ENVIRONMENTAL EFFECTS OF THE OLD DUNBRACK MINE DUMP, MUSQUODOBOIT HARBOUR, NOVA SCOTIA

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Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Sciences, Honours
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Dalhousie University, Halifax, Nova Scotia
March 16, 1998

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Musquodoboit Harbour, Nova Scotia

Degree BSc. **Convocation** May **Year** 1998

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ABSTRACT

The Dunbrack Pb-Cu-Zn prospect, located 5 km north of Musquodoboit Harbour and 45 km east of Halifax, Nova Scotia, ceased operations in 1920. The Devonian Musquodoboit Batholith hosts the minerals in a ca. 300 Ma quartz vein which occupies the contact between the batholith and a felsic dyke. The dump from the deposit is in the woods 50 m from Highway 327 and 200 m from the Musquodoboit river system. This thesis attempts to evaluate whether the dump poses an environmental risk in terms of releasing base metals. Samples of minerals, balsam fir, and lichens from the vicinity of the dump were studied. In addition an experiment was carried out to assess the solubility of base metals in rainwater.

Analysis of heavy mineral concentrations from a grab sample from the Dunbrack mine dump by atomic adsorption spectrometry gave 45 % Pb, 3.5 % Cu, and 1 % Zn. Textural relationships between the main sulphides give the following order of estimated relative ages: chalcopyrite, galena, bornite, covellite, then sphalerite. Results from an experiment involving rainwater combined with crushed dump sulphides show a drop in pH of 0.81 and 0.93 pH units and an increase in the rainwater of Pb, Cu, and Zn concentrations by factors of 100-1000.

The balsam fir and lichens in the vicinity of the dump contain anomalous concentrations of lead, copper, zinc, and cadmium, although the only obvious stunting of the biota occurs directly on the dump. The balsam fir lead concentrations at a distance of 60 m to the north and east of the dump are 1.8-20 times greater than a control location. Concentrations on the dump are 175 times higher than the control location. Other heavy metal concentrations (Cu, Zn, and Cd) are 1.5 to 5 times greater than the control location at a distance of 60 m from the dump, and are up to 13.5 times greater on the dump. Lichens from the dump and surroundings are enriched 2-4.5 times in Cu, Zn, Pb, and Cd, particularly the more sensitive species *Parmelia sulcata.* It is concluded that the dump has anomalous amounts of base metals in the balsam fir and lichens surrounding the dump, but beyond a few hundred metres from the dump it poses little risk.

Keywords: Dunbrack, dump, Musquodoboit Batholith, heavy metals, textural relationship, biogeochemistry, pH, sulphides, balsam fir, lichens (*Parmelia sulcata*, *Hypogymnia physodes*).

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Acknowledgements

I wish to thank first and foremost my supervisor, Dr. D. B. Clarke for his generous support and scientific and technical guidance throughout the thesis process. I thank Dr. M. Zentilli for his support in the process and thesis defense. I thank Pierre Taschereau and Marion Sensen for their field assistance and expertise with plants and lichens. I thank Marc Lamoureau and David Slauenwhite from Saint Mary's University for their generous help with the preparation and analysis of the lichens, and David Richardson also from Saint Mary's University for literature and information pertaining to lichens. I thank Cyril Cole and the Mineral and Resources Centre at Daltech (formally known as TUNS) for the AA and XRF balsam fir and water analyses. I thank Sandy Grist for the use of equipment in the Fission Track Lab at Dalhousie University, and Milton Graves and Greg Pemberton for their advice and support. I thank Don Fox for his advice and the use of lab space and pH meter equipment. I thank Gordon Brown for his preparation of the polished thins (Thin Section Lab, Dalhousie University). I thank Rob White from the Department of Chemistry for the use of the mechanical shaker. I thank Bob MacKay for his help with the microprobe, and Tom Duffett for his help with the rock crushing equipment at Dalhousie University. I thank Dr. Boudreau from the Oceanography Department for his advice with sulphides, and Heather Cross for her advice and literature on water. I thank David Mitchell for his field assistance.

CHAPTER 1 INTRODUCTION

1.1 The Dunbrack Deposit

The Dunbrack Cu-Pb-Zn deposit is located 5 km north of Musquodoboit Harbour along Highway 357, which is about 45 km east of Halifax, Nova Scotia (Fig. 1.1). The dump from the small mine workings are in the woods 20 m from Highway 327 and 200 m from the Musquodoboit river system. The dump itself is from Shaft #2, the richest of the assays, which yielded an estimated 540 metric tons of 2% lead ore (Hayes 1917). The deposit was explored for lead but found uneconomic, and today about 8000 tonnes of rock, including high concentrations of lead, zinc, and copper minerals, are leaching heavy metals to the surrounding region.

The ore mineralization occurs in a vein within the Musquodoboit Batholith. Galena with chalcopyrite and bornite and secondary copper minerals occur within a quartz vein associated with a felsic dyke that intrudes the batholith.

The dump has not accumulated much plant material in the past 75 years, but this may be as much a result of people searching for minerals, as from the toxicity of the rocks. Mosses and lichen grow over parts of the dump (Fig. 1.2).

The Dunbrack deposit is a potential environmental hazard. Crushed rock from the Pb-Cu-Zn deposit has been sitting in a dump since major exploratory operations finished in 1920. It is the intent of this report to examine the environmental hazards associated with this site.

Geobotany and biogeochemistry both have applications within the scope of this

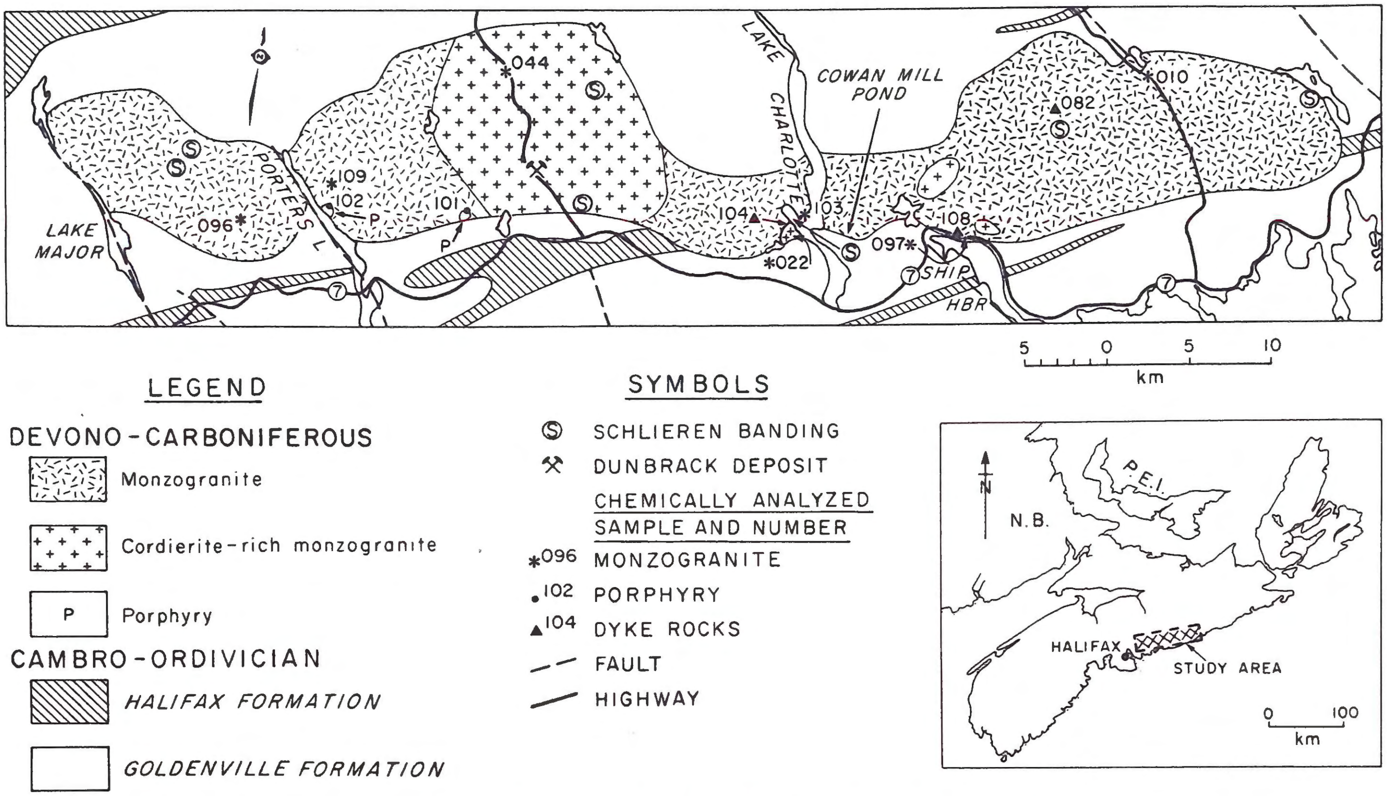

Fig. 1.1 Geologic map of the Musquodoboit batholith showing the location of the Dunbrack deposit (from MacDonald and Clarke 1985).

Fig. 1.2 Photograph of the author on the Dunbrack dump.

thesis. The plant material surrounding the dump (it is a wooded region) can offer indications of the toxicity of the dump, both from their physical reactions to toxic amounts of lead and copper, which can inhibit growth by replacing necessary metals, and from measuring the concentration of heavy metals in the biota.

1.2 Purpose/Scope

The first purpose of this thesis is to examine to geologic background of the Dunbrack deposit. The second purpose of this thesis is to examine the heavy metal uptake by balsam fir and lichens in the immediate vicinity of the dump. These effects were monitored using an experiment involving freshly crushed rocks from the dump to model the uptake of heavy metals in rainwater, and by analysing balsam fir twigs by Atomic Absorption and lichens by X-Ray Florescence Spectrometry. This thesis includes microprobe results of five sulphides at Dunbrack, the paragenetic sequence of these sulphides and their textural relationships, and a discussion on the environmental significance of the Dunbrack dump.

1.3 Claim

The Dunbrack dump is high in lead and copper content and is leaching heavy metals to the surrounding plants, but it does not appear to be environmentally hazardous to the surrounding region.

1.4 Organization

This thesis first examines the regional and local field geology in Chapter 2, and describes the mineralogy of the dump. Chapter 3 presents the methods and results for electron microprobe data, lichen XRF analyses and balsam fir AA analyses, and the results of a heavy metal dissolution experiment. Chapter 4 reviews the effects heavy metals, specifically lead and copper, have on the environment, and discusses the findings. Chapter 5 examines the effects that the Dunbrack dump may be having on the local environment based on the findings of this thesis.

CHAPTER 2 REGIONAL AND LOCAL GEOLOGY

2.1 Introduction

This chapter describes the regional and local geology of the Dunbrack Cu-Pb-Zn deposit. The Musquodoboit Batholith (372 ±2 Ma (MacDonald and Clarke 1985)) hosts a felsic dyke through which the mineralized quartz vein occurs. The quartz vein and mineralization are dated at ca.300 Ma.

2.2 Regional Geology

The Meguma Supergroup of southern Nova Scotia is Cambrian to Lower Devonian in age (Schenk 1997), and consists of two groups, the Halifax shales and the Goldenville sandstones. The succession is from deep-sea fan complexes to coastal facies (Schenk 1997).

The Meguma Supergroup was deformed and metamorphosed during the Acadian orogeny (Schenk 1997). Kilometre-scale, E-NE trending anticlines and synclines (Muecke and Reynolds 1978) formed as a result of this 395-388 Ma collision (Hicks and Jamieson 1995). Greenschist-lower amphibolite facies metamorphism and cleavage formation was part of regional deformation at 410-400 Ma (Dallmeyer and Keppie 1988).

The Meguma Group was later modified by the emplacement of granitic plutons (Tate 1995), including the Musquodoboit Batholith. A contact aureole, a few hundred metres wide and containing cordierite prophyroblasts, developed along the exocontact (Kontak 1996).

2.3 Musquodoboit Batholith

The Musquodoboit batholith is late Devonian (372 ±2 Ma) in age (MacDonald and Clarke 1985). The batholith is petrologically uniform and consists of a light-grey, coarse-grained, two-mica leucomonzogranite. Coarse cordierite grains and alkali feldspar phenocrysts are common in the central part of the batholith (MacDonald and Clarke 1985). The Dunbrack deposit is situated in the southern section of the batholith, but the host rock near the deposit does not contain cordierite (Dickie 1978).

A system of faults and joints, striking NW on average 320^{o} and 220^{o} (Dickie 1978), was probably active during the emplacement of the Musquodoboit Batholith. According to Fyson (1966), post-granite S-kinking in the Meguma Group was a result of E-W compressional stress.

Glacial till covers much of the Musquodoboit Harbour area, in the form of unstratified ablation till, stratified kame terraces, and stratified outwash gravel (Dickie 1978). Stea and Fowler (1979) describe the till as yellow-brown, loose, sand with angular granite clasts of pebble to boulder size, ranging in thickness from 2-5 m. The topography of the region consists of hummocky ground moraine overlying the granite bedrock, mantled in some areas with rounded boulders (Stea and Fowler 1979).

2.4 Dunbrack geology

The Dunbrack deposit (Fig. 2.1) occurs in a quartz vein that occurs in a felsic dyke that is hosted by the Musquodoboit Batholith. The following description of the Dunbrack geology is based on several reports (MacMichael 1977, Dickie 1978, Wroth 1937) and observation by the auther.

