Draft

Supplemental Environmental Impact Statement

In-Pit Tailings Disposal Project
Ispat Inland Mining Company
Virginia, Minnesota

APPENDICES

MINNESOTA DEPARTMENT OF NATURAL RESOURCES

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LIST OF APPENDICES

APPENDIX A

In-Pit Disposal of Taconite Tailings: Geochemistry

Final Report

Minnesota Department of Natural Resources
Division of Lands and Minerals
Reclamation Section

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In-pit disposal of taconite tailings: geochemistry

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Summary

Field, experimental, and theoretical studies have been conducted to help predict the effect of in-pit disposal of taconite tailings on the chemistry of groundwater in the Mesabi Range Iron District, NE Minnesota. The purpose of this report is two-fold: (1) to provide a range-wide data base on the chemistry of water in and near taconite processing plants on the Mesabi Range and (2) to evaluate how in-pit disposal of taconite tailings might affect chemistry of water in the Biwabik Iron Formation.

Municipal drinking water supplies derived from the Biwabik have near-neutral pH, are dominated by Ca, Mg, and HCO_3^-, and have locally elevated concentrations of $SO_4^=$. Hydrogen and oxygen isotope compositions suggest that the tapped groundwater supplies we sampled were derived from rainfall and snow melt that infiltrated the ground relatively recently, much of it within the last four to five decades. The most recently infiltrated waters, those which contain tritium from 1950's bomb testing, have experienced some evaporation signifying that they probably resided in a pit for some time prior to infiltration. Regardless of when or how they infiltrated, the Biwabik groundwaters are all close to saturation with respect to Ca- and Mg-carbonates and fine grained silica, but only the older waters (without tritium) approach saturation with respect to siderite, an Fe-carbonate mineral that is abundant in the formation. Most waters are highly undersaturated with Fe-silicate minerals commonly found in the Biwabik Iron Formation including minnesotaite and greenalite. Thus, except for Ca and Mg carbonate and minor sulfide minerals (where they exist), many phases known to be present in the Biwabik Iron Formation either react slowly or are not in direct contact with the water.

Because grinding and refining of taconite ore takes place under air-saturated conditions, there is much reaction between minerals and water during taconite processing. Taconite processing waters, as a result, have high pH (≥8.5) and high concentrations of most major elements compared to Biwabik Iron Formation groundwaters. Process waters stored in tailings basins are diluted by runoff and local precipitation, but the pH remains elevated compared to local groundwaters. Concentrations of most major elements increase when water stored in tailings basins infiltrates into tailings, while pH, and the concentrations of some trace elements, most notably Mo and F, decrease. Elements of potential regulatory concern include Mn, F, Mo, As, and B. The highest levels of F, Mo, and As are found in raw process waters, while the highest levels of Mn and B are found in tailings pore fluids. Concentrations of all of these elements are relatively low in Biwabik Iron Formation groundwaters.

Experiments were used to determine reactions taking place between water and minerals in tailings. Although many reactions that took place in the laboratory were also found to take place in the field, additional reactions were observed to take place in the field. A carbon isotope study performed to identify the reason for the differences, revealed that CO_2 derived from local decay of plant matter was participating in reactions at some field sites, but not in experiments. Local vegetation, buried during construction and filling of the tailings basin impoundments, is probably the source of this CO_2. Background organic carbon is also present within the Biwabik Iron Formation and its oxidation helps to account for carbon isotope values and chemistry of pore fluids generated in experiments.

Overall, it appears that the availability of oxygen has an important influence on chemical reactions that take place in water penetrating tailings. When oxygenated process waters react with tailings there is a decrease in pH to near neutral values, which leads, in turn, to partial adsorption of F, Mo, and As. Reactions leading to the decrease in pH

during tailings/water interaction involve oxidation of reduced carbon to carbonic acid and oxidation of reduced sulfide to sulfuric acid. In most cases, carbonate minerals in the iron formation neutralize the acid that is produced. Little reaction occurs if the tailings are intruded by groundwaters lacking dissolved oxygen, and although elements such as Mn, F, As, and Mo are partially remobilized by groundwater, their concentrations remain relatively low. If tailings are infiltrated by dilute oxygenated water (e.g., rainfall), however, additional dissolution of tailings occurs along with low level remobilization of some of the adsorbed As, Mo, and F.

