of the trace elements are from 50 to 80 percent. Ingested Ni, on the other hand, is poorly absorbed and excreted mostly in the feces. Nickel carbonyl is apparently excreted in the urine (Belilles, 1975).

Nickel has been associated with cancer of the lungs in animals. Animals inhaling inorganic nickel compounds have developed respiratory changes and deleterious health effects (IARC, 1973; Graham, 1975). Nickel dust, nickel sub-sulphide (Ni_3S_2), NiO, nickel carbonyl and nickel bicyclopentadiene are carcinogenic in experimental animals after inhalation. There is, however, no evidence of carcinogenicity after oral exposure. Nickel carbonyl, $NiCO_4$, is the most toxic of all the nickel compounds. It has caused death after exposure of humans to 30 mg/kg for 30 minutes (Belilles, 1975). Mice can tolerate 5 mg/L of nickel acetate in their drinking water over their lifetime but animals fed 1600 mg/L showed a reduction in growth and degrees of inappetence (Underwood, 1971). Growth rate was reduced in chicks fed on diets containing 700 mg/kg or greater as either the sulphate or acetate. The growth of rats, on the other hand, fed nickel carbonate, nickel soaps and nickel catalyst at 250, 500 and 1000 mg/kg in the diet for 8 weeks was not affected. Dogs and cats are able to tolerate daily doses of 4 to 12 mg/kg Ni for 200 days with no ill effects.

Nickel is poorly absorbed from the intestine although the mucosal lining of the gut can be irritated by Ni (Gough and Shacklette, 1976). The symptoms of Ni toxicity in animals fed Ni are hyperglycemia, and gastrointestinal as well as nervous system disorders.

C.14 NICKEL - (Cont'd)

Abnormalities have developed in the kidney of calves fed nickel carbonate. Nickel chloride fed to young male rabbits decreases liver glycogen and also increases muscle glycogon and produces prolonged hypoglycemia after a galactose dose.

The symptoms of acute poisoning by nickel carbonyl are respiratory problems, leukocytosis and cyanosis. It can also delay the symptoms of fever. The mechanism of toxicity may be in part, due to inhibition of adenosine triphosphate (ATP) utilization, it might also produce a metabolic block at the level of messenger RNA.

Nickel in soils will usually occur as divalent cations, its availability being influenced by CEC of the soil (Berry and Wallace, 1974). Nickel cations will be bound more tightly to neutral or slightly alkaline soils while becoming more available in acidic soils due to their increased solubility. Soil levels of Ni are commonly in the range of 10 to 1000 mg/kg (Allaway, 1968). Nickel has been shown to inhibit nitrogen mineralization in soils (Liang and Tabatabai, 1977).

Nickel can be toxic to plants via the airborne route as well as through uptake by the roots (USEPA, 1976). There are very few data addressing the toxicity of airborne Ni. Entry to plants is primarily through the root system where the metal is subsequently translocated in the xylem and deposited in the leaves (Tiffin, 1971). The toxicity of Ni to plants now appears to be caused by a decrease in the cation exchange capacity of the roots (USEPA, 1976). Nickel seems to be evenly distributed between the roots and shoots of plants (Wallace and Romney, 1977). Whitby et al., (1976), however, report that Ni was higher in the roots than the shoots. Red Maple (Acer rubrum) trees accumulated Ni to 30 mg/kg, 20 km from the Sudbury, Ontario smelters (Whitby et al., 1976). They related the increased uptake to the increased acidity of soils close to the smelters. Analyses of field

grown plants showed that they had very high levels of Ni in the foliage of the seedlings. Water extracts of the field collected soils showed that there was a high percentage of soluble Ni in the soils. Water extractable Ni at concentrations to 20 mg/L and as high as 420 mg/L was found in surface soils. Root growth in a number of plant species has been found to be reduced by as much as 50 percent in solution concentrations of 2.0 mg/L or less (Whitby et al., 1976).

Barley developed the symptoms of white chlorosis characteristic of nickel toxicity in cereals when grown on soils containing 320 mg/kg Ni (Wiltshire, 1974). Yields were also reduced in conjunction with symptoms. The concentrations of nickel were high (293 mg/kg) in the roots. Wiltshire (1974) also observed that certain populations were more tolerant of the Ni than others. Oddly, the more tolerant populations of several species took up as much Ni as less tolerant populations, but translocated less from the root to the sensitive shoot.

Vanselow (1977) demonstrated that Ni is toxic to a number of plants when grown in sand and solutions containing 0.5 to 1.0 mg/L Ni. A concentration of 8 mg/L in solution kills barley quickly while levels of 0.5 and 2.0 mg/L produce chlorosis in buckwheat and ben respectively (Chapman, 1966). McKee and Wolf (1963) indicated that Ni was extremely toxic to citrus. Tomato seedlings were injured by 0.5 mg/L Ni and hop plants were adversely affected at 1.0 mg/L (USEPA, 1976). A concentration of 500 mg/kg in the soil and 60 mg/kg in oat grain reduced crop yields. Yields were also reduced in oat straw and alfalfa at concentrations of 28 and 44 mg/kg (Chapman, 1966).

The symptoms of Ni toxicity to plants is a chlorosis that is usually described as resembling the symptoms of iron deficiency. In cereals, the chlorosis is in the form of white or of yellow and green

C.14 NICKEL - (Cont'd)

stippling, chlorosis in dicotyledons gives a mottled appearance. In severe toxicity, chlorosis may be followed by necrosis and death of the plant (Chapman, 1966). The only way to detect excessive Ni in the soils is to analyze the leaves. Certain species such as birch trees and conifers, however, may serve as indicator species for plant exposure to Ni.

Nickel is present in natural waters at concentrations ranging from 0.003 to 0.08 mg/L (USEPA, 1976) and in sediments from roughly 1 to 135 mg/kg (Leland et al., 1978). As a pure metal, Ni is not a problem in water pollution because it is not affected by, or soluble in water. A number of Ni salts are, however, soluble in water (USEPA, 1972).

The toxicity of Ni to fish varies with the species tested and the quality of water used in the experiments. The 96-hour LC50 of Ni for fathead minnows ranges from approximately 5 mg/L in soft water to 43 mg/L in hard water under static test conditions (Table C-8). A similar relationship of Ni toxicity is observed for bluegills. The results of one study found that 96-hour LC50 values for Ni ranged from 6.2 to 46.2 mg/L for six species of fish under static conditions (Rehwoldt et al., 1971). The survival curves for sticklebacks in soft tap water indicate a lethal limit of 0.80 µg/L Ni (Jones, 1939).

The 96-hour LC50 values for two species of aquatic insects were found to be 4.0 and 33.5 mg/L Ni (Warnick and Bell, 1969). Biesinger and Christensen (1972) found that the 3 week LC50 value for Daphnia magna in soft water was 0.130 mg/L Ni, 0.095 mg/L caused a 50 percent impairment in reproductivity and 0.03 mg/L caused a 16 percent impairment.

In studies of the chronic toxicity of Ni to the fathead minnow, the MATC was found to be 0.38 mg/L. This concentration did not

TABLE C-8

96-HOUR LC_{50} OF NICKEL FOR VARIOUS FISH SPECIES

Species	Temp °C	DO mg/L	pH	Hardness mg/L-$CaCO_3$	96-hour LC_{50}	References
Fathead minnow	-	-	-	Hard	24.0	Tarzwell & Henderson, 1960
Fathead minnow	-	-	-	Soft	4.0	Tarzwell & Henderson, 1960
Fathead minnow	25	7.8	7.5	20	4.58, 5.18	Pickering & Henderson, 1966
Fathead minnow	25	7.8	7.4 to 8.4	360	42.4, 44.5	Pickering & Henderson, 1966
Bluegill	25	7.8	7.5	20	5.18, 5.36	Pickering & Henderson, 1966
Bluegill	25	7.8	7.4 to 8.4	360	39.6	Pickering & Henderson, 1966
Goldfish	25	7.8	7.5	20	9.82	Pickering & Henderson, 1966
Guppy	25	7.8	7.5	20	4.45	Pickering & Henderson, 1966
Killfish	17	6.5	7.8	53	46.2	Rehwoldt et al.; 1971
Striped bass	17	6.5	7.8	53	6.2	Rehwoldt et al.; 1971
Pumpkinseed	17	6.5	7.8	53	8.1	Rehwoldt et al.; 1971
White perch	17	6.5	7.8	53	13.6	Rehwoldt et al.; 1971
American eel	17	6.5	7.8	53	13.0	Rehwoldt et al.; 1971
Carp	17	6.5	7.8	53	10.6	Rehwoldt et al.; 1971
Fathead minnow	25	6.9	7.8	207	27 to 32	Pickering, 1974

C.14 NICKEL - (Cont'd)

adversely affect the survival, growth or reproduction in the species (Pickering, 1974). Nickel concentrations of 0.73 mg/L caused a significant reduction both in the number of eggs per spawning and in the hatchability of eggs. A nickel concentration of 0.095 mg/L reduced reproduction during a 3 week exposure in soft water (45 mg/L $CaCO_3$) and a Ni concentration of 0.03 mg/L had no effect (USEPA, 1972).