The main components of the vein are: alkali feldspar, quartz, including milky, amethystine, and smokey varieties, and possibly tridymite (Table 2.1).

metal/element	Mineral	Formula	Reference
Lead	Galena	PbS	Chatterjee (1991)
	Anglesite	$Pb(SO_4)$	Chatterjee (1991)
	Cerussite	$Pb(CO_3)$	Chatterjee (1991)
	Pyromorphite	$Pb(PO_4)_3Cl$	Chatterjee (1991)
	Meneghinite	$Pb_{13}CuSb_7S_{24}$	Chatterjee (1991)
Copper	Chalcopyrite	$CuFeS_2$	Chatterjee (1991)
	Bornite	Cu_5FeS_4	Chatterjee (1991)
	Azurite	$Cu_3(CO_3)_2(OH)_2$	Chatterjee (1991)
	Malachite	$Cu_2(CO_3)(OH)_2$	Chatterjee (1991)
	Chalcocite	Cu_2S	Chatterjee (1991)
	Djurleite	$Cu_{1.96}S$	MacMichael (1975)
	Digenite	Cu_9S_5	MacMichael (1975)
Zinc	Sphalerite	ZnS	MacMichael (1975)
Other	Quartz	SiO_2	Kontak (1996)
	Tridymite?	SiO_2	Friedlander (1968)
	Calcite	$Ca(CO_3)$	MacMichael (1975)
	Fluorite	CaF_2	MacMichael (1975)
	Pyrrhotite	$Fe_{1-X}S$	MacMichael (1975)
	Ilmenite	$FeTiO_2$	MacMichael (1975)

Table 2.1 A summary of the main minerals of the Dunbrack deposit.

2.4.1 TheDunbrack dyke

The dyke is a fine-grained, red-grey, porphyritic rock. The one-metre wide dyke cuts the leucomonzogranite and strikes N47°W and dips 62°NE (MacMichael 1975). The dyke was probably a major channel for the solutions to pass through (MacMichael 1975). The dyke next to the mineralized section of the vein is highly altered (Kontak 1996, MacMichael 1975). According to Kontak (1996), the vein is related to the

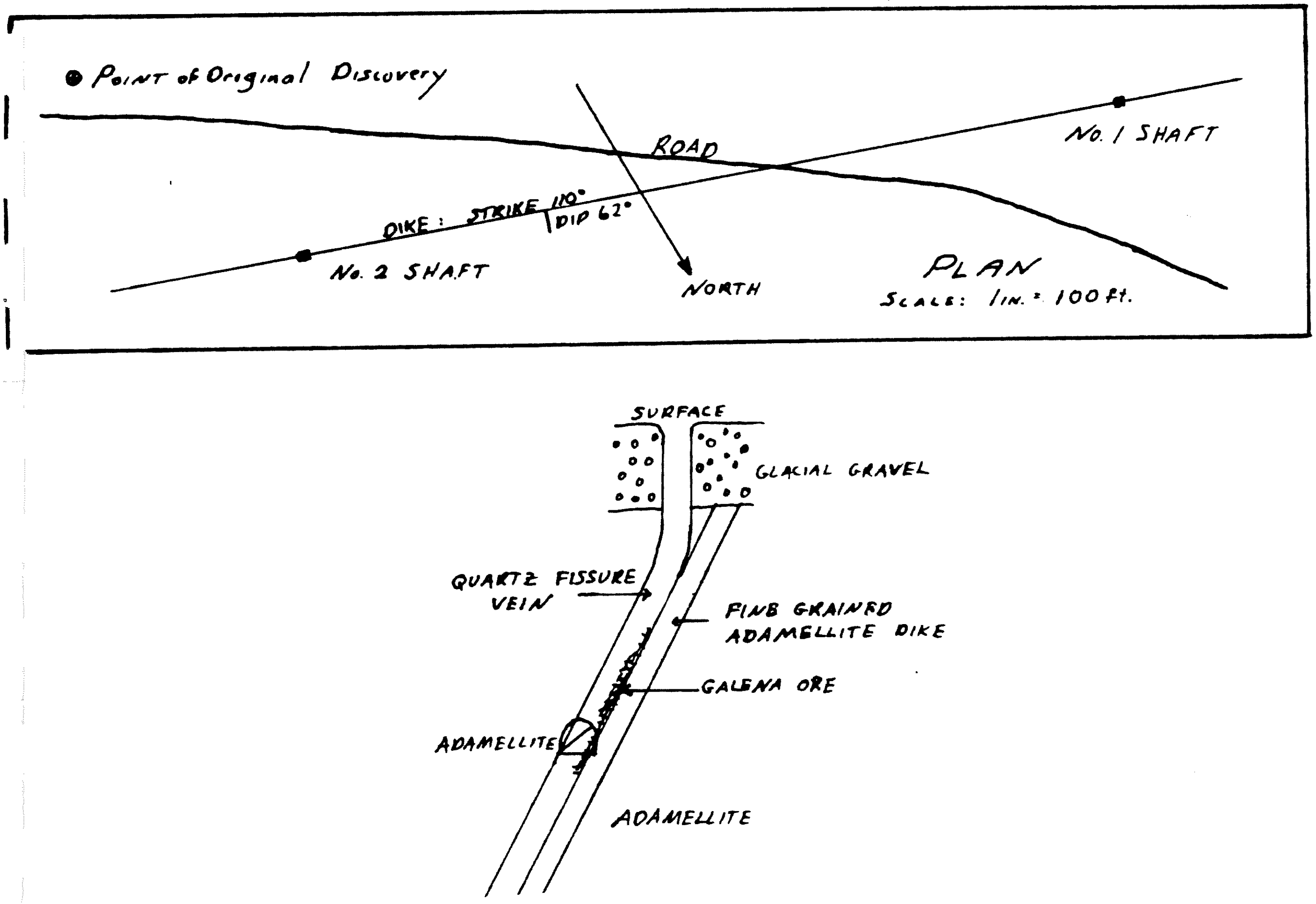

Fig. 2.1 Plan and cross-section of the Dunbrack deposit (after MacMicheal, 1975).

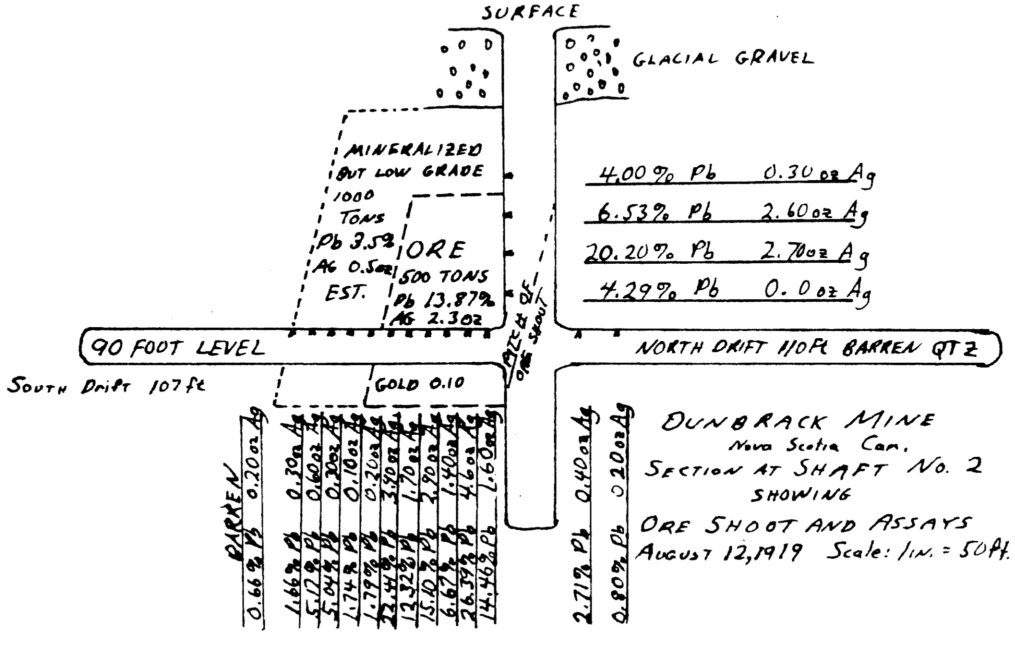

Fig. 2.2 Schematic view of the stratigraphy showing ore grades at Shaft #2 (after MacMicheal 1975).

movements of faults within the Musquodoboit Batholith, and may not be temporally or genetically related to the dyke.

2.4.2 The Dunbrack host vein

At the contact between the dyke and the leucomonzogranite hanging wall is a 1m-2m wide quartz vein. The vein is 299±12 Ma (MacMichael 1977). Sulphide mineralization occurs in the quartz vein, and is most abundant close to the footwall dyke and is sparse towards the hanging wall. Fig. 2.2 shows a schematic view of the stratigraphy in Shaft #2. According to Wroth (1937), the mineralized section of the vein at Shaft #2 is only 15 m long, otherwise the vein is barren.

According to Hayes (1917), the vein first precipitated quartz and feldspar and then further fracturing allowed the introduction of metallic minerals. Subsequent supergene enrichment resulted in the replacement of chalcopyrite by chalcocite and bornite, and the formation of chalcocite rims (MacMichael 1975).

For discussions on the formation and source of the deposit, see Kontak (1996), Dickie (1978), and MacMichael (1975).

2.6 Summary

The Dunbrack deposit occurs within a mineralized vein at the boundary between a reddish fine-grained dyke rock and the Musquodoboit Batholith. Lead, copper, and zinc sulphides are the main host minerals to the mineralization. Chapter 3 looks at microprobe data of the main Dunbrack sulphides and sets out the methods and results of experiments designed to monitor the effect that the Dunbrack dump is having on the local biota.

CHAPTER 3 METHODS AND RESULTS

3.1 Introduction

This thesis deals with various aspects of the mineralogy of the Dunbrack dump and how material in the dump affects the local biota. This chapter presents a description of the mineralogy and reports heavy metal concentrations in several materials including:

1. opaque minerals using an electron microprobe;
2. water from an experiment involving freshly crushed rocks from the dump to model uptake of heavy metals in rainwater, and;
3. lichens and balsam fir twigs collected from the Dunbrack site and from a control location, using both X-ray fluorescence (XRF) analysis and atomic absorption (AA) analysis.

This chapter describes the methods for each of the approaches above and gives the analytical results.

3.2 Microprobe Analysis

Polished thin sections made from Dunbrack rocks were analyzed with the electron microprobe at Dalhousie University. Complete results from the analyses are in Appendix 1, and a summary for each of the main sulphides, galena, sphalerite, bornite, chalcopyrite, and covellite, is in Table 3.1. The polished thin sections were prepared by Gordon Brown in the Thin Section Preparation Lab at Dalhousie University. They were carbon-coated and then probed in the JEOL 733 Electron Microprobe at Dalhousie University.

The analytical methods employed by the JEOL 733 Electron Microprobe, which has four wavelength dispersive spectrometers and an Oxford Link eXL energy dispersive system, have a resolution of 137ev at 5.9Kev, and detection limits for most elements of 0.1 to 0.3 weight percent. The beam current for each analysis was 15nA, with an accelerating voltage of 15 Kv, and it took 40 seconds to acquire each spectrum. The beam diameter was 1 micron. The Link ZAF matrix correction program was used to correct the raw data. Instrument precision on cobalt metal (used for instrument calibration n=10) was ± 0.5% at 1 standard deviation, with an accuracy for all major elements of ± 1.5 to 2.0 %. Calibration used geological standards.

Point	Fe	Cu	Pb	Zn	Sn	Ag	Au	As	S	Total
Galena (n=9)										
Mean			86.12						12.72	99.10
Std Dev			0.34						0.13	0.41
Sphalerite (n= 8)										
Mean	1.92	1.35		63.92	0.27				32.80	100.41
Std Dev	0.69	0.98		2.06	0.28				0.22	0.84
Bornite (n= 10)										
Mean	13.36	52.99				0.27			30.52	98.10
Std Dev	4.18	3.80				0.25			2.08	4.43
Chalcopyrite (n= 11)										
Mean	29.81	34.97							34.70	99.98
Std Dev	0.48	0.46							0.18	0.82
Covellite (n= 10)										
Mean		61.78	2.95			1.69			28.74	95.67
Std Dev		5.42	4.06			1.23			3.35	3.32

Table 3.1 Chemical composition of the principal sulphide minerals at Dunbrack.

For each mineral, the results show fairly consistent elemental constituents (Table 3.1), except for bornite, which may be because the measurements are more affected by the surrounding grains. Silver concentrations range from 0.00 % to 3.49 % with a mean of 1.69 % in covellite. The silver was previously thought to be in the galena, but these microprobe data show that silver instead tends to be more concentrated towards the edges of the covellite grains.

3.3 Paragenetic sequence

This section deals with the textural relationships and paragenetic sequence of the five main metallic sulphide minerals at the Dunbrack deposit as determined from reflected light microscopy.

Galena is the main lead mineral. It ranges in size from 0.1 mm specks within the quartz and feldspar to cubes several centimeters in diameter. The galena is commonly mantled by covellite and sphalerite, indicating that galena is older (Fig. 3.1). Sphalerite principally occurs as rims on galena, but also occurs as inclusions in galena. In rare cases, galena occurs as rims on sphalerite (Fig. 3.2), suggesting a second stage of galena growth, or a shared growth period.