Significant differences can exist among the various operations owing to differences in ore composition, mineral processing, and water budgets:

Maximum manganese concentrations, which can be predicted based on solubility of $MnCO_3$ can approach 10 mg/kg in waters reacting in the presence of an acid source (plant matter decomposition or sulfide oxidation) and in the absence of Ca and Mg carbonate minerals. When Ca and Mg carbonate minerals are present, the water that evolves has high Ca and Mg concentrations rather than high Mn. Thus, Mn concentrations in waters reacting with tailings or within the Biwabik Iron Formation are typically maintained at relatively low levels ($\leq$ 1 mg/kg) because of an abundance of ankerite $(Ca,Mg,Fe)CO_3$ in the iron formation. Anomalously high Mn concentrations in wells and seeps near Inland's tailings basin are attributed to reactions taking place in the substrate buried beneath the tailings basin.

Fluoride concentrations become elevated in taconite processing streams when a wet scrubber system is used to collect particulates from gases evolved during pellet induration. Gaseous HF that is evolved when the pellets are heated to high temperatures is collected by water in the wet scrubber system and introduced back into the process stream as dissolved F^-. This F^- may partially adsorb to tailings or combine with Ca to precipitate as CaF_2. Maximum possible F values in waters at taconite operations can be reasonably predicted based on an empirical inverse relationship between Ca and F. For operations where Ca and F concentrations are below the fluorite saturation level, however, adsorption/desorption criteria must be used to evaluate potential F release from tailings. F can accumulate in process waters that are recycled between the plant and the tailings basin.

Mo is derived possibly from the ore, but may also be released during corrosion of grinding media or from dissolution of lubricating agents. This element is present in processing waters as $MoO_4^=$ ion. Although $MoO_4^=$ ion adsorbs to Fe-oxides under neutral pH conditions, it does not adsorb as effectively at the high pH levels ($\geq$8.5) associated with taconite processing. Thus, like F, concentrations of Mo accumulate when process waters are recycled between the processing plant and tailings basin. $MoO_4^=$ ion adsorbs readily to tailings under the near neutral pH generated in tailings/pore fluid environments but may be released gradually at subdued levels into other waters circulating through the tailings at a later time.

Arsenic is readily adsorbed onto the surfaces of Fe-oxides under the alkaline pH levels ($\geq$8.5) of taconite processing streams. It also adsorbs effectively under conditions prevailing in tailings pore fluids or found within the Biwabik Iron Formation. This element is probably derived from the grinding and oxidation of trace sulfide minerals in the primary ore, but it may also be present as adsorbed arsenic on the surfaces of primary Fe-oxides. Conditions needed to mobilize high concentrations of As, as the soluble species $As(OH)_3^0$, were not encountered in this study, but somewhat elevated concentrations (25 μg/kg) were found in basin waters at one site (LTV) where sulfide oxidation was suspected to be taking place within the tailings. Arsenic should not accumulate in waters cycled between the processing plant and the tailings basin because it is adsorbed nearly quantitatively to Fe-oxides.

B is released from tailings at only one of the operations studied. In this case, B release to water occurred during taconite processing, within tailings basin pore fluids, and in experiments. Calculations suggest that the B release process is probably not related to desorption from Fe-oxides. Like F and Mo, concentrations of this element accumulate when waters are recycled between the processing plant and the tailings basin. Data in the literature indicate that B mobility in nature is generally limited by adsorption onto clay minerals.

Introduction

Taconite is a very hard, relatively low grade, silica-rich iron ore that forms the basis of the iron mining industry in NE Minnesota (Ojakangas and Matsch, 1982). The currently preferred taconite mining method in Minnesota involves grinding of the rock into a fine powder, magnetic separation of ore from non-ore minerals, agglomeration and induration of the ore concentrate into pellets, and deposition of fine tailings and associated processing waters into large above-ground tailings basins. In some operations a flotation process is used to further remove silica from the ore concentrate prior to rolling and induration of the pellets.