Nickel contamination in fresh water lakes of 6 mg/L has been implicated in the reduction of algal biomass and species (Whitby et al., 1976). Nickel has been shown to be toxic to algae at a concentration of 0.5 mg/L (Hutchinson, 1973).

In a study of accumulation of iron, Ni, Zn, Pb and Cu by algae collected near a zinc smelting plant, it was found Ni exhibited the lowest concentration factor for all the metals tested. Nickel accumulates in sediments reflective of the inputs from industrial activity. (Hutchinson et al., 1976). Levels of Ni in the water varied with input source but correlated well with levels in periphyton, zooplankton and minnows which is suggestive that the metal was accumulated. Some concentration factors for Ni by aquatic organisms are: 10.3 for duckweed, Lemna minor (Hutchinson and Czyrska, 1975); 1700 for bryophytes (Dietz, 1973); 100 for fresh water invertebrates and 100 for fresh water fish (Vaughan et al., 1975).

Nickel is non essential to vegetation but is apparently required in the diet of animals. It is apparently of more concern to aquatic organisms as it is not of environmental concern to terrestrial animals that ingest the metal.

C.15 SELENIUM (Se)

Coal combustion is the principal source of selenium contamination in the environment (IARC, 1975). Elemental Se and Se oxides are the most likely forms of Se to be released (Davidson et al., 1974).

C.15 SELENIUM - (Cont'd)

During coal combustion, Se is considered to be volatized to the extent of 50 percent or greater (Ruch et al., 1973; Klein et al., 1975). Selenium dioxide may be emitted from coal combustion in vapour form although the majority is most likely in particulate form.

Selenium generally is not essential to plants but a few angiosperms seem to have a requirement for the element (Bowen, 1966). Animals require selenium for normal growth. Chickens and lambs, for example, develop dystrophy with Se deficiency (Prosser, 1973). Chickens also exhibit poor feathering and pancreatic effects without selenium. Selenium can also replace Vitamin E and occurs in a few amino acids and many proteins. It also prevents hepatosis dietetica in pigs as well as promoting growth, improving fertility and reducing postnatal losses in sheep (Underwood, 1975). A dietary intake of 0.1 mg/kg for sheep and cattle is sufficient to prevent Se deficiency. A dietary requirement of 0.04 mg/kg is recognized as essential for animals in general (Kothny, 1973). Selenium has also been shown to protect against the effects of mercury induced mortality in mice, (Taylor, 1978).

Selenium is likely adsorbed onto particulates of submicron size which can readily deposit in the alveolar portions of the lungs where they are available to the bloodstream and subsequent transport to the internal organs. Natusch et al., (1974) estimate that absorption efficiencies for trace elements in submicron particles from the lung are roughly from 50 to 80 percent.

Selenium compounds are inhaled through the lungs in dust or fumes, absorbed through the skin or ingested (Gough and Shacklette, 1976). Excess Se in the body from any route can cause adverse effects. Although Se in elemental form may be relatively nontoxic, inhaled Se dust and fumes are irritating and may give rise to pneumonitis (Goodman and Gilman, 1970). The main absorption site of Se in animals is the gastrointestinal tract, specifically the duodenum. Elemental Se is poorly absorbed but inorganic salts of Se such as selenate, selenite

C.15 SELENIUM - (Cont'd)

and Se analogues of cystine and methionine are absorbed much better (Underwood, 1975).

The effects of excess Se inhalation have been observed in humans under occupational exposure. It was shown to cause mucous membrane irritation, catarrh, nosebleed, loss of sense of smell and dermatitis. Selenium is rapidly eliminated at first then more slowly afterwards, being excreted in the feces and urine, the amounts and proportions dependent upon the level and form of uptake (Chapman, 1966; Underwood, 1975). Acute exposure to elemental Se causes headache, difficult breathing, mucous membrane irritation and central nervous system effects (Stahl, 1969). Acute exposure to selenium dioxide causes similar symptoms including dermatitis, burning of the eyes, lacrimation, conjunctival congestion, garlic breath, dizziness and lassitude. Chronic exposure to airborne selenium dioxide causes gastrointestinal disorders, nervousness, liver and spleen damage, anemia, mucosal irritation and lumbar pain (Goodman and Gilman, 1970). The general adverse effects of Se inhalation are concentrated on the epidermis (skin and hair) and gastrointestinal systems. Chronic Se poisoning in animals is characterized by dullness and lack of vitality, emaciation and roughness of coat, loss of hair from mane and tail of horses and body of pigs, soreness and sloughing of hooves and a number of other symptoms (Underwood, 1975). Movement of the animal can be restricted which would lead to limited availability to food resources and water resources. In severe cases the animals could expire.

Selenium has also been implicated as being carcinogenic. Animal toxicological studies have demonstrated both carcinogenic and anticarcinogenic activity (Schrauzer, 1976). It has also been implicated as a teratogen in one human occupational study (IARC, 1975).

When chickens are fed 3 to 4 mg/kg Se, no adverse effects are observed in hens and eggs, but 5.0 mg/kg can reduce hatchability (Valkovic, 1975). Animals consuming feed containing 5 to 40 mg/L Se for

C.15 SELENIUM - (Cont'd)

several weeks may be poisoned but 0.6 mg/L in feed is not toxic to sheep over a 15 month period (Chapman, 1966). Kothny (1973) states that a level of 4 mg/L in feed is toxic to most animals. Chronic poisoning may occur in rats and dogs ingesting 5 to 10 mg/kg Se; 20 mg/kg Se in food may cause animals to refuse food. Selenosis may develop in young pigs in 2 to 3 weeks while concentrations of 8 mg/kg in sheep may result in food consumption and body weight reductions after 5 to 6 months of treatment and 16 mg/kg can eventually result in death (Underwood, 1975). Underwood (1975) states that the minimum toxic level for grazing livestock is 5.0 mg/kg.

Chronic poisoning of livestock could result from daily ingestion of cereals and grasses containing 5 to 20 mg/kg Se (Gough and Shacklette, 1976). According to Underwood (1975) a dietary intake of 1 mg/kg provides a satisfactory margin of safety against any dietary variable or environmental stress likely to be encountered by grazing sheep and cattle. Allaway (1969) indicates that a dietary intake of 0.04 to 2 mg/kg is required to prevent deficiencies whereas concentrations of 4 to 5 mg/kg are toxic.

Cases of livestock poisoning by Se in water have not been reported although some spring and irrigation waters have been found to contain over 1 mg/L Se (USEPA, 1972).

The soil concentration of Se varies in the United States (Heit, 1977). The chemistry of Se in soils is not well understood. Selenium usually occurs as divalent anions in the soil solution. It reacts similarly to phosphate in that it is more soluble in neutral or alkaline soils (Berry and Wallace, 1974). In acid soils (pH 4.5 to 6.5), Se is usually found as a basic ferric selenite of extremely low solubility. In alkaline soils (pH 7.5 to 8.5), Se may be oxidized to selenate ions and become water soluble. Selenium demonstrated a slight inhibition of nitrogen mineralization in soils (Liang and Tabatabai, 1977).

C.15 SELENIUM - (Cont'd)

Plants may be exposed to Se via the airborne route or through the soils. There are few data addressing the first mechanism but Se uptake by plants has been observed. The absorption and accumulation of Se by plants depend upon the concentration and distribution of Se in the soil, the chemical nature of Se, seasonal variation in rainfall, plant species, stage of growth, physiological condition of the plants, available sulphur, proteins and amino acids. Plants grown in neutral or alkaline soils will accumulate Se to a greater extent because the Se is more mobile being dissolved in the soil solution. Elemental Se is moderately stable in soils and is not readily available in this form to plants (Lakin, 1973). At low concentrations, Se appears to have a stimulatory effect on plant growth (Chapman, 1966).

Selenium can be concentrated in plant tissues to levels that are toxic to livestock (Allaway, 1969). For example, Se at concentrations exceeding 200 mg/kg (dry weight) has been found in sweet clover growing on beds of fly ash (Gutenmann and Bache, 1975). The Se content of plants seems to vary more than any other trace element, ranging from traces to 15 000 mg/kg. Corn grown in culture solutions containing 5 mg/L of selenite or organic selenium accumulated 200 and 1000 mg/kg Se respectively (Chapman, 1966).

Certain plant species accumulate Se in large amounts and apparently require it for normal growth. Plants belonging to the geni Astragalus, Conopsis, Stanleya, Xylorrhiza, Aster and Atriplea exhibit these characteristics (Chapman, 1966; Valkovic, 1975). These plants can also be used as "indicators" of the Se in soils since they only thrive in such areas. According to Lakin (1973), certain species of Astragalus utilize Se in an amino acid peculiar to members of this genus. Toxic concentrations for chrysanthemum, sargho, tomato and wheat range from 101 to 1350 mg/kg in leaf foliar tissues (Chapman, 1966). Plants grown on soils containing 30 to 325 mg/kg Se developed Se Toxicity symptoms. Plants grown on nearby uncontaminated soils (<2.0 mg/kg Se) were unaffected (Chapman, 1966).