Chalcopyrite is less abundant than galena. It occurs as individual grains, as grains directly adjacent to galena, or as small discrete grains within the galena, indicating that the chalcopyrite is earlier than the galena, although they probably grew simultaneously for much of their growth. Chalcopyrite is commonly rimmed by covellite and sphalerite, and cut by bornite (Fig. 3.3). This relationship suggests galena and chalcopyrite were present before the growth of covellite, sphalerite, and bornite.

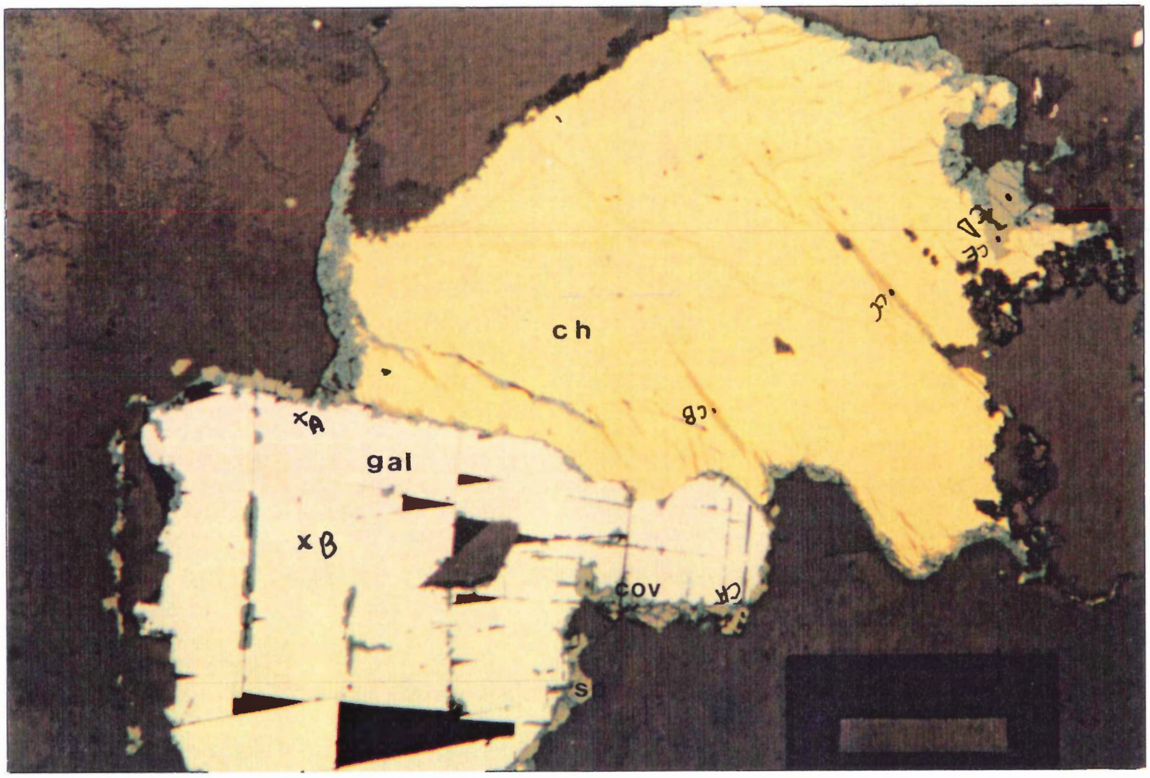

Fig 3.1. Galena (gal) rimmed by covellite (cov) and sphalerite (sp) in reflected light (width of photo is 150 mm).

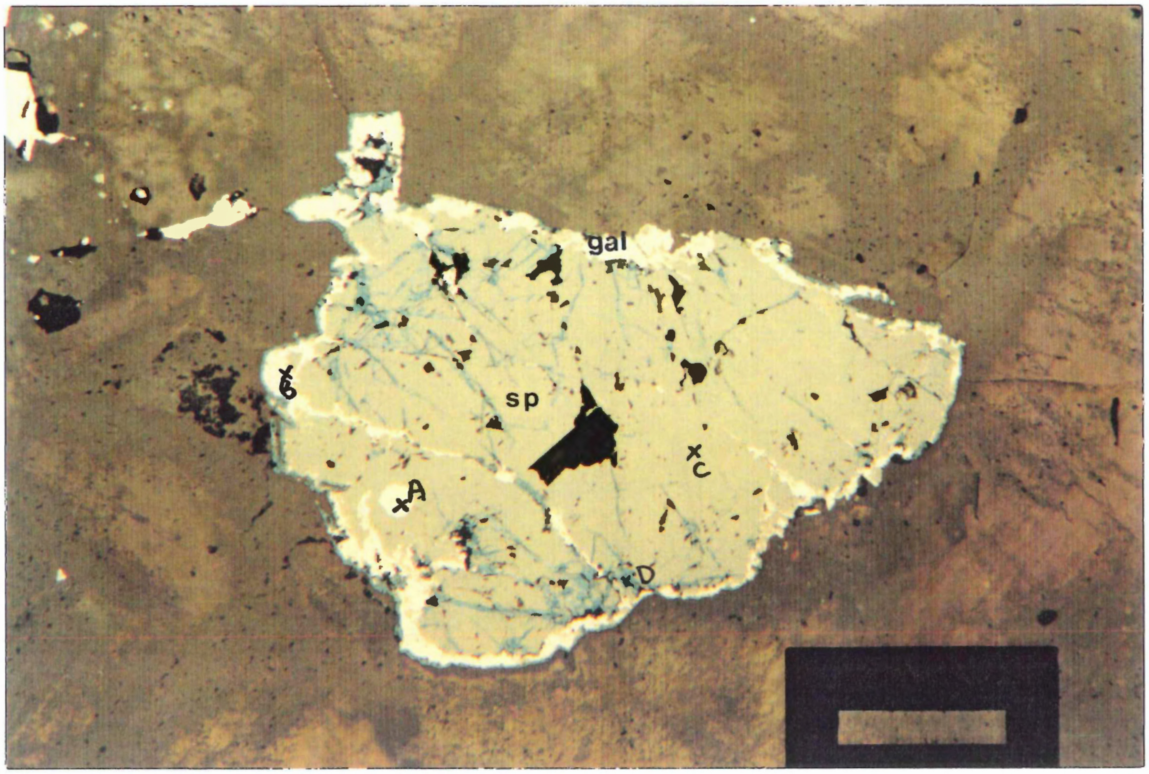

Fig. 3.2 Sphalerite with covellite veining rimmed by galena. In reflected light (width of photo is 150 mm).

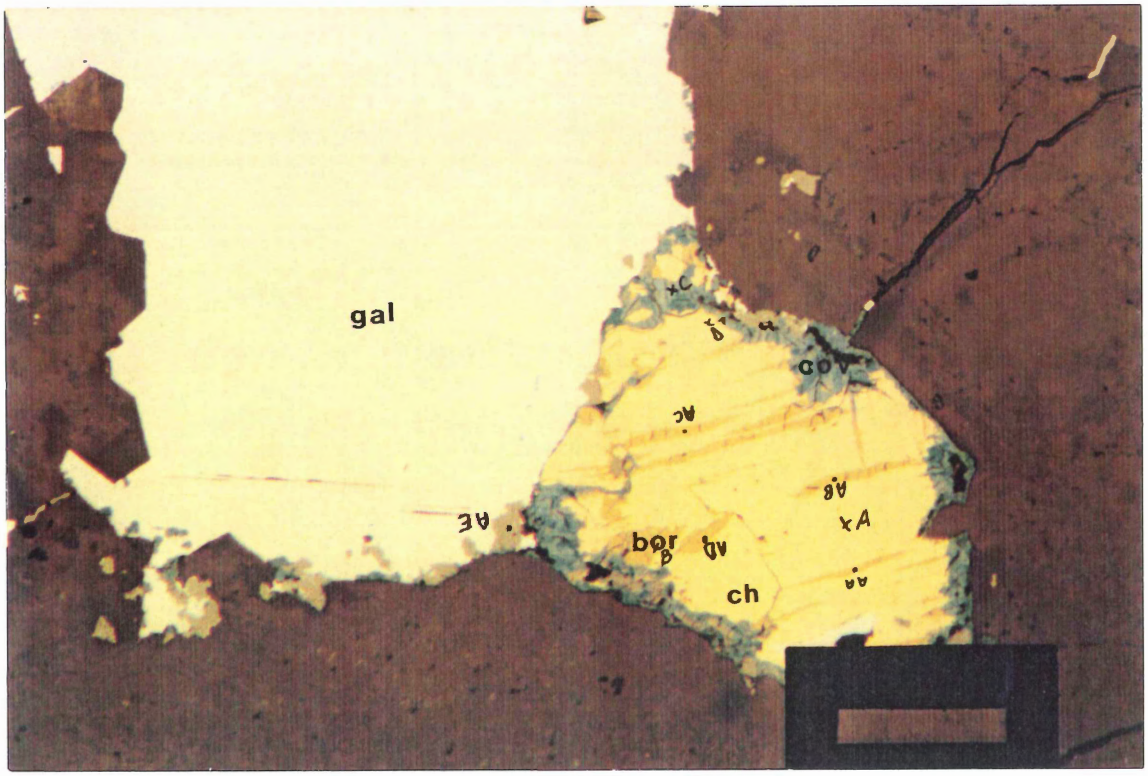

Fig. 3.3 Chalcopyrite (ch) rimmed by covellite and sphalerite, and veined by bornite (bor) in reflected light (width of photo is 150 mm).

Covellite occurs commonly as a mantle to galena, but covellite also occurs in galena and, therefore, may share a later part of the growth history of galena. Sphalerite also contains covellite veins (Fig. 3.2), indicating that the covellite is younger, however most commonly covellite and sphalerite mantle galena (Fig. 3.1). Because neither covellite nor sphalerite rims the other, they appear to have grown simultaneously. In rare cases, covellite occurs as inclusions within sphalerite, indicating that some covellite may be older (Fig. 3.5).

Bornite flames extend inward from the chalcopyrite rims, and both are rimmed at the edges by covellite and sphalerite. In some instances, this entire suite of minerals replaces galena (Fig. 3.6). Chalcopyrite is therefore older than the bornite, and bornite and chalcopyrite are older than the covellite and sphalerite. In Figure 3.4, a chalcopyrite grain with small bornite laths occurs as an inclusion within a sphalerite vein, also indicating that sphalerite is later than chalcopyrite and bornite.