Largely to avoid the need to construct and maintain tailings basins, mining companies in NE Minnesota are exploring the possible use of mine pits in the Biwabik Iron Formation for tailings disposal. Other possible benefits of in-pit disposal include elimination of the risk of tailings dam failure as well as reductions in dust generation, the area of land (including wetlands) disturbed by mining, and the amount of energy used for pumping tailings. Thus, laws preventing in-pit disposal of tailings have been modified recently making it possible for regulatory agencies to issue permits to fill pits with fine tailings, provided it can be shown that ground water supplies in the Biwabik Iron Formation will not be adversely impacted. The Biwabik Iron Formation is the only major bedrock aquifer in the region.

Tailings deposited in a pit may be exposed to water derived from a variety of sources, depending on local geographic and hydrologic factors. In active tailings basins, it is clear that the pore fluids within the deposited tailings are dominated by downward migration of process waters stored within the basins (Myette, 1991; Berndt and Lapakko, 1997 a,b). In a pit environment, however, local groundwaters and/or surface runoff may displace processing waters within the pores of the deposited tailings. Full evaluation of the potential impacts and merits of in-pit disposal of taconite tailings must consider, therefore, the potential consequences of reactions that may take place between tailings and water derived from a variety of sources, including process waters, groundwater, and precipitation.

Berndt and Lapakko (1997 a, b) previously identified Mn, F, Mo, As, and B as potentially problematic based on analysis of samples collected over a one year time period from active tailings basins and taconite processing plants and based on the results of experiments and calculations. The present study expands the earlier results in both time and scope: field sampling has been extended to three years for tailings basins and has been broadened to include groundwaters from the Biwabik Iron Formation. Experiments were also conducted to evaluate reactions taking place in tailings infiltrated by groundwater and local runoff. Isotopic samples were collected to help resolve former discrepancies between field and experimental measurements. The results are integrated to evaluate the likely geochemical consequences of in-pit disposal of taconite tailings on water quality on the Mesabi Iron Range district.

This study was initiated by the Minnesota Department of Natural Resources, supported by a grant from the Iron Ore Cooperative Research Program, and executed jointly by the University of Minnesota and Department of Natural Resources. John Folman is acknowledged for assistance in collecting and processing samples and for performance of all analysis carried out at the DNR laboratory in Hibbing (alkalinity titration, pH, Eh). Jim Walsh of the Minnesota Department of Health is acknowledged for assisting with oxygen isotope, hydrogen isotope, and tritium analysis and interpretation of Biwabik Iron Formation groundwaters. Rick Knurr, at the University of Minnesota is acknowledged for his careful analysis of cations and anions. Scott Alexander at the University of Minnesota is acknowledged for assistance with carbon isotope interpretation.

Methods

Chemical analysis

Water

Each water sample was analyzed for a large array of parameters including pH, alkalinity, temperature, and major and trace cations and anions. Temperature and pH (Beckman model 11 meter with Ross model 8165 combination electrode) were determined on site, while alkalinity titrations were conducted at the Minnesota Department of Natural Resources (MN DNR) laboratory in Hibbing. The concentrations of numerous cations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer mode-SCIEX-Elan 5000) while anions were measured using ion-chromatography (IC, Dionex Ion Chromatograph fitted with GP40 gradient pump, CD20 conductivity detector, and two AS4A anion exchange columns) at the University of Minnesota. Tables 1 and 2 list a subset of inorganic species that were analyzed along with approximate detection limits and the analytical technique used. Major cations were analyzed on water diluted by a factor of 10, while trace elements were analyzed directly on undiluted samples. Some elements (Fe, Mn, Sr and Ba) were analyzed at both dilutions to serve as a crosscheck on the analyses.

Tailings

Samples of the tailings used in experiments were dried and sent to the Midland Research Center, Nashwauk, MN, where they were analyzed chemically (ICP), mineralogically (X-ray diffraction, thermal gravitational analysis, heavy metal separation, scanning electron microscopy with energy dispersive detectors, and light microscopy), and physically (grain size analysis). A sample of tailings was also collected just above a high-Mn seep at Inland Steel's outer containment dike and analyzed by scanning electron microscopy.