C.15 SELENIUM - (Cont'd)

The symptoms of Se toxicity in plants are usually characterized by a snow-white border chlorosis of the leaves of cereals. As wheat plants grow to maturity, there is a progressive diminution of chlorosis in successive leaves. Roots take on a pinkish complexion when injured by selenite. A garlic like odor emanates from some forage plants in range areas that have accumulated Se (Chapman, 1966).

Selenium is found in natural waters and sediments at relatively low concentrations, the levels for water ranging from 0.001 to 0.40 mg/L and in sediments generally averaging from 0.1 to 1.0 mg/kg (USEPA, 1976; Adams and Johnson, 1977). The Se content of surface waters is a function of pH being higher in alkaline (pH 7.8 to 8.2) than slightly acidic (pH 6.1 to 6.9) waters (Lakin, 1973). Selenium is quantitatively precipitated as a basic ferric selenite at pH 6.3; to 6.7; at a pH of about 8.0, selenite may be oxidized to the soluble selenate ion.

Selenium has been regarded as one of the dangerous chemicals reaching the aquatic environment. The toxicity of Se is sometimes counteracted by the addition of arsenic which acts as an antagonist (USEPA, 1972). Selenium is both chronically and acutely toxic to aquatic organisms.

Ellis et al. (1937) showed that goldfish could survive for 98 to 144 hours in soft water over a pH range from 6.4 to 7.3 at 10 mg/L sodium selenite. The same species exposed to 2 mg/L Se died after 18 and 46 days, preceded by equilibrium loss and lethargy (Ellis et al., 1937). At 5 mg/L, death occurred in 5 to 10 days. For Catfish (Ictalurus punctatus) an intraperitoneal injection of 3 mg/kg was fatal in less than 40 hours at 10°C.

Zebrafish (Brachydanio rerio) exposed to Se concentrations ranging from 0.5 to 10 mg/L caused embryo mortalities at all levels

C.15 SELENIUM - (Cont'd)

(Niimi and Lattam, 1975). After hatching, mortality increased in concentrations of 3.0 mg/L or greater. Huckabee and Griffith (1974) demonstrated that the toxicities of mercury and selenium were synergistic to the eggs of carp.

Bringmann and Kuhn (1959) demonstrated the threshold effect of Se as sodium selenite on a fresh water crustacean (Daphnia), an alga (Scenedesmus sp.) and a bacterium (Escherichia coli). In 2 days the median threshold effect occurred at 2.5 mg/L with Daphnia, in 4 days the threshold level was 2.5 mg/L with Scenedesmus, 90 mg/L with Escherichia coli and 138 mg/L for the protozoan, Microregma. Selenium as selenous acid slightly stimulated growth at 5 to 15 mg/L but as selenite it completely blocked growth at all concentrations tested, 3 to 20 mg/L, in selected aquatic animals (Bovee, 1978).

Dietary Se appears to be the most important source of Se to many fresh water organisms (Phillips and Russo, 1978). Fish do not appear to concentrate Se to dangerous levels but the accumulation of Se by fish may be beneficial both to the fish and the consumer because of the presumed protective action Se provides against Hg. Barnhart (1958) reported, however, that mortalities of fish stocked in a reservoir were caused by Se leached from bottom deposits, passed through the food chain and accumulated to lethal concentrations in their liver. Concentration factors for fresh water fish and invertebrates are reported to be 250 and 167 (Vaughn et al., 1975). It has been reported that duckweed, an aquatic macrophyte, concentrated selenium (Rodgers, et al., 1978).

Selenium accumulates in terrestrial plants but to a lesser extent than aquatic and terrestrial animals. Animals appear to be more sensitive to the element, especially livestock feeding on contaminated forage.

C.16 SILVER (Ag)

Silver is emitted from the stacks of coal-fired powerplants. It is largely retained within the plant in bottom ash and precipitated fly ash (Ruch et al., 1974; Klein et al., 1975; Curtis, 1977).

There is almost no information on the toxicity of silver to animals via inhalation. It is not generally known as a gaseous pollutant nor is it essential to plants or animals. Silver does not normally occur in animal tissues. It can be absorbed from both the lungs and gastrointestinal tract although absorption is very slow (Goodman and Gilman, 1970; Belliles, 1975). Silver is slowly absorbed as Ag ions are readily fixed to proteins; thus the ions are captured before they diffuse far into the tissues. Ag can, however, enter the body from mucous membranes. Excretion of ingested Ag is primarily via the gastrointestinal tract (Belliles, 1975). Studies of the metabolism of silver in the rat showed only about 2 percent of the element entered the blood from the gastrointestinal tract and the biological half-life was roughly 3 days (Scott, 1949). The spread of damage occurs only when the dose of Ag overwhelms the capacity of tissues to fix it (Goodman and Gilman, 1970).

Ingestion of soluble silver salts in sufficient concentration leads to corrosion of the mucosa of the digestive tract. The fatal oral dose of silver nitrate is 10 g in man. Chronic ingestion of Ag leads to a local or generalized impregnation of the tissues known as argyria. This is due to deposition of Ag in subepithelial portions of the skin. A study of the toxic effects of Ag added to drinking water of rats showed pathological changes in kidneys, liver and spleen at concentrations of 0.40, 0.70 and 1.0 µg/L (USEPA, 1976).

The concentration of Ag in soils appears to average approximately 3.0 mg/kg (Ragaini et al., 1977). No information was found concerning the soil chemistry of silver.

C.16 SILVER - (Cont'd)

Silver can apparently be taken up by plants in polluted areas. Ragaini et al., (1977) showed that grasses grown on Ag - enriched soils accumulated the metal accordingly. The movement of Ag in plants however, would seem to be restricted to the shoots thus limiting the amounts accumulating in the aerial portion (Wallace and Romney, 1977). This would also minimize the amounts of Ag ultimately being ingested by herbivorous species. Klein and Russell (1973) sampled soils and vegetation near a coal-fired powerplant. They found that although there was some enrichment of soils with Ag near the plant, there was no attendant increase in plant concentration. This suggests the element is relatively immobile and unavailable to plants. The discrepancies between Klein and Russell's (1973) work and that of Ragaini et al., (1977) are unexplained.

Silver is rarely detected in water above 1 µg/L (USEPA, 1972), its concentration in sediments is also quite low being less than 0.5 mg/kg (Leland et al., 1978). Silver is one of the most toxic metals to aquatic life, ranking ahead of mercury on a relative acute toxicity basis (Doudoroff and Katz, 1953). Due to the low solubility of most Ag compounds in water, however, it is not generally regarded as a hazard to aquatic life.

Sticklebacks were killed by a 20 µg/L concentration of silver nitrate in 2 days (Doudoroff and Katz, 1953). In differing concentrations, the average survival times were: 1 week at 40 µg/L, 4 days at 10.0 µg/L and only 1 day at 100 µg/L. Jones (1948) reported that the lethal concentration limit of silver applied as silver nitrate for sticklebacks at 15 to 18°C was 0.003 mg/L which compared favourably with Anderson (1948) who found 0.0048 mg/L to be the toxic threshold for the same species.

Rainbow trout exposed to concentrations of Ag from 0.09 to 0.17 µg/L as Ag displayed no significant mortalities but the results

C.16 SILVER - (Cont'd)

did not address the possible effects on reproduction. Silver nitrate in concentrations of 1000 and 100 µg/L killed 16 out of 20 and 12 out of 20 fish respectively, while silver carbonate was lethal to all test fish at a concentration of 1000 µg/L (USEPA, 1976).

Silver is not present in aquatic animals at very high concentrations because most of its compounds are virtually insoluble in water (Phillips and Russo, 1978). In addition, Ag has a very short biological half-life and does not accumulate significantly in the edible portions of fish. Concentration factors for duckweed (Lemna minor) as well as fresh water fish and invertebrates have been estimated at 82, 2 and 769 (Hutchinson and Czyrska, 1972; Vaughan et al., 1975). Obviously, there is no biomagnification of Ag from insect prey to predator fish.

There are limited data on the toxicity of Ag to the terrestrial biota but it is likely the metal is relatively immobile in soils. Animals ingesting Ag would likely secrete the majority of it as it is not accumulated in body tissues. Silver is very toxic to aquatic organisms but its abundance is low in the aquatic environment due to its low solubility in water.

C.17 THALLIUM (Tl)

Thallium is volatilized by about 50 percent or greater during the combustion of coal (Ruch et al., 1974; Klein et al., 1975). It is emitted in the vapour phase of coal-fired powerplant stack emissions (Ray and Parker, 1978). Thallium oxide is believed to be the main species of Thallium released by the combustion of coal (Cavanaugh et al., 1975).

Thallium is not essential for plants and animals. It has been cited as having a very high pollution potential due to its reported toxicity to bacteria, higher plants and animals (Bowen, 1966).