The following paragenetic sequence is consistent with the estimated relative ages of galena, chalcopyrite, sphalerite, bornite and covellite (Fig. 3.4).

```
Chalcopyrite               ----------
Galena                        ----------------- - - -                        -----
Bornite                                              ---------
Covellite                                                     --------
Sphalerite                                                         ---------
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Fig. 3.4 Paragenetic sequence based on the estimated relative ages of galena, chalcopyrite, sphalerite, bornite and covellite.

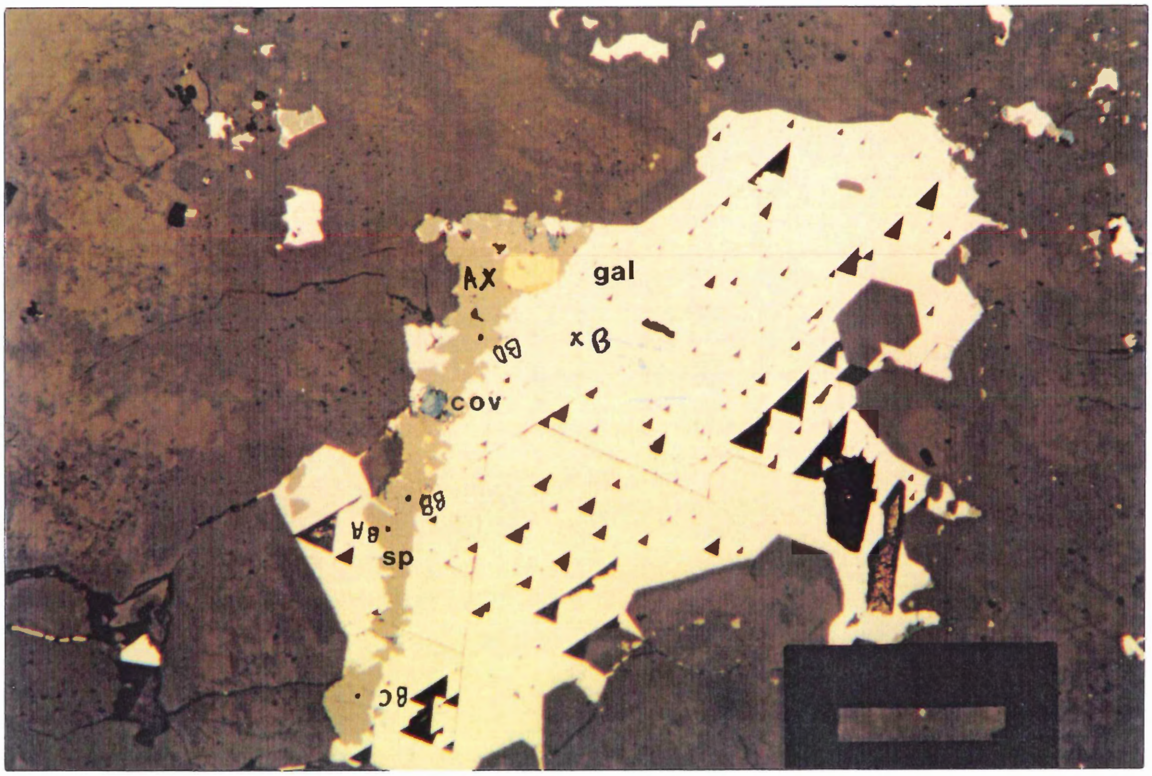

Fig. 3.5 A sphalerite vein within galena containing covellite inclusions in reflected light (width of photo is 150 mm).

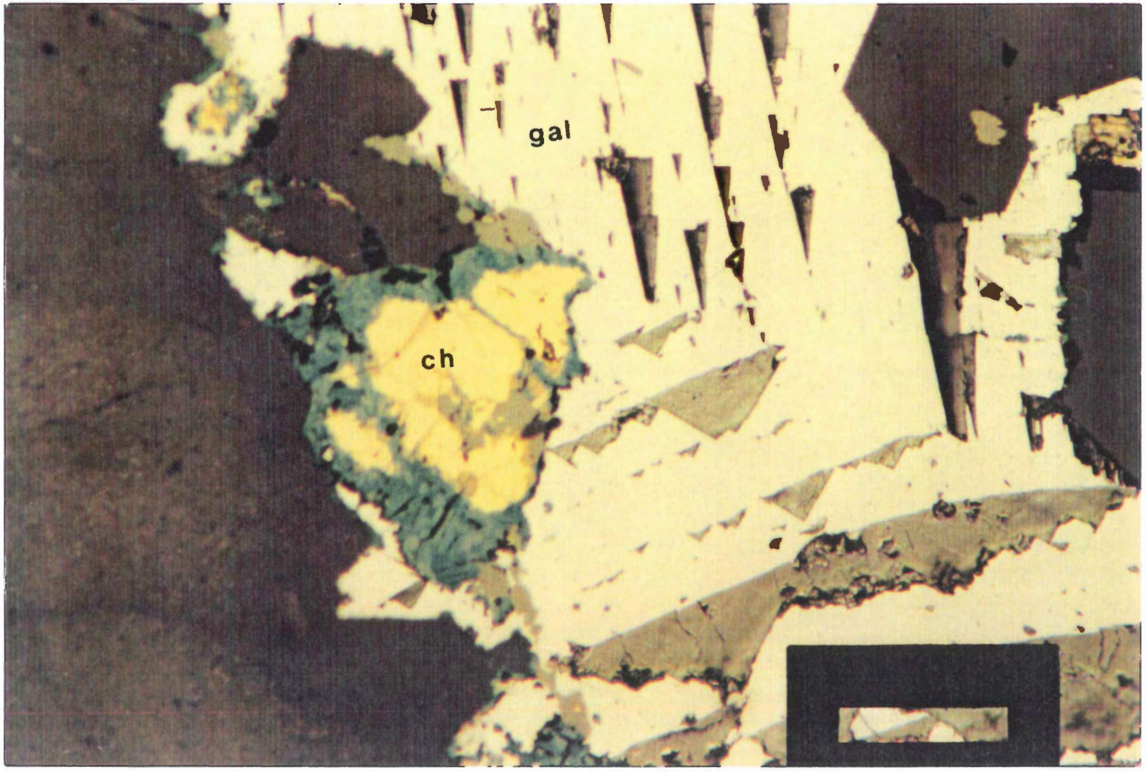

Fig. 3.6 Galena partially replaced by chalcopyrite. The chalcopyrite contains bornite veins and is rimmed by covellite and sphalerite in reflected light (width of photo is 150 mm).

3.4 Dunbrack Rock Analysis by XRF

3.4.1 Introduction

Sulphidic rocks from the dump at Dunbrack were collected in a grab-bag fashion. These samples include fist-sized or smaller samples containing visible sulphides and their alteration minerals, in particular malachite, azurite, and cerussite, as well as silicates typical of the quartz vein which contained sulphide veins. These samples were crushed to large sand size in order to expose large surface areas of the sulphides, and then were split into homogeneous fractions with a rock splitter in the Department of Earth Science crushing room at Dalhousie University, and then made into rock pellets at Saint Mary's University using 9 parts silica to 1 part rock powder to simplify the analysis.

3.4.2 Rock Pellet Results

The rock pellet results were found by the XRF spectrometer at Saint Mary's University in Halifax were set with standard parameters, with the collimator mask set at 27 mm, and the medium chosen was a vacuum. The alpha corrections were done internally by the spectrometer.

%	L.O.I.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
KS-D-97-A	1.63	90.18	0.051	2.26	0.38	0.006	0	0.07	0.05	0.52	0.073
KS-D-97	1.72	91.44	0.054	2.29	0.4	0.007	0.02	0.08	0.07	0.53	0.07
ppm	Sc	V	Cr	Co	Zr	Ba	Ce	Nd	Ni	Cu	Zn
KS-D-97-A	16	33	15	54	306	0	385	150	25	4066	1282
KS-D-97	18	38	6	57	308	0	372	140	24	4113	1115
ppm	Ga	Rb	Sr	Nb	Sn	Pb %	Th	U			
KS-D-97-A	75	140	880	32	58	5.23	3160	20			
KS-D-97	77	142	879	37	52	5.17	3138	28			

Table 3.2 Rock powder element concentrations for two pellets made from samples from the Dunbrack dump, KS-D-97 and KS-D-97A, analyzed by X-ray fluorescence spectrometry at Saint Mary's University, Halifax. (L.O.I.: loss on ignition). Note: High silica content due to the addition of silica to the rock powder before analysis. *Abnormal Th values are unexplained.

Rock powder analysis shows that the Dunbrack dump rocks are very high in lead, aluminum, iron, zinc, copper, and thorium.

3.5 Heavy Metal Dissolution Experiment

3.5.1 Purpose

The purpose of the pH experiment is to evaluate the effect of heavy-metal-rich rocks from the abandoned Dunbrack deposit on rainwater, because if there is an effect on the rainwater this rainwater will travel to the surrounding biota and have an effect on it. The procedure involved adding rainwater to crushed fresh sulphides from the dump, monitoring the pH of the rainwater, and analyzing the water by AA after the experiment. This process mimics, as closely as possible, the natural environment. In the natural environment rainwater percolates through the surficial dump rock and soil, and travels quickly to the surrounding biota. The effects of the sulphides on the rainwater during this experiment are then estimated and discussed in Chapter 4.

This experiment kept external factors constant in order to be sure that the change in pH and chemistry can be deduced to be resulting from the rocks. The natural environment will have other factors affecting the pH of the rainwater after it seeps through the rocks, such as the temperature (which was kept constant in this experiment at approximately 20^0C), presence of decaying organic matter, and the circulation of fresh air, all of which can encourage growth of bacteria and can result in a change in pH. The changes occuring at the control location can be deduced to be resulting from external factors and not a product of the rocks, and therefore can be deducted from the changes in the other bottles.

3.5.2 Procedure

A clean 1 gallon plastic container was rinsed with distilled, de-ionized water, dried, and then used to collect rain from a drainpipe in Halifax in October 1998, approximately 40 km from the Dunbrack site. The container was then rinsed with rainwater, and then more rainwater was collected in it. This rainwater may not be exactly the same as rainwater from the Dunbrack dump area, but will result in the same relative change in pH and composition, and therefore the starting point need not be absolute.

Sulphidic rocks from the dump at Dunbrack were crushed and homogenized (Section 3.4.2). Seven 250 ml plastic bottles were similarly cleaned with distilled, de-ionized water and then rinsed with rainwater.

Each bottle was filled with 125 ml of crushed rock, and then 100 ml of rainwater was added to each bottle, enough to cover the samples once the water had permeated the rock. Three bottles remained static at room temperature, and their pH was measured, about 5 minutes after the rainwater had been added, and again after 24 hours had passed. After 1 week, the water was drained from one bottle through a filter, the pH was recorded, and the water was kept for chemical analysis. The same was done with water from another bottle after 2 weeks, and to water from another bottle after 4 weeks. A bottle of rainwater was kept separate for a control and had its pH measured after 1 week, 2 weeks, and 4 weeks.

Three more bottles containing the same amount of rocks and rainwater were put in a mechanical shaker at approximately 120 shakes per minute, in the Department of Chemistry, Dalhousie University. This experiment was done in order to see if the rate of dissolution would be increased by shaking the samples. A bottle was removed, the water was filtered, and the pH was checked after 1, 2 and 4 weeks. The seven bottles (with one control rainwater bottle) were then sent to the Minerals Engineering Centre at the Dalhousie Polytechnic (formally known as TUNS) in Halifax for atomic absorption (AA) analysis.

3.5.3 pH experiment results

Table 3.3 gives the results from the pH experiment. The pH meter (Model 290A manufactured by Orion) is accurate to 0.005 pH units, and was calibrated with a buffer solution of 4.00 dated December 1995 and a buffer solution of 7.00 dated May 1997. These buffers are slightly outdated, and as a result the precision has a standard deviation of 0.024 pH units.

	Before pH	Day1 pH	Week1 pH	Week 2 pH	Week3 pH	Week4 pH
Static Bottle	5.82	5.26	4.68	4.70	4.86	5.01
Shaken Bottle	5.82	5.26	4.54	5.00	4.95	4.89
Control Water (full)	5.83	5.75	5.49	5.49	5.65	5.82

Table 3.3 The pH of rainwater when added to crushed sulphides and silicates from the Dunbrack dump as measured over a 4 week period.

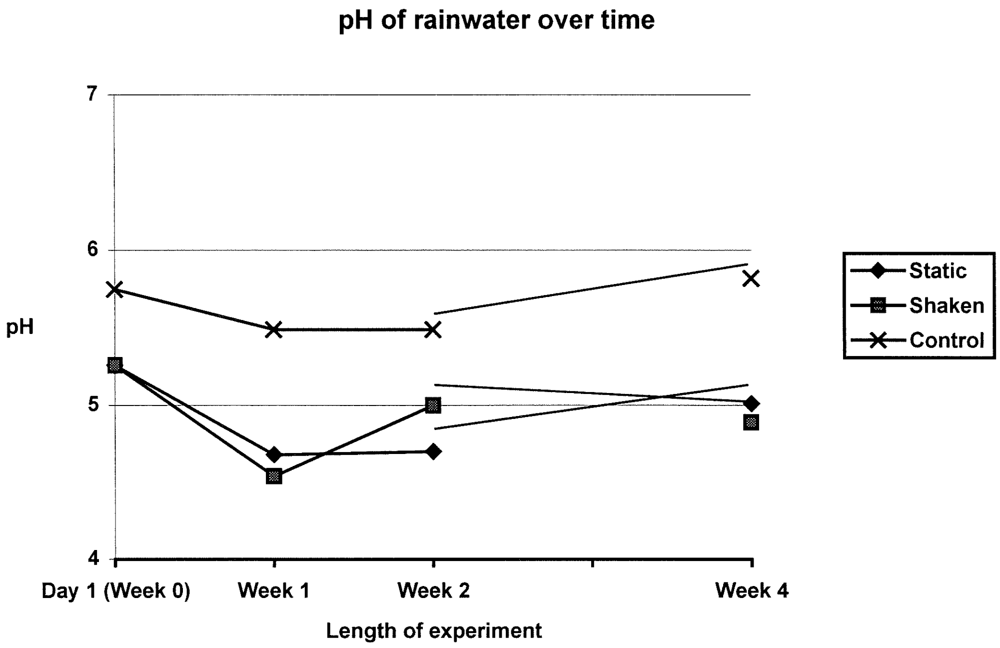

Fig 3.7 Change in pH of rainwater in contact with crushed sulphides from the Dunbrack dump.

The final difference in pH is a decrease of 0.81 units for the static bottle and a decrease of 0.93 units for the shaken bottle, whereas the control remains approximately constant. The pH dropped significantly (0.49 units) after being in contact with the sulphides for 24 hours, and continued to drop over the next week, and then changed less over the following 3 weeks.

3.5.4 Water Analysis

Rainwater analysis for seven bottles of rainwater from the pH experiment were sent to the Minerals Engineering Centre at the Dalhousie Technical University in Halifax for analysis by AA. Background correction was used on all elements, and the water was measured by direct aspiration after having been diluted by 1/10. Results are accurate within 2-5 % of the amounts present. Table 3.4 gives the results.

Sample		Pb ppm	Cu ppm	Zn ppm	Cd ppm
Control		<0.03	<0.01	0.05	<0.002
Week 1	Static	33 ± 1.65	3.02 ± 0.15	2.64 ± 0.13	0.013 ± 0.001
Week 2	Static	33 ± 1.65	2.89 ± 0.14	2.98 ± 0.15	0.018 ± 0.001
Week 4	Static	31 ± 1.55	1.43 ± 0.07	3.68 ± 0.18	0.019 ± 0.001
Week 1	Shaken	31 ± 1.5	3.72 ± 0.19	4.06 ± 0.20	0.016 ± 0.001
Week 2	Shaken	28 ± 1.4	2.89 ± 0.15	4.26 ± 0.21	0.024 ± 0.001
Week 4	Shaken	25 ± 1.25	0.60 ± 0.03	3.98 ± 0.20	0.025 ± 0.001

Table 3.4 Heavy metal concentrations in rainwater after contact with crushed Dunbrack rock for periods of 1, 2, and 4 weeks. Half of the samples were shaken.

The water analysis shows that the concentration of heavy metals in rainwater after having been in contact with fresh sulphides from the Dunbrack dump is enriched by >1000X for Pb, >300X for Cu, > 60X for Zn, and > 10X for Cd.

3.6 Balsam Fir Analysis

The balsam fir were collected from four locations (Fig 3.8); from the Dunbrack dump (Location 1); from a location 60 m to the SE of the dump (Location 2); from a location 60 m to the NE of the dump (Location 3); and from a control location approximately 100 km from the dump (Control), in the Pockwock watershed region off Highway 103, 50 km west of Halifax. This location is in the woods at least 200 m from a dirt road, and 3.5 km from the 103 Highway, with no known dumps or smokestacks in the region. It provides control material from a relatively pristine environment.. Five years of growth were collected in September of 1997 from chest hight at Location 2, 3, and the control location. Balsam firs receive their nutrients primarily from the soil.

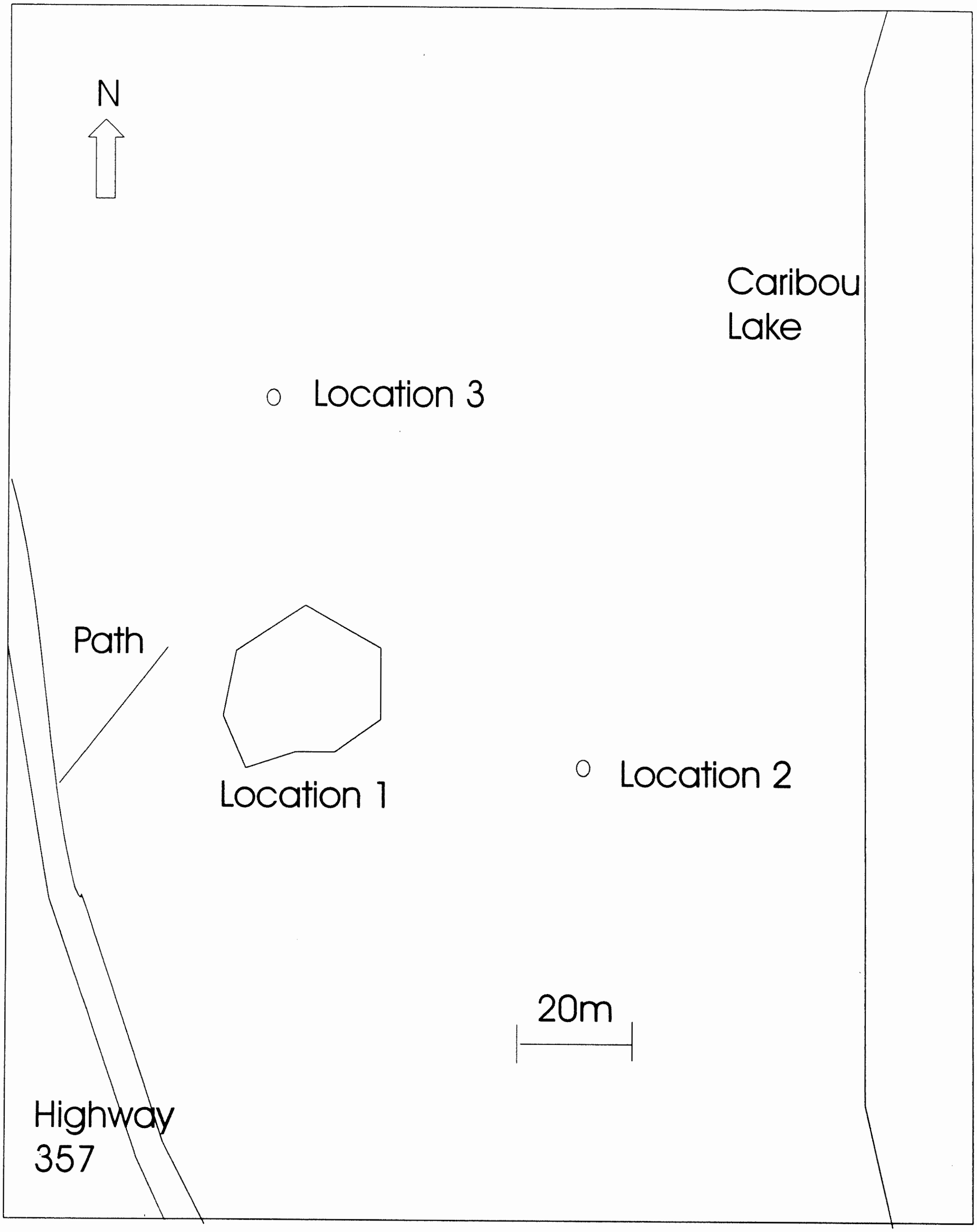

Fig. 3.8 Sketch map of the Dunbrack dump (Location 1) and the lichen and balsam fir

locations (Location 2 and Location 3). The balsam fir twigs were dried at 100°C for 3 hours, stripped of their needles, washed, and given to the Mineral Engineering Centre at the Dalhousie Technical University in Halifax for analysis. The twigs were ashed in an electric muffle furnace at 550°C. The percentage of ash was measured and weighed. The ash was leached with Aqua Regia (3 parts HCl and 1 part HNO_3) and filtered into a 100 ml flask, which was directly analyzed by atomic absorption spectrometry for elements.

Sample In branch (ppm)	Pb	Cu	Zn	Cd
Control	1.39	2.22	30	0.11
Location 1	243.00	30.00	79	0.44
Location 2	27.60	5.30	150	0.53