Isotopes

Carbon

The carbon cycle in natural fluids is intimately related to water chemistry and on the presence or absence of sources of dissolved CO_2 and $CO_3^{=}$. One means to distinguish between different chemical processes is to measure carbon isotope ratios ($\delta^{13}C$). Samples for carbon isotope analysis were collected from three column experiments, three tailings basin reservoirs (National, Inland, and LTV), and either a seep or a well at the edge of each of the tailings basins. All samples were collected in 70 ml bottles and sent directly to the Waterloo Isotope Lab at the University of Waterloo, Waterloo, Ontario, Canada. They report an error in analyses of approximately 0.3 ‰ for $\delta^{13}C$.

Hydrogen and oxygen isotopes (and tritium)

Samples of water from the Biwabik Iron Formation were collected and sent to James Walsh at the Minnesota Department of Health for processing of $\delta^{18}O$ (per mil difference of the $^{18}O/^{16}O$ ratio relative to seawater standard), δD (per mil difference of the $^{2}H/^{1}H$ ratio relative to a seawater standard), and ^{3}H (tritium concentration). Actual analyses were performed at the Waterloo Isotope Lab at the University of Waterloo, Waterloo, Ontario, Canada. This lab reports a precision of 0.2 per mil (‰) for $\delta^{18}O$ and 3.0 ‰ for δD. Errors in ^{3}H measurement are reported to be 0.3 to 0.4 TU (Tritium Units where 1 TU = 1 ^{3}H per 10^{18} hydrogen atoms = 3.19 $pCi \cdot kg^{-1}$) for waters having low concentrations and about 10% of the measured value when ^{3}H concentrations exceed 3 TU.

Tailings basin study

Over 80 water samples have now been collected from active tailings basins spanning the time period from June, 1996, through April, 1999. Sites visited in these studies include the tailings discharge pipe (where tailings and process waters are pumped into the basin), the water return barge (where water is recycled from the tailings basin back to the processing plant), and seeps and wells in or near the tailings basin dike (water from the tailings basin which has presumably reacted with tailings). One-liter grab samples were collected when possible. Samples from wells were collected using either a one-liter Teflon bailer or a battery operated pump system. For well sampling, a volume of water greater than or equal to three well volumes was collected and discarded before sample processing procedures were begun.

Water discharging into tailings basins from processing plants contained large amounts of suspended material that required settling before the sample could be processed. Thus, the initial sample for these sites was collected using a clean 20-liter pail. Temperature and pH were measured immediately in the slurry, but water used for analysis was decanted from the container after the tailings had settled out at the base of the pail. All samples were filtered in the field immediately after sample collection but prior to acid preservation, when applicable.

Three Minnesota taconite mining operations participated in the three year tailings basin portion of this study (See Fig. 1): National Steel Pellet Company near Keewatin (National), Inland Steel Mining Company near Virginia (Inland), and LTV Steel Mining Company near Hoyt Lakes (LTV). Each of these companies currently disposes tailings in above-ground tailings basins, but the processing methods vary. National uses nothing beyond magnetic separation to process their ore, Inland uses flotation to decrease SiO_2 in their pellets, while LTV uses flotation and softens their water. Inland and LTV both use a wet scrubber system to remove particulates from their gas emissions, while National uses a dry mechanical collector. Possibly significant, is the fact that LTV placed 262,652 LT of sulfur bearing (3.19% average) hornfelsic waste rock from the Virginia formation and 31,468 LT of dolomitic limestone in their tailings basin in 1994 (LTV, 1996). These differences in processing techniques and tailings basin construction lead to distinct differences in water quality at each site.

National

Plant discharge and intake (return from tailings basin) samples were collected on each visit to National's tailings basin. No seeps were available for sampling at National's tailings basin, however, two wells were found on the south side of the basin in October, 1997 (wells 12 and 14). Well 12 had a depth of approximately 15 feet, the bottom 5 of which was filled with water. Well 14 was 28 feet deep, the bottom 11-13 feet of which was filled with water. Both wells were located at road level, approximately 12-15' below the top of the tailings dike. Drill logs for these wells are provided in the appendix. Both wells bottom out in glacial materials located beneath the dike, however, based on hydrologic considerations, it can be determined that the water in the wells originated in the tailings basin.