C.17 THALLIUM - (Cont'd)

There is little information on the toxicity of gaseous Tl to animals. Thallium is not a normal constituent of animal tissues but can be absorbed both through the skin and gastrointestinal tract. Humans accumulate Tl in the kidney with lesser amounts in other tissues and is excreted slowly through the urine with small amounts in the feces (Beliles, 1975). Thallium is quite toxic with a lethal dose for humans estimated to be about 12 mg/kg.

The toxic concentrations of Tl to a variety of animals range from 0.8 to 50 mg/kg when administered orally (Bowen, 1966). A level of 750 mg/kg per day has been reported lethal to rats. Rat studies have indicated that thallium oxide is more toxic when taken orally than when administered by injection (Beliles, 1975). Thallium compounds have been widely used for controlling rodents and predators because of the extreme toxicity of the compounds (McMurtrey and Robinson, 1938). When poisoned bait is scattered on the soil, the effects last for several years.

Very few data are available which describe the soil chemistry of Tl or its effects on plants grown in such soils. It appears that thallium-rich soils provide poor substrates for vegetation. Zyka (1972) reports that Tl in the ash of herbaceous plants from an area known to be high in soil concentrations of Tl ranged from 10 to 17 000 mg/kg. These data demonstrate the cumulative potential of plants for Tl. Thallium has been reported to inhibit photosynthesis and transportation in plants (Bazzaz et al., 1974).

Thallium is observed in natural water at a very low concentration of less than 0.01 µg/L (Bowen, 1966). Thallium displays both acute and chronic toxicity to aquatic organisms. Adverse effects of thallium nitrate have been reported for rainbow trout at levels of 10 to 15 mg/L; for perch (Perca fluviatilis) at 60 mg/L; for roach (Rutilus rutilis) at 40 to 60 mg/L; for Daphnia at 2 to 4 mg/L and

C.17 THALLIUM - (Cont'd)

Gammarus at 4 mg/L (Zitko et al., 1975). Damage occurred within 3 days. Exposure to lower concentrations also resulted in injury. The 96-hour LC50 for salmon is 0.03 mg/L (Zitko, 1975). Zitko also reports that 0.4 mg/L was lethal to tadpoles and growth inhibition occurs at levels of 20, 390 and 200 mg/L for Azobacter, Proteus mirabilis and Aspergillus niger respectively. Thallium is apparently as acutely toxic to juvenile Atlantic salmon (Salmo salar) as copper. It kills the salmon slowly allowing them to incorporate high gill, liver and muscle concentrations prior to death. Fresh water fish and invertebrates readily accumulate Tl from the aquatic environment. Concentration factors for the metal in invertebrates is given as 15 000 and 10 000 in fish (Vaughan et al., 1975).

Thallium is also concentrated by some fresh water plants (Zitko et al., 1975). In studies with marine clams (Mya arenaria) and mussels (Mytilis edulis), Zitko and Carson (1975) found that neither organism accumulated the metal. They concluded it was not an environmental hazard to aquatic molluscs.

Thallium is moderately toxic to fish but its movement and potential toxicity to the aquatic biota is largely not understood. It is accumulated in plants and may be passed onto herbivorous species by ingestion.

C.18 THORIUM (Th)

When coal is burned, nearly all the Th is collected and retained within the plant in bottom ash and precipitated ash (Ruch et al., 1974; Klein et al., 1975; Curtis, 1977). The percentage emitted is estimated at only 0.11 percent (Section 3).

Thorium is considered more from a radiotoxicological standpoint than the chemical. The element contributes to dose levels in

C.18 THORIUM - (Cont'd)

biotic receptors. Thorium is not considered a gaseous pollutant from coal-fired powerplants, this is obviously due to the fact that so little of the element is emitted. No data were found which discussed the toxicity of Th via inhalation to animals.

In soils, Th is accumulated in the fine earth particles. The minutely dispersed fraction of soils which contain Th (<0.001 mm) are delivered to plants with ascending water flow. It is readily absorbed onto the roots of plants but translocation to the leaves is negligible. (Mercer and Morrison, 1962; Squire, 1963). Generally, under natural conditions, Th is absent from plant tissues due to its retention in the solid phases of the soil and its general immobility in biological systems (Russell and Smith, 1966).

The mobility and intensity of the incorporation into biological objects depends on the solubility of its compounds (Verkhovskaja et al., 1967). This solubility is low and the element is highly immobile usually making it unnecessary to consider the transfer of Th through a food web.

The impacts of Th on the aquatic environment are not well documented. Water concentrations are typically very low as it is readily precipitated to sediments and is relatively immobile (Russell and Smith, 1966). Thorium is moderately accumulated by fresh water invertebrates and fish. Concentration factors were 500 and 30 for invertebrates and fish respectively (Vaughan et al., 1975). The element is not biomagnified as the concentration factor for fish is less than that of the invertebrates. Algae and macrophytes are reported to display concentration factors varying from 4 to 10 (Polikarpov, 1966).

Pendleton et al., (1964), however, studied the effects of an accidental release of wastes from a uranium ore refining plant. They

C.18 THORIUM - (Cont'd)

found that high concentrations of Th were found in environmental samples and in muskrats living in the area but carp appeared to contain relatively low levels.

Thorium was shown to be toxic to bacteria and an alga (Scenedesmusp) at 0.8 and 0.4 mg/L. (Bringmann and Kuhn, 1959). No data were found for the toxic effects of Th to higher aquatic organisms.

Thorium is essentially immobile in both the aquatic and terrestrial ecosystems. It is not biomagnified through the food chain and is generally not considered as a significant contaminant in food-chain relationships.

C.19 TIN (Sn)

Recent mass balance studies of coal-fired powerplants have shown that tin is concentrated in the ash, while a percentage is released into the environment as particulate or gas (Ruch et al., 1974; Klein et al., 1975; Lim, 1979).

Tin is believed to be essential to animals although a precise role for the metal is unknown (Underwood, 1975). Inhaled inorganic Sn remains in the lungs whereas organic Sn may enter the bloodstream and accumulate in the liver with smaller amounts entering other organs (Belilles, 1975). In humans, most of the ingested inorganic Sn is not absorbed and 90 percent of the element is recovered in the feces; absorbed inorganic Sn accumulates in the liver and kidneys.

Generally, inorganic Sn may be considered nontoxic to most organisms except at high concentrations, e.g. 500 mg/kg for 14 months (Belilles, 1975). Organic Sn, however, is extremely toxic to mammals, including man. Laboratory determined toxic doses of Sn for various

C.19 TIN - (Cont'd)

animals range from 40 to 1200 mg/kg (Bowen, 1966). Rabbits experienced depressed weight gain and mild gastroenteritis as well as a reduction in peripheral red blood cells when given oral doses of 20 mg/kg per day of dibutyl tin chloride (Wakashin, 1975). Tin has also been shown to affect the liver, kidney, spleen and nervous system as well as to cause growth inhibition and decreased food utilization efficiency (Charyer, 1975; Wakashin, 1975).

Little is known about tin in the environment. The toxicity of Sn to plants via the airborne route is largely undocumented. In soils, Sn occurs largely as a divalent cation, its availability being determined in part, by the CEC of the soil (Berry and Wallace, 1974). Generally, Sn is bound more tightly in neutral or slightly alkaline soils and is more mobile in acidic soils by comparison. Tin is relatively low in concentration in soils (Peterson et al., 1976). Tin has been reported to inhibit nitrogen mineralization in soils.

Plants can accumulate Sn from soils but the literature contains relatively few reports on the subject. Peterson et al., (1976) indicate that, in a number of investigations the concentration of Sn has been reported to be below the limit of detection for most of the samples analyzed. Peterson et al., (1976) have, nevertheless, reported the accumulation of Sn by some plants collected near the tailings of a tin mine in Malaysia. The concentrations of Sn varied between plant species and sampling locations. The values for the concentration of Sn in plants studied were higher than those reported from other countries. The results of the work described above by Peterson et al., (1976) contrast the statement that tin is effectively excluded by plants (USEPA, 1972).

In water, tin levels are reported to be about 0.001 to 0.17 mg/L (Peterson et al., 1976). Little information is available on the toxic effects of Sn to aquatic organisms. Bowen (1966) however,

C.19 TIN - (Cont'd)

reports that Sn is toxic to green algae. The 48-hour LC50 for fish exposed to electroplasting tin solutions was 100 mg/L (Karija et al., 1969). Tin was accumulated by the gills, skin and mucous of exposed fish. It has recently been shown that inorganic tin can be alkylated by bacterial action. The resulting organic species may be volatilized and released into the atmosphere (Peterson et al., 1976). One can recall the environmental implications of methylmercury within this context. Tin is accumulated by fresh water invertebrates and fish with concentration factors reported as 1000 and 3000 respectively (Vaughan et al., 1975).

Tin is relatively immobile in the natural environment and is moderately toxic to fish and animals. Its methylated forms from bottom sediments should be considered a potential threat to the biota although specific data are lacking.

C.20 TUNGSTEN (W)

Tungsten is released into the environment from coal combustion. The majority of the W is retained within the plant in the bottom ash and precipitated ash fractions (Ruch et al., 1974; Klein et al., 1975). A small percentage (0.03) is released into the atmosphere as the particulate and gaseous form (Section 3).