Location 3	2.58	4.20	49	0.20
In ash (ppm)	Pb	Cu	Zn	Cd
Control	79	126	1706	6.21
Location 1	13280	1636	4291	24.18
Location 2	1758	338	9576	33.94
Location 3	149	243	2812	11.59

Table 3.5 Results from the balsam fir twigs and from the ash of the twigs done by the Minerals Engineering Centre at the Dalhousie Technical University in Halifax.

Heavy metals in the balsam fir are highly concentrated on the Dunbrack dump (Location 1), and are considerably less highly concentrated at Location 2 and Location 3. The lead at Location 2 is 10 times more concentrated than at Location 3, the zinc is 3 times more concentrated, copper is 1.3 times more concentrated, and cadmium is 3 times more concentrated at Location 2.

3.7 Lichen analysis

Lichens are good bioindicators. They receive their nutrients from the air and the tolerance levels for lichens are well known. Lichens were collected and analyzed from the Dunbrack area in order to determine their heavy metal concentrations. This will be discussed further in Chapter 4.

3.7.1 Preparation

To investigate the heavy metal uptake by the biota surrounding the dump, lichens of the varieties *Parmelia sulcata* and *Hypogymnia physodes* were collected from trees at a height of approximately 1-2 metres from twigs were collected from the same 4 locations as the balsam fir (section 3.6). These lichens were analyzed by XRF at Saint Mary's University in Halifax.

The lichens were prepared for analysis by XRF by the following procedure. First, I used tweezers and a microscope to separate them from the woody branch they were living on, then they were dried overnight at 70^0C. Next, they were crushed to a fine powder at Saint Mary's University in Halifax, using a ceramic mortar and pestle in which the lichens were covered by liquid nitrogen. The powder was sieved through a 50 mesh stainless steel sieve (opening 0.3 mm), and re-crushed and re-sieved, until about 0.5 g to 1.0 g of lichen powder was produced for each species of lichen for each location. The lichen powder was stored in new glass vials. They were then dried again (at 80^0C overnight), and combined with 1 g of silica, 0.5 g of Hoechst micronized wax, and enough pure cellulose was added to the lichen powder to make a combined total of 2 g of material. Table 3.5 shows the exact distribution of material in each pellet.

Location	Lichen type	Lichen	Silica	cellulose	Wax	total
Location 1	*H.P.*	1.3923	0.9997	0.6077	0.5000	3.4997
	P.S.	0.8968	1.0001	1.1031	0.4999	3.4999
Location 2	*H.P.*	1.6419	1.0002	0.3549	0.5001	3.4971
	P.S.	0.3741	0.9998	1.6262	0.5001	3.5002
Location 3	*H.P.*	0.6641	1.0003	1.3362	0.5000	3.5006
	P.S.	0.6552	0.9998	1.3449	0.5000	3.4999
Control	*H.P.*	1.6619	1.0005	0.3385	0.4999	3.5008
	P.S.	0.3602	1.0001	1.6397	0.5001	3.5001
	Blank sample	0.0000	1.0001	2.0001	0.5000	3.5002

Table 3.6: *Hypogymnia physodes* (H.P.) and *Parmelia sulcata* (P.S.) distribution of material in the lichen pellets with all values in grams.

This material (a total of 3.5 g of combined material) was shaken for 10 minutes and then was pressed into pellets using a hydraulic press set at ten tons for a period of ten seconds. The pellets were placed in plastic pouches and put in a desiccator. A blank pellet of 2.0 g of pure cellulose, 1.0 g of silica, and 0.5 g of wax was prepared in the same way.

3.7.2 Lichen Results (XRF)

Standard curves were prepared from pellets made from lichen powders previously analyzed using AA spectrometry and XRF spectrometry at Saint Mary's University in Halifax, and from the blank sample.

SAMPLE ppm	Al	Cu	Zn	Cd	Hg	Pb
H.P. Location 1	130.3	5.1	103.0	0.7	0.84	28.6
H.P. Location 2	647.4	4.1	24.7	1.4	0.50	0.0
H.P. Location 3	265.6	0.8	41.2	0.7	0.60	0.0
H.P.control	640.8	1.7	28.3	1.2	1.00	0.0
P.S. Location 1	398.3	3.00	98.5	0.5	0.65	54.5
P.S. Location 2	147.6	2.90	10.9	0.5	0.00	19.9
P.S. Location 3	291.6	3.35	42.5	0.6	0.00	3.4
P.S. control	98.6	0.30	9.1	0.2	0.20	0.0
TP-26	1087.3	7.4	100.4	0.9	0.5	33.1
TP-26 book	1108±56	7.1±0.4	100±4	0.57±0.05	0.5±0.05	39±4

Table 3.7: *Hypogymnia physodes* (H.P.) and *Parmelia sulcata* (P.S.) element concentrations from the Dunbrack dump analyzed by XRF spectrometry.

The accuracy of the spectrometer for each element can be checked by comparing the known sample (TP-26 book) with the results obtained by the Saint Mary's University spectrometer (TP-26). The results for Al, Cu, Zn, and Hg have good accuracy, Pb, Cd, and Cr have reasonable accuracy, and the Ni values should not be judged as reliable.

The lichen analyses show that the samples from the Dunbrack area have a much higher concentration of Cu, and Pb than the control location in the Pockwock watershed region. The lichen species *Parmelia sulcata* shows a much higher concentration of metal ions than the species *Hypogymnia physodes*. For leafy lichens, the species *Parmelia sulcata* is of higher sensitivity to pollution than *Hypogymnia physodes* (Richardson 1997).

3.8 Summary

Microprobe results found are fairly standard for galena, sphalerite, bornite, chalcopyrite, and covellite, except that silver was found to be in the covellite, not in galena. Dunbrack rock powder analysis results have 45 % Pb, 3.5 % Cu, and 1 % Zn. When rainwater was added to these sulphides the pH dropped by 0.81 and 0.93 pH units. The rainwater was enriched by factors of 100-1000 with Pb, Cu, and Zn, and by a factor of 10 with Cd.

Balsam fir lead concentrations from 1.8-20 times that of the control location were found 60 m from the dump, and concentrations 175 times higher were found directly on the dump. Concentrations of Cu, Zn, and Cd increased by 1.5 to 5 times around the dump, and up to 13.5 times on the dump. Lichen from the dump and surroundings was enriched by 2-4.5 times in Cu, Zn, Pb, and Cd, particularly the more sensitive species *Parmelia sulcata.*

The next chapter presents a discussion of these results.

CHAPTER 4 DISCUSSION

4.1 Introduction

This chapter reviews lead in soils and in plant matter, and the effects lead and copper can have on the biosphere in general and on balsam fir and lichens in particular. This chapter also discusses the analytical results of Chapter 3 for the minerals and textural relationships, the pH experiment and water analysis, the lichen analysis, and the balsam fir analysis.

4.2 Literature Review

This section reviews the geochemistry and biochemistry of lead and copper.

4.2.1 Geochemistry of Lead

Lead is the heaviest of the common metals, with an atomic weight of 207.2. Lead is typically present in soil in concentrations of 2-200 ppm, averaging approximately 16 ppm (Tidball 1976). The lead in soil near an ore deposit however can range from 1,000 to 10,000 ppm (Huff, 1976). Natural lead deposits do have a toxic effect under certain conditions where soil fertility, organic matter, and colloidal content are very low (Lovering 1976). The dump at Dunbrack may be an example. In such a situation, more lead is directly available for uptake, because the dispersal of heavy metals has been artificially enhanced by excavation of the deposit. Excavation of the deposit results in a greater proportion of free sulphides.

Lead from natural ore bodies in soil or ground water is not substantially mobile because any lead dissolved from sulphide ore typically combines with carbonate or sulphate ions to form insoluble lead carbonate or lead sulphate compounds. The insoluble compounds are then relocated by mechanical weathering (Huff 1976). However, at Dunbrack (and other lead deposits), the lead can be mobilized relatively quickly because as the sulphides weather, they produce acidic components through the following reactions:

$$PbS + 4\ H_2O \rightarrow Pb^{2+} + SO_4^{2-} + 8H^+ + 8e$$

$$2PbS + 4\ H_2O \rightarrow 2Pb^{2+} + S^o + SO_4^{2-} + 8H^+ + 8e$$

These lead components may be sorbed onto other soil components such as clay minerals, or converted into weathering products, such as anglesite ($PbSO_4$), cerussite ($PbCO_3$), or pyromorphite ($Pb(PO_4)_3Cl$). Also, during weathering, galena may be slowly oxidized to either anglesite (when the pH is less than 6), or cerussite when the pH is greater than 6 (Pauli 1975):

$$PbS + 2O_2 \rightarrow PbSO_4 \text{ (anglesite)}$$

$$PbS + CO_2 + H_2O + 2O_2 \rightarrow PbCO_3 + H_2SO_4 \text{ (cerussite) (Huff 1976).}$$

The CO_2 for cerussite formation is usually available in the soil, in limestone, or in the atmosphere if the galena is exposed. Galena becomes coated with a light oxidation product (anglesite or cerussite) which is resistant to leaching. The low solubilities of these secondary minerals, as well as the strong binding capacity of lead, result in a low geochemical mobility of lead, much less so than for copper or zinc.

4.2.2 Geochemistry of Copper

Copper is the least mobile metal (Deutsch 1997) of the three, with lead being the second least mobile, and occurs in trace amounts in the common igneous rocks. In granite, copper is typically present at 15 ppm, and in the earth's crust, copper abundance estimates are 24-55 ppm (Cox 1979). It exists as sulphide inclusions in silicate minerals, and by substituting for Na^+ and Mg^{2+} in the silicate lattices. Copper forms sulfides, sulfates, sulfosalts, and carbonates.

Copper in soils is usually present in its divalent form, Cu^{2+}, and can be replaced by Zn^{2+}, Mg^{2+}, and Fe^{2+}. It ranges from 1 ppm to 50 ppm (averaging 20 ppm) but soils with a mineralized parent source can be much higher (Cox 1979). Factors that influence the abundance of copper in the soil are the degree of weathering of the parent material, the pH, the capacity of the soil to absorb copper, the amount of organic matter in the soil, the mobility of the copper in that environment, and the type of vegetative cover.

4.2.3 Biogeochemistry of lead and copper

Other metals present may be affecting the region as well. Copper concentrations of 4 % are present in the Dunbrack dump and the effects of copper and lead combined are probably greater than the sum of the effects of each heavy metal.

The threshold for background Pb in plant material is about 1.6-2.0 ppm in the dry weight, or 16-40 ppm in ash (Cannon 1976). Concentrations above this threshold constitute an anomaly, but concentrations should be above at least 30 ppm to be significant (Cannon 1976). The reaction of an individual plant depends on the plant species and its age. The main toxic effect caused by lead in plants is growth reduction. One hypothesis for this effect (Cepp 1979) is that the lead replaces phosphate, and an insufficient supply of phosphate causes the cells to die.