Tungsten is not essential to plants or animals and is not usually found in animal tissue. Tungsten is absorbed by the gastrointestinal tract and retained in the bone with lesser amounts accumulated in the spleen, liver and kidney. Oral toxicity does not appear to be a problem and it may be antagonistic to the uptake of molybdenum (Belilles, 1975).

There is virtually no information on the toxicity of W to plants or its uptake from soils and nutrient cultures. The USEPA (1972) has stated that the element is effectively excluded by plants.

C.20 TUNGSTEN - (Cont'd)

This statement is confirmed by the data of Ragaini et al., (1977) who indicated that W was not detectable in plants even when grown on W-enriched soils. Tungsten has been shown to be slightly inhibitory to nitrogen mineralization in soils (Liang and Tabatabai, 1977).

There is a paucity of information on the toxicity of W to aquatic organisms. Catfish (Ictalurus melas), however, accumulated W after 4 days exposure, the biological half-life was relatively short at 2.75 days (Reed, 1969). Fish dosed in a simple feeding lost tungsten at two rates; one component had a half-life of 14 hours and the other 6 days. After 8 days, flesh, gills, liver and gut together contained 78.6 percent of the total content.

In nature, concentrations of W in aquatic biota receptors are very low (Fukai and Meinke, 1959, 1962). Tungsten does not appear to be biomagnified in the aquatic food chain. The concentration factor for the element in fresh water fish is 1200 compared with 30 for sea water species. The concentration factor for fresh water invertebrates is only 10 (Vaughan, et al., 1975).

The dearth of information available on W is insufficient to evaluate its potential for adverse effects in the environment. Vaughan et al., (1975), however, indicated that W was considered to merit some concern and perhaps a more intensive evaluation of potential for adverse effects in terrestrial ecosystems.

C.21 URANIUM (U)

When coal is combusted, a small percentage of the uranium content (1 percent, Table 3-1) escapes into the atmosphere in particulate and/or gaseous form (Curtis, 1977). The remainder is retained within the plant in the bottom ash and collected precipitator ash.

C.21 URANIUM - (Cont'd)

The quantities of U inhaled under normal exposures do not appear to be of dosimetric significance (on the basis of radiotoxicity). The major contribution to doses comes from the gaseous members of the series, radon and thoron and their solid daughter products. Inhalation of uranium dioxide dust at a concentration of 5 mg/m^3 for 5 years produced no evidence of toxicity in mammals (Belilles, 1975). Uptake of the soluble uranylion (UO_2^{2+}) may result in acute renal damage.

Uranium in soils is generally in the form of the water soluble uranyl ion which can be carried away by leachate waters (Hansen et al., 1960). Uptake of U by plants depends on several factors which include plant species and mostly the availability of U in the soil. Small quantities of U have been identified in many plants. It is believed that U enters the vegetation mainly as the uranyl ion (Hansen et al., 1960). The concentration of U varies widely among plant species, with the highest levels usually found in perennial plants with concentrations as high as 100 mg/kg in the ash of plants grown on soils rich in uranium (Cannon, 1953). This has, on occasion, been used in the "biological prospecting" for uranium. Once in the bark, stems, tree branches and shrubs, the uranium deposited there will remain to the end of the plant's life. The U in grass, however, will be returned back into the soil after decomposition, thus enriching its upper layer.

The ratio of U in plant material, to that of "mobile" uranium in the soil, differs between species. The ratio is a little above unity for grains, legumes, tubers, roots and hay (Garner, 1972). Available U can penetrate plants as a result of ion exchange or in a complex combination with organic acids given off by plant roots (Kovalsky et al., 1967). The mobile forms of U compounds in soils make up from 2 to 19 percent of the total U content in the soil with the proportion of mobile forms increasing with soil depth. The presence in the soil of U compounds readily assimilated by plants leads to its accumulation in some food components of the rations of farm animals

C.21 URANIUM - (Cont'd)

(Reid et al., 1977). Uranium has been observed in the tissues of pigs, poultry and in milk presumably from the consumption of plants contaminated with U; most of the U ingested by animals is found in the bones, wool and skin (Kovalsky et al., 1967).

Roughly 0.9 to 2.5 percent of the daily U intake by a hen is eliminated in the egg, with uranium apparently concentrating in the yolk. Wildlife may incorporate U depending on their life habits and feeding characteristics (Verkhovskaja et al., 1967). Digging animals, for example, may accumulate U when digging burrows and these animals may in turn be taken by predators.

The concentration of natural U in water is usually very low (Welford and Baird, 1967). Concentrations for sea water are less than 3 µg/L (USEPA, 1972). Bringmann and Kuhn (1959) determined the threshold effect of uranyl nitrate as U at 28 mg/L on a protozoan (Microregma), 1.7 to 2.2 mg/L on E. coli, 22 mg/L on the alga Scenedesmus, and 13 mg/L on Daphnia. Tarzwell and Henderson (1960) found the sulphate, nitrate and acetate salts of U more toxic to fathead minnows on 96-hour exposure in soft water than in hard water, the 96-hour LC50 for uranyl sulphate being 2.8 mg/L in soft water and 135 mg/L in hard water. Tarzwell and Henderson (1960) found that the LC50 values in hard water for U were 10 to 100 times greater than those obtained in soft water.

Natural U is concentrated from water by the algae (Ochromonas) by a factor of 330 in 48 hours (Morgan, 1961). Aten et al., (1961) calculated the concentration factor of U by marine fish to be about 20. This compares with the value of 10 suggested by Vaughan et al., (1975) for both fresh and sea water fish. The work of Kovalsky et al., (1967) showed that U accumulates in aquatic organisms indirectly via the food chain and that the amount of U accumulated by

C.21 URANIUM - (Cont'd)

fish differs with the species, corresponding to the amount of U absorbed with the food. The largest amounts were absorbed by plant-eating fish such as carp and the least amounts by predatory fish such as trout.

Uranium is accumulated by plants and aquatic organisms. It is relatively mobile through food chain but its toxicity is moderate.

C.22 VANADIUM (V)

The burning of coal contributes a substantial amount of V to the environment (NRC, NAS, 1974). This V is most likely emitted as solid compounds in the particles of fly ash.

Vanadium is considered to be non essential for higher plants and animals although there is some evidence to indicate it is beneficial to some fungi, algae, bacteria, chicken and rats (Bowen, 1966; Gough and Shacklette, 1976). Vanadium is present in tissues of many animals in small amounts (0.1 mg/kg). It may function in some cellular oxidations (Prosser, 1973). The dietary requirements to promote optimum growth for U by rats appears to be about 0.10 mg/kg of diet (Prosser, 1973). In plants, V may play a role in enzyme activation in nitrogen fixation by soil microorganisms and may replace Mo as an essential element by some N_2 fixing bacteria (Chapman, 1966).

Fly ash particles of submicron size may enter the alveolar portions of the lung, where the V in these particulates can gain access to the bloodstream and internal organs (Natusch et al., 1974). Particles less than 0.5 mm contain the highest concentrations of V, particles of this size are readily deposited in lungs. Consequently, V poses a toxicological threat via the inhalation route to animals. In fact, the V inhalation threat increases with decreasing aerosol size (Underwood, 1975). Soluble V compounds which are inhaled in concentrations greater than 50 $\mu g/m^3$ are thought to accumulate in the lung

C.12 VANADIUM - (Cont'd)

and cause irritation (Babu, 1973). Vanadium is more readily absorbed via inhalation than ingestion. The toxic action of V is largely confined to the respiratory tract in humans (Belilles, 1975).

The toxicity of Vanadium compounds is related to their valence states. Vanadium oxide compounds are most likely to be present in coal combustion emissions, of these, vanadium pentoxide presents the greatest hazard. Vanadium is not, however, generally considered to be a toxic element. In humans, an asthma-like condition results from occupational exposure, in such conditions a relationship is observed between urban atmospheric vanadium and bronchitis as well as pneumonia in males (Babu, 1973). Experimentation with animals exposed to large amounts of V produces toxicity and death. At high concentrations (industrial exposure for example), gastrointestinal disorders, kidney damage, and cardiac palpitations have been observed. Heart disease in humans has been postulated to be related to the V concentration in the air (Belilles, 1975).

In animals the toxic effects of inhaled V include: diarrhea, enzyme system dysfunction, growth depression and irritation to the lungs (Underwood, 1975; Gough and Shacklette, 1976). Vanadium may also be toxic to animals when ingested. It has, however, a low order of oral toxicity to mammals as it does not affect growth, life span, nor produce tumours in rats or mice when given in concentrations of 5 mg/L in their dietary water (Schroeder, 1971). Chicks can tolerate 20 to 35 mg/kg (Underwood, 1975). Toxic symptoms in rats were induced by 25 mg/kg of sodium vanadate while 30 mg/kg depresses weight gain and 200 mg/kg results in high mortality (Valkovic, 1975). Rats developed gastrointestinal irritation that lead to death when fed 160 mg/kg V. The highest concentrations of V in animals are in the hair and bones (Bowen, 1966).