An effective method of sampling the biosphere to show heavy metal concentrations has been to use biogeochemistry, especially of balsam fir twigs. This type of prospecting is practical, inexpensive, and effective (Rogers and Dunn 1993; MacDonald and Boner 1993). Detailed sampling of balsam fir twigs at known Au occurrences in Nova Scotia produced distinctive geochemical signatures, (Rogers and Dunn 1993).

Where the soil is rich in lead, the plants are likely to be rich in lead as well. The granite hosting the mineralization typically has lead contents of 10-20 ppm (Fleischer 1976). For the lead to enter the plant root systems, lead must be dissolved in the soil solution (the rainwater percolating through the dump to the soil). Lead in the soil almost always stays bound to organic or colloidal materials, or exits in solid form (Cepp 1979). This solid-phase lead replenishes lead to solution as plant roots remove the ions from the solution during growth. Once the roots absorb the lead, only a small amount is transported to the shoots (Cepp 1979). This process, called translocation, is made difficult for the plant by physical processes such as lead binding to the cell walls, nuclei, and cytoplasm of the cells within the roots (Cepp 1979).

Natural lead deposits have not been shown to cause appreciable toxic reactions in plants. According to Cepp (1979): "Lead taken up by roots generally has no toxic effect on plants, except at extremely high root media concentrations that have little relevance to natural conditions. This general lack of lead effect from high Pb concentrations in roots has led to the hypothesis that most Pb taken up by roots is quickly inactivated through deposition in the roots." The lead is localized in the cell walls of the roots (Cepp 1979), and even though lead concentrations may be high, the effect on plant growth is minimal.

Copper in soil is not always available for uptake by plants because it is strongly held on inorganic and organic exchange sites (Thorton 1979). The number of copper ions absorbed by plants from solution varies with the concentration of ions in solution. The pH of the water also affects copper absorption, with an increase in pH decreasing the amount of copper in soil solution (Thorton 1979). Copper is passively absorbed by roots and becomes chelated (an equilibrium reaction between a metallic ion and an organic molecule) once it reaches the xylem (Lepp 1979). In these cases, reduced plant growth, branching, thickening of branches, and dark colouration may occur in the roots of many plants.

The bio-accumulation of metals depends on the bio-availability; that is, bio-accumulation depends on the ionic supply in the soil solution (Fig. 4.1), and not the total supply, which includes the solid phase of the metals (Jackson and Bistricki 1995). The solubility and bio-availability of metals will increase as the soil pH decreases because an increase in the activity of H^+ will increase the amount of trace elements in the soil solution and decrease the amount of trace elements in solid phase (Pierzynski et al. 1994). A change in the pH of the soil solution can change the trace-element containing soluble species present. At $pH < 6$ for example, Pb^{2+} is the dominant species, whereas at pH 6-11, $PbOH^+$ is the dominant species (Pierzynski et al. 1994).

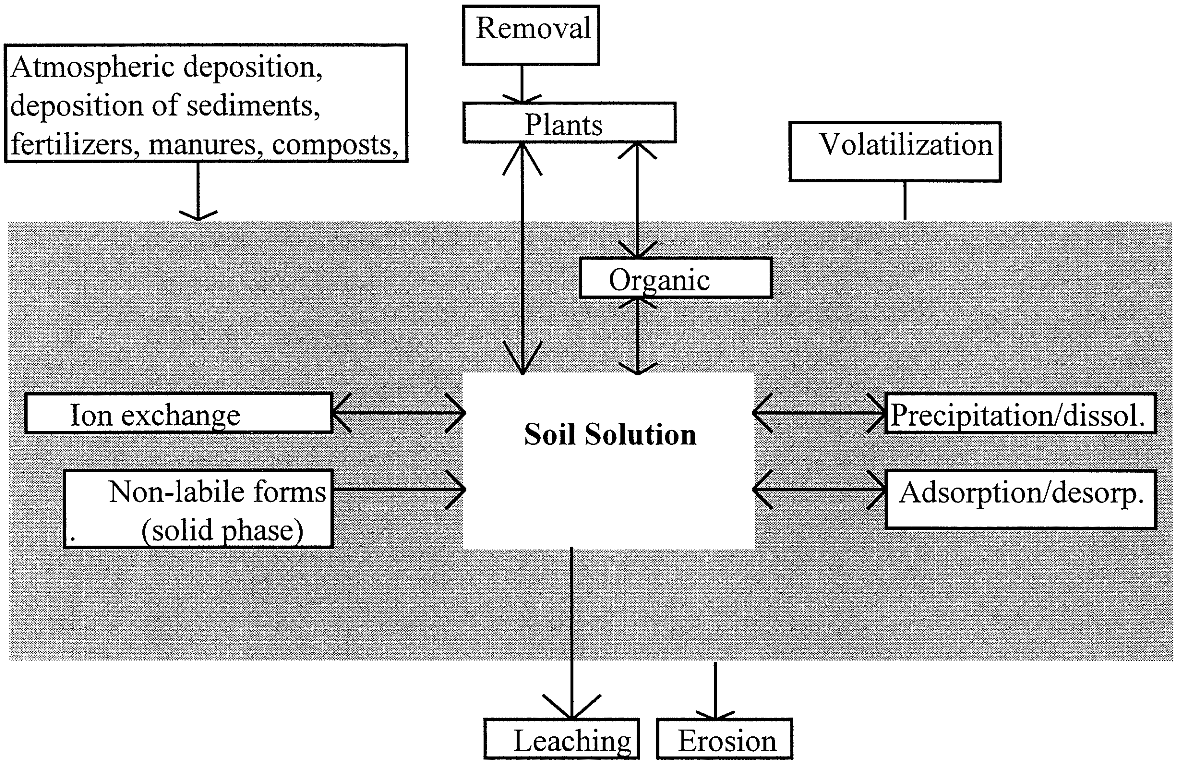

Figure 4.1 Generalized cycle of trace elements in soil. The gray box represents the soil boundaries (from Pierzynski et al. 1995).

4.3 Discussion of the heavy metal dissolution experiment

The pH of the water affects heavy-metal absorption of soil, with a decrease in pH increasing the amount of heavy metals in soil solution (described for copper by Thorton 1979). Small shifts in water pH can result in sharp concentration changes of dissolved metals (Salomons 1995).

When sulphides oxidize, acid drainage results, with a corresponding decrease in the pH of the water (Salomons 1995), but only if there are no minerals in the rock, such as clays, feldspars, and carbonates that will neutralize the acid produced. The pH experiment results show that the pH of the rainwater decreased when added to crushed sulphides by up to 0.93 pH units over a period of 4 weeks. However, this amount may have been buffered in the natural environment. The main acid-producing sulphide at Dunbrack, galena, is partially coated by anglesite and cerussite. This coating can slow the production of acid by protecting the sulphides from further rapid degeneration and limiting the amount of free raw sulphides available to the rainwater, but it also results in less buffering of the acid products that are already present. Acid is also consumed by reactions with silicates, creating a long term buffering action (Salomons 1995).

The experiment on pH conducted for this thesis is relevant because the lead uptake by plants such as balsam fir and lichens is affected by the pH of the water and the concentrations of other pollutants. The material in the dump is coarse-grained, and this allows more oxygen advection and diffusion, which in turn results in higher acid production (Salomons 1994).

The dump today has caused concentrations of lead, copper, zinc, and cadmium in local lichen and balsam fir to increase. At the original time of the removal of the sulphides, many fresh surfaces would have been available, increasing the effects of the dump on the local biota. The experiment tends to reconstruct a worst-case scenario of the dump at the time of its creation when fresh surfaces were created. The biota in the region may have had some time to recover, but obvious evidence of the presence of lead today is shown in lead values as high as 27.6 ppm in balsam fir twigs 60 m from the dump.

The oxidation of the minerals may not all have occurred after excavation. Some of the oxidation and weathering may also have taken place through deeply circulating fluids at the time of deposition (300 Ma), during Cretaceous to Tertiary weathering, or by post-glacial weathering. Therefore, the lead that has left the sulphides may not all have left recently, though some of the contamination is likely to have been caused by creating fresh surfaces during excavation of the area. Some of the contamination would probably have occurred naturally, both through the sulphides and the secondary minerals (sulphates), but it has been aggravated by excavation, and the combined amount of damage to the biota is what remains to be seen today.

4.4 Textural Relationships and Dissolution Rates

The real dissolution of grains from the Dunbrack dump today and their effect on the surrounding environment depends on how available for dissolution the metal sulphides are. For instance, if the sulphides are fully enclosed ("locked") by the surrounding galena, they are not available for dissolution by rainwater, as they are when the material is broken up, liberating the sulphides. In the natural environment, a proportion of the sulphides will be fully locked, a proportion will be semi-enclosed, and a proportion will be free. In the disturbed Dunbrack environment, a higher proportion of sulphides are free or partially enclosed.

The heavy-metal dissolution experiment involved liberated sulphides, purposely crushed to expose fresh surfaces to the rainwater. This experiment models the worst-case scenario for the dump today. In order to determine the real situation, I have examined the availability of the five sulphides, galena, chalcopyrite, covellite, bornite, and sphalerite in relation to their concentrations. Those that are mainly unenclosed or only partially enclosed pose the worst threat to the local environment.

Galena grains are the most exposed. In thin section, galena is approximately 90 % -95 % surrounded by (or available to) the host silicates. The edges of most galena grains are slightly indented by the silicates, or in rare cases (<2%) silicate rims have formed on the galena grains. Covellite and sphalerite rim 5-10 % of the galena grains, but certain rare grains are rimmed over 85% of their edges. Chalcopyrite is present as discrete grains within galena, covellite, and sphalerite. It is mostly locked by these minerals.

Covellite and sphalerite rim galena. Covellite rims galena and chalcopyrite, and occurs as discrete grains within galena. Approximately 80% of covellite is rimmed by silicates, not locked by other sulphides. Sphalerite occurs as grains and rims at the edges of galena and chalcopyrite. It is approximately 50 % available to the silicates. Bornite occurs primarily within sphalerite, and is approximately 97 % locked, so the copper in bornite is generally not available to the local biota.

4.5 Balsam Fir

Results for balsam fir show that the lead in the balsam fir of the dump and of the locations 60 m away from the dump have concentrations well above the threshold (1.6-2.0 ppm in dry weight, and 16-40 ppm in ash) in both the branch and the ash (Cannon 1976). The concentration of lead in balsam fir at the control is 1.39 whereas at Location 2 it is 27.6 ppm, 20 times more concentrated. Copper in the balsam fir of the control location is 2.22 ppm, whereas it is 5.3 ppm, more than twice as concentrated. Zinc is more than 5 times more concentrated at Location 2, where it has a concentration of 150 ppm. The concentration of zinc at the control location is 30 ppm. Lead concentrations in balsam fir growing on the Dunbrack dump are extremely high (243 ppm), and have resulted in stunted growth. Yearly growths (evident from new branching) in the balsam fir growing on the dump are about 2 cm, as compared to yearly growths of about 5 cm for the Location 2 and Location 3 balsam firs.

4.6 Lichens

4.6.1 Introduction

Lichens can be a qualitative indicator of air pollution because they accumulate nutrients and pollutants from airborne particles and rain. Lichens are useful for monitoring airborne pollutants because their tolerance levels and reactions to various levels of pollution are known. Tolerant lichen species which survive in polluted regions are also useful because chemical analyses can give an indication about the type and concentrations of the pollutants. Median lead concentrations in the ash of uncontaminated lichens are the highest of natural vegetation at 1000 ppm (Lovering 1976). The metal content can be high without damaging the lichens, depending on the type of metal. Lead, zinc, and copper can be harmful to lichens because excess amounts of these metals can affect the function or structure of the cell membrane or chloroplasts, by replacing essential metal ions (Richardson 1997) such as phosphur, sodium, or potassium.