C.22 VANADIUM - (Cont'd)

There are few data which describe the effects of airborne V in plants. In soils, V is found usually as a divalent cation. Its availability in soils is dependent upon the CEC of the soil. (Berry and Wallace, 1974). In neutral or slightly alkaline soils it is tightly bound but is more mobile in acidic soils. Vanadium has an affinity for soil organic matter (Jacks, 1976). It has also been shown to inhibit nitrogen mobilization is soils.

Vanadium has been shown to accumulate in forest litter, humus, lichens, mosses and the needles of spruce trees (Ruhling and Tyler, 1973). The accumlated V generally remains in the roots of plants with little reaching the stem and leaves. Plant shoots seldom contain more than 1 mg/kg V (Berry and Wallace, 1974). Some food plants can accumulate high levels of V without toxic symptoms. Some concentrations found were: 600 mg/kg (ash) in snap bean; 50 mg/kg in cabbage; 30 mg/kg in tomato fruits and asparagus (Gough and Shacklette, 1976).

A concentration of 500 mg/L V in a nutrient solution was toxic to both the roots and tops of barley (Chiu, 1953). Vanadium was toxic to germinating seeds and even more toxic to plants at later growth stages (Scharrer and Schropp, 1935). A concentration as low as 1 mg/L V as vanadium chloride added to solution and sand cultures was injurious to barley. At 10 mg/kg V added to sandy soils depressed the growth of orange seedlings and at 150 mg/kg the plants died (Chapman, 1966).

Concentration of 2 mg/kg (dry weight) in the tops of pea or soybean plants may be indicative of V toxicity (Chapman, 1966). Levels greater than 0.5 mg/L in nutrient solutions are toxic to plants, additions of the element to soils has caused plant toxicity. The following concentrations of soluble V are slightly toxic: 10 to 20 mg/kg for soybeans, 25 mg/kg for beets, 40 mg/kg for barley, 20 mg/kg for wheat and 22 mg/kg for oats.

C.22 VANADIUM - (Cont'd)

There is little information on the occurrence or toxicity of V in the aquatic biota. Vanadium as vanadyl sulphate had no effect on the growth of the protozoan, Tetrahymena at concentrations of 1 to 3 mg/L; 5 to 15 mg/L were slightly stimulatory; above that (20 to 25 mg/L) growth was depressed (Bovee, 1978). Several species of marine algae, invertebrate ascidians and tunicates concentrate vanadium to high levels (Goldberg et al., 1951; Vinogradov, 1953; Swinehart et al., 1974). Concentration factors for fresh water and marine invertebrates are estimated at 3000 and 50 respectively (Vaughan et al., 1975).

Vanadium shows some essentiality to animals but not to plants. It is generally non toxic to animals. Data on V in the aquatic environment are lacking.

C.23 ZINC (Zn)

Zinc is most probably emitted through coal combustion as solid compounds in particulate form (Ruch et al., 1974; Klein et al., 1975). Much of the Zn is retained in the powerplant in the bottom ash and precipitated ash with a small percentage (1.5, Section 3) being emitted in the particulate and/or gaseous phases.

Zinc is found in almost all living organisms and is an essential element for most plants and animals (Prosser, 1973). Zinc is an essential component of carbonic anhydrase and is an essential activator for pancreatic carboxypeptidose and occurs in glutanic and lactic dehydrogenases, alcohol dehydrogenase and alkaline phosphatases. Zinc is essential for growth, bone growth, wound healing, reproduction, carbohydrate metabolism and learning behaviour (Underwood, 1975).

Generally, the inhalation of Zn is not an important exposure route. Some information pertaining to this subject is available from situations of occupational exposures. Illness from exposure to excess

C.23 ZINC - (Cont'd)

zinc occurs primarily as "zinc fume fever". Concentrations greater than 15 mg/m^3 have caused this fever (Goodman and Gilman, 1970). Inhalation of Zn and zinc oxide powder cause inflammation of the upper respiratory tract in workers (Schrauzer, 1976). Large doses of inhaled and ingested Zn have caused illness or death to experimental animals but the concentrations were even higher than those that would be encountered in industrial settings.

Animals are exposed to Zn through air, water and food (Chapman, 1966). Zinc is absorbed primarily in the small intestine, it is excreted in the feces and sweat. The metal is also accumulated in bones, the central nervous system and hair. The biological half-life of Zn is relatively long. Zinc has been observed to accumulate in the eye choroid, prostate, kidney, feathers, red blood cells and snake venom (Bowen, 1966; Maniloff et al., 1970; Underwood, 1975).

Zn is comparatively non toxic to both mammals and birds. There is quite a difference in the normal levels of intake compared with those that produce deleterious effects. Domestic animals are quite tolerant to high levels of Zn in their diet; this tolerance is related to other elements (Cu, Fe and Cd) which affect Zn absorption and utilization (Underwood, 1975). Levels as high as 2500 mg/kg, 1000 mg/kg, 500 mg/kg and from 1200 to 1400 mg/kg Zn had no ill effects in rats, weanling pigs, steers and chickens respectively (Gough and Shacklette, 1976). A concentration of 5000 mg/kg of zinc chloride depressed growth and caused mortality in young rats, 5000 to 10 000 mg/kg of zinc carbonate produced anemia and inhibited growth, induced anorexia and ultimately death at the latter concentration (Underwood, 1975). In another experiment, Dunker et al., (1927), found that while Zn intake resulted in Zn accumulation in rat tissues, its accumulation was not great and the levels fell rapidly after the termination of the experiment. The fetuses of female rats are resorbed at a concentration of 4000 mg/kg, levels of 4000 to 8000 mg/kg are lethal to weanling pigs

C.23 ZINC - (Cont'd)

while 3000 mg/kg causes growth and appetite depression in chickens. The growth, physiology and food consumption in lambs were adversely affected at concentrations from 900 to 1700 mg/kg (Underwood, 1971). A concentration of 1 mg/kg Zn taken in by dogs reduced the leucocyte count and 4 mg/kg bound to serum proteins resulting in lassitude, decreased tendon reflexes, blood enteritis and diarrhea (Valee, 1959).

In birds, the LD50 of zinc phosphide for pheasants in the field was from 8 to 27 mg/kg (Janda, 1972). Janda also reported that smaller doses caused blood disorder and adversely affected the nervous system, liver and kidneys. Zinc carbonate at concentrations ranging from 3000 to 12 000 mg/kg was toxic to mallard ducks under laboratory conditions (Gasaway and Buss, 1972).

Zinc toxicity to plants via the airborne route is not as significant as that taken up by roots from soils or nutrient solutions. In the soils, Zn usually occurs as divalent cations, the availability being determined partially by the CEC of the soil (Berry and Wallace, 1974). It is bound tightly to slightly neutral or alkaline soils and is more mobile in soils that are acidic. Zinc reacts with organic matter to form zinc humates that are quite unavailable (Ermolenko, 1966). Zinc has been shown to inhibit nitrogen mineralization in soils which may inhibit the growth of detritus microorganisms (Liang and Tabatabai, 1977).

Plants can accumulate Zn from quite dilute soil solutions as the element is a micronutrient for plants. If the soil concentration of these elements is increased, so is the proportionate amount accumulated. Tissues of plants deficient in Zn usually contain less than 15 to 20 mg/kg Zn while plants containing greater than 400 mg/kg Zn show toxicity symptoms (Nash, 1975). Toxic concentrations to the plant itself or grazing herbivores may be reached in this fashion (Dvorak and Lewis et al., 1978). Plants also vary in their ability to accumulate

C.23 ZINC - (Cont'd)

Zn. Some plants may accumulate Zn to such high levels they have been suggested as "indicators" of high soil Zn levels as is the case with ragweed, Abrosia sp. (Chapman, 1966). Other "indicators" of high Zn levels in soils are the Caryophyllaceae, Compositae, Cruciferae, Gramineae, Phymbaginaceae, Rutaceae and Violaceae families (Gough and Shacklette, 1976).

According to Wallace and Romney (1977), zinc is uniformly distributed in the shoots and roots of plants. Van Hook et al., (1977), however, found that Zn was higher in the roots than other plant parts in selected trees. Accumulations of Zn by mosses were greater in urban than rural areas which was related to the greater sources of Zn in the urban sites (Barclay-Estrup and Rinne, 1978). Zinc was mobilized in soils and accumulated in all tissues of the red maple (Jackson et al., 1978). It appeared that most of the accumulated Zn tends to be tied up in insoluble form in the cell wall and hence exerts only limited metabollic activity.

Zinc distribution and cycling in a mixed deciduous forest was studied by Van Hook et al., (1977). The woody component of forest vegetation incorporated an amount equal to 50 percent of the estimated Zn input. The watershed retained less Zn with respect to input, stream output was 26 percent of estimated input. The watershed soils, however, were the major sink for Zn. Although the transport of Zn through vegetation was rapid, the slow response of soil and the potential for recycling resulted in the retention of Zn within the system. These data were similar to those described by Jackson et al. (1978) in a similar study.