Lichens receive nutrients not primarily from root sources but from airborne nutrients. Lichens absorb metal ions into their cell walls through ion exchange. In so doing, they release hydrogen ions or metal ions with a low binding capacity. Lichens also accumulate metals by trapping insoluble oxides, sulphates, and sulphides (Richardson 1997). Around contamination sites, such as (potentially) the abandoned Dunbrack deposit, lichens can accumulate the metals without harm if the metals are in insoluble form.

Lead is present in natural atmospheric concentrations that may be much less than 0.019 ug/m^3 (Cannon 1976). However, lead may be taken into the atmosphere as the wind disperses heavy metals in small particles. This airborne lead is usually not absorbed by plants but remains on their surfaces where it is a problem for grazers.

4.6.2 Environmental Impact

The lichens to the east of the dump at Location 2 (Fig. 3.8) show a higher concentration of copper and lead than the lichens at Location 3 to the north, though the concentration of zinc is higher at Location 3. This shift in concentration is probably related to wind dispersal and topographical dispersal, which in this case, does appear to be more disposed to the east. The topography, though highly uneven, generally decreases in the direction of the east. The pattern shown in the lichens is similar to the pattern in the balsam fir, where higher concentrations of metals occur in the balsam firs to the east of the dump.

Wind is a key dispersal agent for airborne particles. The lichens near the Dunbrack dump show lead levels ranging from 8-88 ppm, and up to 100 ppm on the dump itself, with *Parmelia sulcata* having higher values than *Hypogymnia physodes*. Zinc values were 25 ppm and 107 ppm at 60 m from the dump, and 123 and 183 ppm on the dump itself, with *Parmelia sulcata* again having the higher values. Copper values for the lichens are relatively low: concentrations of 2-13 ppm at 60 m from the dump are actually on average higher than the concentrations found on the dump itself: 5 and 6 ppm. Lead values over 100 ppm are considered elevated concentrations above the background, whereas copper values of 15-1100 ppm and zinc values of 1000-25000 ppm respectively are considered elevated (Shaw 1989).

The efficiency with which the lichens trap these particles is strongly dependent on the particle size. Epiphytes, such as moss and lichens, are not particularly sensitive to submicron-sized particles (Nriagu 1976). The climate, the intensity of the rainfall, and the atmospheric concentrations of other pollutants such as SO_2 also play a part in the particle collection efficiency. The lead aerosols near sites of mining activity consist mainly of the following: PbS, $PbCO_3$, $PbSO_4$, $Pb_5(PO_4)_3Cl$, $PbS*Bi_2S_3$, PbO_x, and Pb-silicates (Nriagu 1976). The composition relates to the particle size.

4.7 Environmental Significance of the lichen and balsam fir results

The results of analysis of balsam fir and lichens show higher concentrations of lead than of copper and zinc at distances of 60 m from the dump, and the concentrations of lead (45 %) in the dump are significantly higher than those of copper (4.1 %) and zinc (1.3 %). The low geochemical mobility of the heavy metals in the dump, and weathering products such as anglesite or cerussite, can protect the lead sulphides from rapid degeneration and slow the effects that the sulphides have on the local environment.

The geochemical mobility of the heavy metals in the dump can be estimated by calculating the relative proportions of the amount of metals in the dump to the amount of metals in the water after it has been in contact with the dump material, and the amount of metals in the balsam firs and lichens 60 m from the dump. Fig. 4.2 is a flowchart of the movement of heavy metals from the dump, and Table 4.1 shows the relative amounts of Pb, Cu, and Zn metals in the balsam firs and lichens.

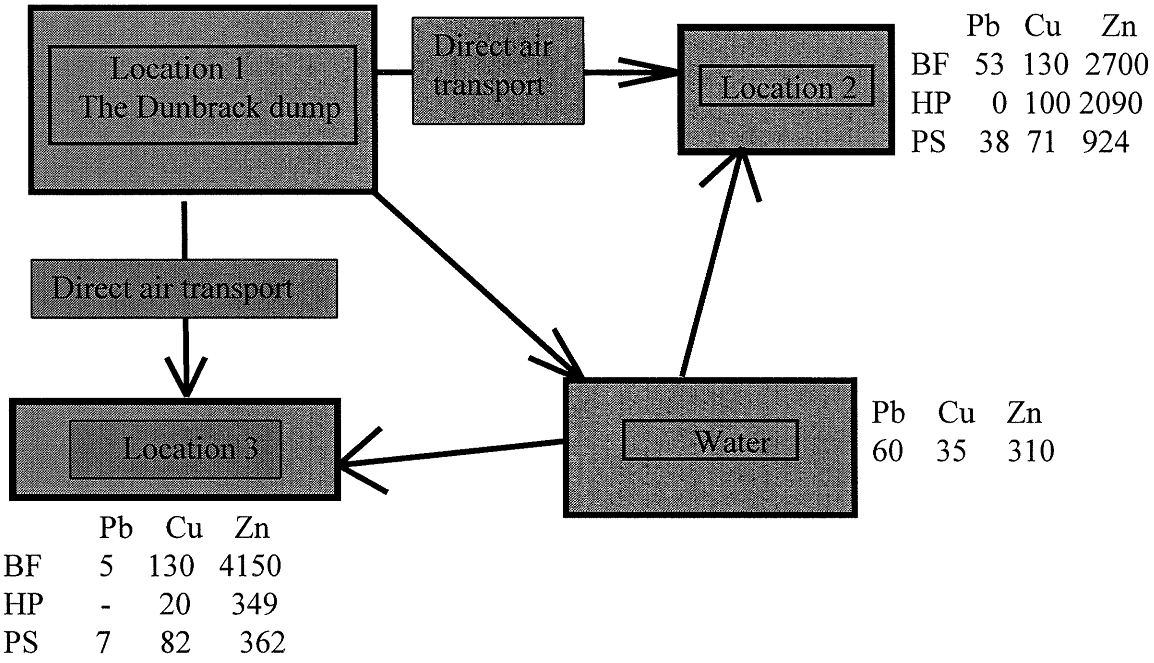

Figure 4.2 Flowchart of the path heavy metals from the Dunbrack dump take to the lichens (by direct air transport) and to the balsam fir (by groundwater), at Location 2 and Location 3. All values are ratios of (heavy metal concentrations in medium / heavy metal concentrations in dump) x 10^6.

		Pb	Cu	Zn
Location1		52%	4.09%	1.18%
Location2	Hypogymnia	0	1 x 10^4	2.09 x 10^3
	Parmelia	3.83 x 10^5	7.09 x 10^5	9.24 x 10^4
Location3	Hypogymnia	0	1.96 x 10^5	3.49 x 10^4
	Parmelia	6.54 x 10^6	8.19 x 10^5	3.62 x 10^4
Water		5.96 x 10^5	3.5 x 10^5	3.1 x 10^4
Location2	Balsam fir	5.31 x 10^5	1.3 x 10^4	a.27 x 10^2
Location3	Balsam fir	4.96 x 10^6	1.03 x 10^4	4.15 x 10^3

Table 4.1 Proportions of heavy metals in the water, lichens, and balsam fir at Location 2 and Location 3 to the amount of heavy metals in the dump material (Location 1).

From the values presented in Fig. 4.2 it is apparent that the amount of lead in balsam fir is less than the amount of lead in water, amounts of copper in balsam fir are also less than the amounts of copper in water, and the amounts of Zn are high in water and in balsam fir, indicating that zinc is highly mobile. Cu and Zn values differ by less than 2X and may indicate non-fractionation in transport from the dump.

4.8 Summary

The environmental effects caused by the Dunbrack dump have resulted in anomalous concentrations of lead, copper, zinc, and cadmium in the balsam fir and lichens in the vicinity of the dump, though there has not been obvious stunting of the biota surrounding the dump as a result. Directly on the dump, however, lead concentrations are high enough to have resulted in severely stunted balsam fir.

The lichen species *Parmelia sulcata* shows a much higher concentration of heavy metal ions than *Hypogymnia physodes*. The lichens to the east of the dump at Location 2 show a higher concentration of copper and lead than the lichens at Location 3, though the concentration of zinc is higher at Location 3. The distribution is probably related to topographical dispersal through water in the soil. Airborne particulates are used to replace nutrients in lichens, and wind dispersal is a key factor in their distribution. There certainnly may be other factors present in the distribution of metals to the lichens. The data shown here is an indication that the dump most likely had a role in the heavy metal supply.

In the heavy metal dissolution experiment, the pH of rainwater when added to crushed rock from the dump caused the pH of the rainwater to drop by 0.81 and 0.93

units, which will generally increase the amount of metals ions in the soil. The rainwater from the experiment became enriched in lead, zinc, copper, and cadmium ions.

Microprobe analysis of five of the main sulphides from the Dunbrack dump, galena, chalcopyrite, covellite, sphalerite, and bornite, show consistent elemental components. Relationships between these sulphides give the following order of estimated relative ages: chalcopyrite, galena, bornite, covellite, then sphalerite. Microprobe analyses also show that the silver is not present in the galena, which is of relatively uniform composition, but in the copper grains, particularly covellite.

Relationships between the grains also show that the most available grain is galena, which is 90-95% exposed to the surrounding silicates, and therefore able to be leached. Covellite and sphalerite are also both available to the silicates, but bornite and chalcopyrite are largely locked by galena, sphalerite, and covellite grains.

Chapter 5 discusses the environmental hazards posed by the Dunbrack dump to the local environment and draws conclusions from this study.

CHAPTER 5 THE ENVIRONMENTAL EFFECTS OF DUNBRACK

5.1 Introduction

This chapter examines the effects that the Dunbrack dump may be having on the local environment, the threat to biota and animals, and discusses any possible necessary remediation tactics, based on the findings of this thesis.

The local environment surrounding the Dunbrack dump has had 75 years to adjust to the last serious human intervention (producing the dump). Soils surrounding the dump are major sinks for pollutant lead, and the soil in turn affects the biota of the region. Soil over a metalliferous vein has a dispersion halo, concentrated at up to several hundred ppm closest to the ore body, so the effects of the lead will decrease with distance from the source. Clearly a supply of lead to the soils surrounding the dump still exists, carried by rainwater after percolating through the dump. High amounts of heavy metals common to the dump, in particular Cu, Pb, and Zn, are present in the balsam firs and lichens surrounding the dump.

5.2 Environment Significance of Dunbrack

The environmental impact of the Dunbrack dump on the local surroundings is determined by the change in concentration of metals in the plants, and the change in pH of the soil solution (Salomons 1994). The change in concentration of metals in the plants was high but only resulted in visible stunting of plant growth on the dump. The experimental change in pH of 0.93 units increases the acidity of the locality, but can probably be judged as an overestimation of the pH change because the proportion of neutralizing factors such as carbonates and silicates was lower in the pH experiment than it is in the dump situation.

Other factors such as the contamination from leaded gasoline and car batteries must also be taken into consideration. Auto exhaust pollutants are not as prevalent today as they were 25 years ago, but their effects on the biota up to 200 m from well-travelled roads are widely documented (Nriagu 1976). The main automotive constituents are $PbCl_2$, $PbBr_2$, PbBrCl, Pb(OH)Br, Pb(OH)Cl, $PbCl_2$, and PbBrCl. Auto exhaust particulates are agglutinated grains with diverse morphologies (Nriagu 1976). There may be residual lead in the soil and biota from this source.

Dumps such as the one at Dunbrack can inhibit microbial activities such as enzyme production, CO_2 production, humification of organic matter, and denitrification (Azcue et al. 1995). Top layers of dumps which are phytotoxic, and have no vegetative cover, are available for erosion by wind and water, with transport to the surrounding environment. This transport can significantly change the soil solution balance, and increase the volume of metal-rich water percolating through the dump to the ground water below. In many such situations the recommended policy is to cap the dump with clean material and vegetation (Azcue et al. 1995).