Zinc can be toxic to plants in sufficient quantities. Concentrations of 16 to 20 mg/L in nutrient solutions produced iron deficiencies in sugar beets (Hewitt, 1948). Hunter and Vergnano (1953) found toxicity to oats at 25 mg/L, and 25 mg/L produced iron deficiency

C.23 ZINC - (Cont'd)

(Millikan, 1947). Chapman (1966) indicated that toxicity occurred at concentrations of from 1700 to 7500 mg/kg of Zn in leaves of oats. Zinc chloride at concentrations from 0.5 to 50 mg/L inhibited plant growth (Weaver and Brock, 1972). Gough and Shacklette (1976) noted that 125 g/kg total Zn in the soil will stunt the growth of most plants. Toxicity levels for tomatoes and oranges range from 526 to 1489 mg/kg and 200 to 300 mg/kg Zn respectively (Chapman, 1966). Turnips grown in soil containing 200 mg/kg reduced crop yields (Kusaka et al., 1971). The toxicity of Zn is highest in clay and peat soils and the least in sands (USEPA, 1972). Excess zinc in soils produces chlorosis in plants as it interferes with required iron uptake.

Zinc has been found accumulated in the tissues of organisms inhabiting Zn-contaminated areas. Earthworms (Dendrobaena rubida) exhibited higher tissue levels of Zn in animals living in soil contaminated by base metal mining (Ireland, 1975). The concentrations were relatively low compared with the high soil levels. Johnson et al., (1978), however, found no difference in the Zn concentration of small mammals (field mice, (Apodemus sylvaticus) and bank voles, (Clethrionomys glareolus)) from control and Zn polluted sites. The densities of forest litter arthropods were shown to be affected by Zn. Strojan (1978) reported that the densities of all major taxonomic groups were lower near a zinc smelter which was correlated to high soil Zn levels.

Zinc is found in natural waters and sediments in concentrations from 0.01 to 1.18 mg/L and 10 to 3500 mg/kg respectively (USEPA, 1976; Leland et al., 1978). In most surface and groundwaters it is generally found in trace amounts. There is some evidence that Zn ions are adsorbed strongly and permanently on silt resulting in the inactivation of the metal in aquatic systems (Skidmore, 1964). Zinc species in fresh waters are divided between labile ionic species (Zn^{2+}) and a stable inorganic form ($ZnCO_3$); very little of the Zn was associated with organic colloids (Florence, 1977).

C.23 ZINC - (Cont'd)

Zinc displays both chronic and acute toxicity to aquatic organisms. The relative toxicity of Zn has been determined, principally, through the case of fish. The acute toxicity of Zn to fresh water organisms varies greatly with the water hardness, dissolved oxygen concentration, pH and temperature. Zinc toxicity in hard water is roughly an order of magnitude lower, the concentration of the alkaline-earth ions (especially calcium) antagonize the toxicity (Jones, 1939). These ions saturate binding sites on the organism and prevent Zn from doing the same. The survival times of rainbow trout to several Zn concentrations were measured at three hardness levels (Lloyd, 1961). It was observed that the survival period lengthened as hardness increased with a ten fold difference between the toxicity of zinc in the hardest (320 mg/L as $CaCO_3$) and the softest (12 mg/L as $CaCO_3$) waters over a 2.5 day exposure at similar pH values. The toxicity of Zn to Atlantic salmon is also less when the fish are exposed in hard water (Sprague and Ramsay, 1965).

Zinc toxicity to Atlantic salmon decreased as the pH was raised from 7.9 to 9.3; these findings have been attributed to the decreased amount of Zn in solution at the higher pH levels (Sprague, 1964). In contrast, fathead minnows were found to be more susceptible to Zn at a pH of roughly 8.0 when the Zn precipitated and coagulation of the gill mucous was apparent (Mount, 1966).

The effects of temperature on Zn toxicity have been examined by a number of investigators. Studies of bluegills acclimatized to 18 and 30°C showed little difference in the toxicity of Zn (Cairns and Scheier, 1957). In a later study of the toxicity of Zn to rainbow trout at four different temperatures, it was revealed that an increase in temperature from 12 to 24°C reduced survival time by a factor of 2.4 (Lloyd, 1961). The survival time of Atlantic salmon has been observed to increase by a factor of roughly four when the water temperature was decreased from 15 to 5°C (Sprague, 1964). Similarly, the reduction of

survival times for bluegills exposed to Zn was a function of the rate at which the temperature was increased (Burton et al., 1972). Similar results have been found for Atlantic salmon exposed to Zn as the temperature was increased (Hodson and Sprague, 1975). Cold-acclimatized salmon survived longer than warm-acclimatized fish.

The sensitivity of fish to Zn varies with species, age and condition as well as the physical-chemical characteristics of the test water. Table C-9 summarizes the results of 96-hour LC50 data for several fish species. The values range from 0.43 to 13.8 mg/L in soft water and 4.2 to 35.5 mg/L in hard water. Salmonids were the most sensitive species tested while the warm water types such as bluegills and goldfish were the most tolerant. Death of fish in acute bioassays is generally accepted as being due to changes in blood flow patterns through the gill lamellae causing a failure of lamellar circulation, resulting in respiratory collapse and death.

Zinc is also toxic to invertebrates. The 96-hour LC50s for pond snails (Physa heterostropha) in water with hardnesses of 100 and 20 mg/L as $CaCO_3$ were 0.303 and 0.434 mg/L Zn (Wurtz, 1945). The 96-hour LC50 for the mayfly (Ephemerella subvaria) in water with a hardness of 44 mg/L as $CaCO_3$ was 16 mg/L (Warnick and Bell, 1969). The 48-hour LC50 for Daphnia in soft water (45 mg/L as $CaCO_3$) was 0.10 mg/L.

Chronic or long-term exposures to Zn by aquatic organisms have caused growth inhibition, changes in swimming movement patterns, alterations in behaviour and blood chemistry and reduction in reproductive capacity. Holcombe et al., (1979) exposed brook trout over three generations to zinc concentrations varying from 2.6 to 534 µg/L without harmful effects. A concentration of 1.37 mg/L, however, reduced embryo and 12-week larval survival. Brungs (1969) found that in water with a total hardness of 200 mg/L as $CaCO_3$, 0.18 mg/L caused

TABLE C-9

96-HOUR LC_{50} OF ZINC FOR VARIOUS FISH SPECIES

Species	Temp °C	DO mg/L	pH	Hardness mg/L-$CaCO_3$	96-hour LC_{50}	References
Bluegill	18	-	-	15	2.9 to 3.8	Cairns and Scheier, 1957
Bluegill	20	-	-	15	1.9 to 3.6	Cairns and Scheier, 1957
Bluegill	18	-	-	11 700	10.1 to 12.5	Cairns and Scheier, 1957
Bluegill	30	-	-	11 700	10.2 to 12.3	Cairns and Scheier, 1957
Bluegill	25	7.8	7.5	20	6.44	Pickering and Henderson, 1966
Bluegill	15	7.8	7.5	20	5.37	Pickering and Henderson, 1966
Bluegill	25	7.8	7.5	20	5.37	Pickering and Henderson, 1966
Fathead minnow	25	7.3	6.0	50	12.5, 13.8	Mount, 1968
Fathead minnow	25	7.9	6.0	100	18.5, 28.0	Mount, 1968
Fathead minnow	25	7.2	6.0	200	29.0, 35.5	Mount, 1968
Fathead minnow	25	6.8	7.0	50	6.2, 13.7	Mount, 1968
Fathead minnow	25	6.8	7.0	100	12.5	Mount, 1968
Fathead minnow	25	6.8	7.0	200	13.6, 19.0	Mount, 1968
Fathead minnow	25	7.4	8.0	50	4.7, 5.1	Mount, 1968
Fathead minnow	25	6.6	8.0	100	8.1, 9.9	Mount, 1968
Fathead minnow	25	7.1	8.0	200	8.2, 15.5	Mount, 1968
Fathead minnow	23	6.7	7.7	203	12.0, 13.0	Brungs, 1969
Fathead minnow	23	1.7 to 10.8	7.4 to 8.3	192 to 221	12.0, 13.0	Brungs, 1969
Fathead minnow	23	1.7 to 10.8	7.4 to 8.3	192 to 221	8.4, 10.0	Brungs, 1969
Fathead minnow	23	6.5	7.8	206	9.2	Brungs, 1969
Rainbow trout	16.2±0.79	6.8±1.07	7.81±0.39	333±27.25	7.21	Sinley et al., 1974
Rainbow trout	12.7±3.40	6.8±1.38	6.81±0.17	26±3.70	0.43	Sinley et al., 1974
Rainbow trout	10	7.0	7.3	362	5.34	Watson, 1975
Rainbow trout	10	7.0	7.3	362	4.20	Watson, 1978
Flagfish	25	7.2 to 9.5	7.1 to 7.8	44	1.50	Spehar, 1976

C.23 ZINC - (Cont'd)

an 83 percent reduction in eggs produced by the fathead minnow. Spehar (1976) reported that a Zn concentration of 0.139 mg/L reduced the growth of flagfish as well as the embryo production in females. The growth of rainbow trout was retarded at a concentration of 1.14 mg/L over an 85 day exposure (Watson and McKeown, 1976). A perturbance of the osmoregulatory enzyme systems also was apparent in the same species during exposure to 0.29 to 1.98 mg/L Zn (Watson, 1978). Reproduction in Daphnia was impaired in a 3-week chronic test upon exposure to 0.07 mg/L Zn (Biesinger and Christensen, 1972).