A few recuperation processes are recommended where the above situation poses a health threat. Only lead concentrations in plant products of at least 30 ppm are considered to pose a threat to animals (Dudka et al. 1995). In adults (humans), under 40 ug/100 ml blood-lead level is normal, and 40-80 ug/100 ml is acceptable (Hepple 1991). These types of blood lead levels would not occur as a result of a natural ore deposit such as Dunbrack, unless perhaps the immediate area was used for agricultural processes and was used as the main food source (which is not the case).

Several procedures are operative today in reclamation sites where dumps pose a health threat and/or obvious aesthetic disadvantage. Trace element bio-availability can be reduced by increasing the soil pH with lime to pH 6.5 and greater (Pierzynski et al. 1994). A vegetative cover of metal-tolerant plants can block the wind erosion and reduce the percolation by 85-90 % (Vangronsveld et al. 1995). Beringite (an aluminosilicate capable of high metal immobilization based on chemical precipitation, ion exchange, and crystal growth) is useful where even metal-tolerant plants cannot survive. When beringite is mixed in with the soil the metal concentration of the particulates is reduced, however, the percolation capacity of the dump increases, so judicious use is recommended (Vangronsveld et al. 1995).

Based on the assumption that the concentrations of heavy metals in balsam fir and lichens decrease linearly away from the Dunbrack dump, the difference in concentrations of heavy metals from the dump to a distance of 60 m from the dump can be extended until concentrations reach background (control) values. In this way the necessary distance from the dump for the balsam fir and lichens to recover to background concentrations of heavy metals can be calculated. By calculations based on the above assumption, the concentrations of Pb, Cu, and Zn in balsam fir and lichens will have decreased to background concentrations by a distance of 144 m from the dump, with the exception of copper in *Parmelia sulcata* at Location 3, which increased away from the dump. This is however based on a very small sample size, and on the assumption that the concentration of heavy metals (Pb, Cu, and Zn) decreases linearly away from the dump.

Further sampling and analysis is required to determine if the biota actually has recovered at a distance of 144 m from the dump.

The distance from the Dunbrack dump to the nearest human habitation is greater than 144 m, and the land surrounding the dump is located in a wooded region and is not used for agricultural purposes. However, although the biota may have recovered by a distance of 144 m from the dump, the area cannot be assumed to be safe for humans at this distance. Further testing of the groundwater and heavy metal levels in the soil is necessary to make judgements on the safety of the region for humans. Although the heavy metal content in balsam fir and lichens 60 m from the dump is anomalous, there has not been obvious stunting of biota in the region (except directly on the dump). Reclamation and revegetation would be helpful for animal and plant species living in the region, but vegetation could presumably cover the dump on its own within 75 years.

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Appendix A Microprobe raw data

Point	Sample	Fe	Cu	Pb	Zn	Sn	Ag	Au	As	S	Total
Galena											
13	KS-10-1D	0.1	0	86.47	0.07		0			12.7	99.33
20	KS-10-2B	0.1	0.16	86.09	0		0.11			12.7	99.12
23	KS-10-3C	0.11	0	85.72	0.08		0.11			12.7	98.74
24	KS-10-4A	0	0.02	86.4	0		0.02			12.8	99.2
25	KS-10-4B	0	0	85.83	0.35		0			12.9	99.12
35	KS-07-1A	0	0.27	86.71	0.3		0			12.7	100
39	KS-07-2A	0.01	0	85.79	0		0.08			12.9	98.76
40	KS-07-2B	0	0.01	85.96	0.17		0.06			12.5	98.72
41	KS-07-2C	0.08	0.05	86.12	0		0.06			12.6	98.9
Mean		0.04	0.06	86.12	0.11		0.05			12.7	99.1
Std Dev		0.05	0.1	0.34	0.14		0.05			0.13	0.41
Sphalerite											
6	KS-06-2A	1.35	0.7		65.44	0.67			0.18	32.8	101.1
9	KS-06-2D	0.92	0.46		66.45	0.16			0.26	33.2	101.4
22	KS-10-3B	1.9	1.28		63.91	0			0.16	32.6	99.88
10	KS-11-CA	2.71	0.59		63.37	0.1			0.15	33.1	99.98
14	KS-11-CE	1.74	3.03		62.69	0.2			0.12	32.9	100.7
15	KS-11-DA	1.48	1.07		66.18	0			0.08	32.5	101.4
24	KS-11-FC	2.91	2.71		60.26	0.72			0.19	32.7	99.51
16	KS-11-DB	2.36	0.96		63.09	0.28				32.7	99.34
Mean		1.86	1.41		64.04	0.26			0.16	32.8	100.6
Std Dev		0.72	1.04		2.2	0.3			0.06	0.23	0.78
Bornite											
27	KS-11-1B	14	53.8		0.11	0	0.29			31.3	99.46
2	KS-11-AB	14.9	52.4		0.15	0.05	0.11	0.43		32	99.93
3	KS-11-AC	14.5	53.5		0.21	0.11	0.12			31.3	99.75
4	KS-11-AD	14.3	53.3		0	0.46	0			31.4	99.38
11	KS-11-CB	0.26	55.4	0.72	7.59	0.1	0.15	0.47		28.7	93.36
12	KS-11-CC	12.4	60.9		0.51	0.13	0.07			27	101.1
17	KS-11-DC	4.14	50	5.1	0.16	0.08	0.5			26.4	86.39
18	KS-11-EA	11	51.4	1.03	0.15	0	0.81			30.6	94.99
19	KS-11-EB	13.4	54		0.39	0.25	0.35			31.4	99.74
20	KS-11-EC	21.1	45.9		0.02	0	0.09			32.7	99.81
Mean		12.7	47.1	2.28	6.05	0.13	0.21	0.45		30.9	97.73
Std Dev		8.16	15.9	2.44	18.09	0.14	0.24	0.03		2.38	4.21

Point	Sample	Fe	Cu	Pb	Zn	Sn	Ag	Au	As	S	Total
Chalcopyrite											
1	KS-11-AA	30.4	34.2		0.24		0	0		34.7	99.56
2	KS-06-1B	29.2	35.5		0.39		0.08	0		34.6	99.8
4	KS-06-1D	30	35.3		0.32		0.08	0.23		34.8	100.7
7	KS-06-2B	30	35.5		0.5		0.14	0.05		35.2	101.2
11	KS-10-1B	29.4	34.5		0.33		0	0		34.7	98.88
21	KS-10-3A	30.2	34.9		0.09		0.01	0		34.7	99.89
26	KS-11-1A	29.9	34.5		0.39		0	0		34.5	99.26
29	KS-11-1D	28.8	34.7		0.3		0	0.23		34.8	98.81
30	KS-11-2A	30.2	35.2		0.16		0.09	0.1		34.6	100.4
31	KS-11-2B	30	35.5		0.59		0.33	0		34.6	101
33	KS-11-2D	30	34.8		0.53		0.09	0.19		34.6	100.3
Mean		2.35	6.55		9.04		0.05	0.05		6.63	20.33
Std Dev		5.62	21.6		28.45		0.03	0.3		17.7	55.83
Covellite											
3	KS-06-1C	0.67	64.3	1.36	0.17		0.2	0.2		22.9	89.81
12	KS-10-1C	0	64.2	0	0		0.55	0.18		32.7	97.7
14	KS-10-1E	0	65.8	0.22	0		2.69	0		26.2	94.84
15	KS-10-1F	0	63.6	3.24	0.27		1.25	0		28.3	96.66
16	KS-10-1G	0.08	50.3	10.7	0.24		2.38	0		26.4	90.02
17	KS-10-1H	0	69.3	0	0.53		2.02	0.12		25.7	97.69
19	KS-10-2A	0.05	61.3	2.25	0.31		1.16	0.26		31.6	96.92
28	KS-11-1C	0.43	62.1	0	0.47		0	0.14		32	95.15
32	KS-11-2C	0.25	66.2	0	0		3.12	0.15		31.6	101.3
37	KS-07-1C	0.11	37.8	32.85	0.36		2.35	0		23.6	96.97
38	KS-07-1D	0.09	61.7	1.7	0.49		3.49	0		31.7	99.15
21	KS-11-FA	13.8	55	0	0.26		0.32	0.01		31.1	100.5
23	KS-11-FB	0	55.2	10.04	0.26		3.12	0.17		29.9	98.72
Mean		1.19	59.7	4.8	0.26		1.74	0.09		28.7	96.56
Std Dev		3.8	8.43	9.2	0.18		1.23	0.1		3.43	3.47

Appendix B Rock Powder and Lichens raw data

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23-Jan-98

Rock Powders

SAMPLE	L.O.I. %	SiO2 %	TiO2 %	Al2O3 %	Fe2O3 %	MnO %	MgO %	CaO %
KS-D-97-A	1.63	90.18	0.051	2.26	0.38	0.006	0	0.07
KS-D-97	1.72	91.44	0.054	2.29	0.4	0.007	0.02	0.08

SAMPLE	Na2O %	K2O %	P2O5 %	Sc ppm	V Ppm	Cr ppm	Co ppm	Zr ppm
KS-D-97-A	0.05	0.52	0.073	16	33	15	54	306
KS-D-97	0.07	0.53	0.07	18	38	6	57	308

SAMPLE	Ba ppm	Ce ppm	Nd Ppm	Ni ppm	Cu ppm	Zn ppm	Ga ppm
KS-D-97-A	0	385	150	25	4066	1282	75
KS-D-97	0	372	140	24	4113	1115	77

SAMPLE	Rb ppm	Sr ppm	Nb ppm	Sn ppm	Pb %	Th ppm	U ppm
KS-D-97-A	140	880	32	58	5.23	3160	20
KS-D-97	142	879	37	52	5.17	3138	28

Lichens

SAMPLE	Al ppm	Cr ppm	Ni ppm	Cu ppm	Zn ppm	Cd ppm	Hg ppm	Pb ppm
KS-D-97-1	155.5	0	0	6.1	123	0.8	1	34.1
KS-D-97-2	738.2	0	0	5.6	182.5	1	1.2	101
KS-D-97-3	640.8	0	0	1.7	28.3	1.2	1	0
KS-D-97-4	454.7	0	0	1.3	41.8	1	0.7	0
KS-D-97-5	655.3	0	0	4.2	25	1.4	0.5	0
KS-D-97-6	655.7	10.8	14.7	12.7	48.6	2.1	0	88.3
KS-D-97-7	664.8	0	0	2.1	103	1.7	1.4	0
KS-D-97-8	739.7	4.7	7.6	8.5	107.7	1.6	0	8.7
TP-26	1087.3	5.9	0.5	7.4	100.4	0.9	0.5	33.1

Appendix C Systematic Botanical Inventory

The following botanical inventory of material surrounding the dump are observations of Dr. P. Taschereau, Department of Biology, Dalhousie University (from September, 1997).

Directly Surrounding the Dump

Tsuga canadensis (L.) Carriere, eastern hemlock

Abies balsamea (L.) Mill., balsam fir

Picea rubens Sarg. X Picea mariana (Mill.) BSP, hybrid red-black spruce

Betula alleghaniensis Britt., yellow birch

Acer spicatum Lamb., mountain maple

Acer rubrum L., red maple

Also some stunted (>50 cm high) balsam fir showing nutrient (magnesium etc) deficiency, and stunted hybrid red-black spruce growing near the top lower margin of the mound, and on the mound some small hybrid spruce along with moss and lichens (Cladonia spp.).

Below the Dump (to the East: See Location Map Chapter 3)

All the species listed above, plus:

Scattered Picea glauca (Moench) Voss, white spruce with a rich forest flora of the species typical of older second-growth, selectively cut, stands of this region, including a ground cover abundant with:

Bazzania trilobata (L.) S.F.Gray, liverwort

Hylocomium splendens (Hedw.) BSG, moss (one example)

Dryopteris carthusiana (Vill.) H.P. Fuchs, fern

Dryopteris carthusiana (Vill.) H.P. Fuchs, fern

Polypodium virginianum (L.) H.P. Fuchs, fern (and others)

Above the Dump to the Highway (to the West)

Acer rubrum L., common

Abies balsamea (L.) Mill., common

Acer spicatum Lamb., occasional

Acer rubens Sarg. X Picea mariana (Mill.) BSP, common

Betula alleghaniensis Britt., common to abundant

Acer rubrum L., very common and scattered throughout

Lonicera canadensis Bartr., Canada honeysuckle, Amer. Fly honeysuckle, occasional

Prunus virginiana L., choke cherry, one speicmen; common above in more open ground by highway

Highway Margin Closest to the Dump

All the typical native and introduced species here continue for miles along the highway margin:

Populus grandidentata Michx., largetooth poplar, common

Picea glauca (Moench) Voss, white spruce, common to abundant

Populus tremuloides Michx., trembling aspen poplar, common

Salix bebbiana Sarg., Bebb willow, beaked willow, occasional to probably common

Salix sp., willow occasional shrub

Diervilla lonicera Mill., abundant subshrub or small shrub

Betula alleghaniensis Britt., very common, forming a stand of young trees

All the above trees and shrubs are more or less shade-intolerant plants, often occurring as pioneer species following forest fires and clear-cutting, but scattered to rare in mature, shady forests.

Expected to Occur on the Dump but not there

Some of the more typical pioneer tree species growing less than 100 m above the mound by the highway.

Picea glauca (Moench) Voss, white spruce

Populus grandidentata Michx., largetooth poplar, common

"Mosses, lichens, and small shrubs on the perimeter of the mound top might cover the sterile central portions of the mound completely within another 75 years"
(Pierre Taschereau, September 1997).