Zinc is accumulated by fresh water organisms from both the food and water but the internal organs and bones accumulate more than the edible tissues (Phillips and Russo, 1978). The biological half-life is relatively long hence most of the Zn is slowly eliminated (Jones, 1978). Atlantic salmon accumulated Zn at a higher rate as temperature increased (Hodson, 1975). Upon entering fish some Zn associates with Cadmium - binding proteins and there is evidence to suggest the presence of Zn-binding protein (Marafante, 1976). The level at which Zn begins to accumulate is near the concentration at which Zn begins to accumulate. Some concentration factors for selected organisms have been found to be 32.6 in duckweed (Hutchinson and Czyrska, 1975), 10 300 in bryophytes, (Dietz, 1973) and 10 000 and 1000 for invertebrates and fish (Vaughan et al., 1975).

Zinc is essential to most plants and animals and is consequently accumulated by these organisms. It is moderately toxic to plants, birds and mammals but is relatively toxic to fish. Its accumulation in the aquatic ecosystem does not pose too great an environmental hazard because of the metal's low toxicity when ingested and because most of it is accumulated in the non-edible portions of fish.

APPENDIX D

MERCURY CONTENT IN HAT CREEK AND THE BONAPARTE RIVER AT SELECTED STATIONS

APPENDIX D

MERCURY CONTENT IN HAT CREEK AND THE BONAPARTE RIVER AT SELECTED STATIONS

CONTENTS

Section	Subject	Page
D.1	Hg CONCENTRATION - BONAPARTE RIVER UPSTREAM OF HAT CREEK, 20 MAY 1980	D - 1
D.2	Hg CONCENTRATION - BONAPARTE RIVER UPSTREAM OF HAT CREEK, 23 JUNE 1980	D - 2
D.3	Hg CONCENTRATION - BONAPARTE RIVER UPSTREAM OF HAT CREEK, 25 JULY 1980	D - 3
D.4	Hg CONCENTRATION - HAT CREEK AT BONAPARTE RIVER, 27 MAY 1980	D - 4
D.5	Hg CONCENTRATION - HAT CREEK UPSTREAM OF BONAPARTE RIVER	D - 5
D.6	Hg CONCENTRATION - HAT CREEK UPSTREAM OF BONAPARTE RIVER	D - 6

MAY 20, 1980 ENVIRONMENTAL LABORATORY
MINISTRY OF THE ENVIRONMENT

WATER QUALITY REPORT FOR SAMPLE 006470W

TO: BC HYDRO 17TH FLOOR
BOX 12121 555 W HASTING
VANCOUVER BC V6B 4T6
ATTENTION OF: BC HYDRO 17TH FLOOR

FOR SITE: BONAPARTE RIVER U/S OF HAT CREEK

SAMPLING DATE(S): MAY 12/80 0000 HRS
SAMPLE TYPE: FRESH WATER
SAMPLING DEPTH: 0
SAMPLED BY: B. C. HYDRO
CHARGE TO: INDEPENDENT AGENCY
DATE RECEIVED BY LABORATORY: MAY 14/80

2613403	MERCURY DISSOLVED	L 0.05 UG/L	2613503	MERCURY TOTAL	L 0.05 UG/L

THE APPROXIMATE COST OF THE ABOVE TESTS IS $ 50.40

REMARKS:

FOR ENVIRONMENTAL LABORATORY

SAMPLERS'S COMMENTS: SAMPLED 3-6 IN BELOW SU

JUNE 23, 1980 ENVIRONMENTAL LABORATORY PAGE 1
MINISTRY OF THE ENVIRONMENT

WATER QUALITY REPORT FOR SAMPLE 0084038

TO: BC HYDRO
BOX 12121
VANCOUVER BC V6B 4T6
ATTENTION OF: BC HYDRO

FOR SITE: BONAPARTE RIVER U/S OF HAT CREEK

SAMPLING DATE(S): JUN 11/80 0000 HRS
SAMPLE TYPE: FRESH WATER
SAMPLING DEPTH: 0
SAMPLED BY: B. C. HYDRO
CHARGE TO: INDEPENDENT AGENCY
DATE RECEIVED BY LABORATORY: JUN 12/80

2613403	MERCURY DISSOLVED	L 0.05 UG/L	2613503	MERCURY TOTAL	L 0.05 UG/L

THE APPROXIMATE COST OF THE ABOVE TESTS IS $ 50.40

REMARKS:

FOR ENVIRONMENTAL LABORATORY

SAMPLERS'S COMMENTS: ATTN: HATHORN

JULY 25, 1980 ENVIRONMENTAL LABORATORY PAGE 1
MINISTRY OF THE ENVIRONMENT

WATER QUALITY REPORT FOR SAMPLE 010937W

TO: B C HYDRO
BOX 12121 17TH FLOOR
VANCOUVER BC V2B 4T6
ATTENTION OF: B C HYDRO

FOR SITE: BONAPARTE RIVER U/S OF HAT CREEK

SAMPLING DATE(S): JUL 13/80 0000 HRS
SAMPLE TYPE: FRESH WATER
SAMPLING DEPTH: 0
SAMPLED BY: B. C. HYDRO
CHARGE TO: INDEPENDENT AGENCY
DATE RECEIVED BY LABORATORY: JUL 15/80

2613403	MERCURY DISSOLVED	L	0.05 UG/L	2613503	MERCURY TOTAL	L	0.05 UG/L

THE APPROXIMATE COST OF THE ABOVE TESTS IS $ 50.40

REMARKS:

FOR ENVIRONMENTAL LABORATORY

MAY 27, 1980 ENVIRONMENTAL LABORATORY MINISTRY OF THE ENVIRONMENT PAGE 1

WATER QUALITY REPORT FOR SAMPLE 006471W

TO: BC HYDRO 17TH FLOOR
BOX 12121 555 W HASTING
VANCOUVER BC V6B 4T6
ATTENTION OF: BC HYDRO 17TH FLOOR

FOR SITE: HAT CREEK AT BONAPARTE RIVER

SAMPLING DATE(S): MAY 12/80 0000 HRS
SAMPLE TYPE: FRESH WATER
SAMPLING DEPTH: 0
SAMPLED BY: B. C. HYDRO
CHARGE TO: INDEPENDENT AGENCY
DATE RECEIVED BY LABORATORY: MAY 14/80

2613403	MERCURY DISSOLVED	L 0.05 UG/L	2613503	MERCURY TOTAL	L 0.05 UG/L

THE APPROXIMATE COST OF THE ABOVE TESTS IS $ 50.40

REMARKS:

FOR ENVIRONMENTAL LABORATORY

SAMPLERS'S COMMENTS: SAMPLED 3-6 IN BELOW SU

JUNE 23, 1980 ENVIRONMENTAL LABORATORY MINISTRY OF THE ENVIRONMENT

WATER QUALITY REPORT FOR SAMPLE 008407W

TO: BC HYDRO
BOX 12121
VANCOUVER BC V6B 4T6
ATTENTION OF: BC HYDRO

FOR SITE: HAT CREEK U/S OF BONAPARTE RIVER

SAMPLING DATE(S): JUN 11/80 0000 HRS
SAMPLE TYPE: FRESH WATER
SAMPLING DEPTH: 0
SAMPLED BY: B. C. HYDRO
CHARGE TO: INDEPENDENT AGENCY
DATE RECEIVED BY LABORATORY: JUN 12/80

2613403	MERCURY DISSOLVED	L 0.05 UG/L	2613503	MERCURY TOTAL	0.07 UG/L

THE APPROXIMATE COST OF THE ABOVE TESTS IS $ 50.40

REMARKS:

FOR ENVIRONMENTAL LABORATORY

SAMPLERS'S COMMENTS: ATTN: HATHORN

JULY 25, 1980 ENVIRONMENTAL LABORATORY PAGE 1
MINISTRY OF THE ENVIRONMENT

WATER QUALITY REPORT FOR SAMPLE 010938W

TO: B C HYDRO
BOX 12121 17TH FLOOR
VANCOUVER BC V2B 4T6
ATTENTION OF: B C HYDRO

FOR SITE: HAT CREEK U/S OF BONAPARTE RIVER

SAMPLING DATE(S): JUL 13/80 0000 HRS
SAMPLE TYPE: FRESH WATER
SAMPLING DEPTH: 0
SAMPLED BY: B. C. HYDRO
CHARGE TO: INDEPENDENT AGENCY
DATE RECEIVED BY LABORATORY: JUL 15/80

2613403	MERCURY DISSOLVED	L 0.05 UG/L	2613503	MERCURY TOTAL	L 0.05 UG/L

THE APPROXIMATE COST OF THE ABOVE TESTS IS $ 50.40

REMARKS:

FOR ENVIRONMENTAL LABORATORY