Inland

Plant discharge and intake (return from tailings basin) samples were collected on each visit to Inland's tailings basin. In addition, a single seep was sampled on the NW side of Inland Steel's tailings basin during our initial visit in June, 1996. This seep was inactive during later visits. Water was also collected from a seep found on the north side of the tailings basin on all subsequent visits. Two monitoring wells were installed by Inland Steel at the north edge of their tailings basin dike on Aug. 22, 1996. The first (MW-5) was drilled to the top of the basement rock (Giants Range Granite) and screened between approximately 7 to 9 feet. The second (MW-6) was bored several feet from MW-5, but only to a depth of approximately 5 feet and screened over the interval between 3 and 5 feet below the surface. Drill logs for these wells are provided in the appendix. Both wells were sampled on all subsequent visits, weather permitting.

LTV

An actively flowing seep was found on the southwest side of LTV's tailings basin during all of visits. Plant discharge and intake (return from tailings basin) samples were also collected on each visit.

USX/Snively pit tailings disposal site

Several samples were also collected from the tailings basin at USX (see Fig. 1) early in our previous study, but later efforts were focused on obtaining water samples from the Snively Pit tailings disposal site. Tailings were deposited by USX within the Snively Pit from 1964 to 1980, providing an ideal opportunity to study the long-term effects of in-pit tailings disposal on groundwater chemistry. Until recently, the only activity in the Snively pit was the pumping of mine-water from the nearby East Pit onto the surface of tailings deposited in the Snively Pit. Most of this water flowed directly back out of the Snively through porous road bed material on the west end of the pit, but a portion of this water may also have percolated into the tailings. The groundwater level in the Snively pit was found to be approximately 60 feet below the surface of the tailings owing to dewatering operations in the nearby East Pit. This made it necessary to drill a well deep into the tailings (89 feet) in order to obtain a representative sample of the pore fluids from this site. After completion of the well in October, 1996, samples were collected periodically, thereafter, beginning in November, 1996. A sample of the water being discharged into the pit was also collected on each visit for comparison purposes. Groundwater levels dropped recently owing to de-watering and active mining operation taking place around the Snively.

Biwabik Iron Formation groundwater

A large amount of data on the composition of water in the Biwabik Iron Formation are presented by Cotter et al (1965), but these data were inadequate for our purposes owing to the age of the dataset and lack of chemical analysis for many trace elements. Eleven water samples were collected from municipal wells along the iron range (Fig. 1) in early May, 1998. These data not only provided us with range-wide information on the background levels of Mn, F, Mo, As, and B of Biwabik Iron Formation groundwaters, but also permitted assessment of reactions that affect chemical transport of these elements through the Biwabik Iron Formation. Field measurements (temperature, pH, conductivity, Eh) and samples were taken at each site with the pump activated and water treatment deactivated (e.g., raw water samples). Samples were filtered on site and analyzed using the same procedures used on samples from tailings basins (see above). Cities participating in this part of the study included Calumet, Nashwauk, Keewatin, Hibbing (Scranton well), Buhl, Kinney, and Mountain Iron. Hydrogen and Oxygen isotope samples were collected in 70 ml plastic bottles while Tritium samples were collected in 1 liter glass bottles.

Laboratory and field experiments

Process water experiments

A series of experiments was conducted to evaluate reaction when tailings are penetrated by process waters. Columns used in experiments were constructed of 2-inch inner diameter plastic tubing, 15 feet in length, fitted with a sampling port at the base. The tubing was secured in vertical orientation and covered with an opaque plastic sheet to eliminate penetration by light. An amount of fluid equal to approximately one pore volume of process water was passed through the column over a time period of 57 weeks prior to injection of groundwater or infiltration by rainwater. Samples were collected periodically throughout this time and analyzed for all of the same inorganic components measured in the field portion of the study. A total of six experiments were conducted involving tailings and process waters from National, Inland, and LTV.

Groundwater injection experiments

Three of the columns used in process-water experiments (with tailings from National, Inland, and LTV, respectively) were reused to investigate tailings reaction with groundwater. Groundwater used in experiments was collected from Keewatin, MN. Hydrology and water chemistry from these wells have been studied previously by Jim Walsh at the Minnesota Department of Health (Walsh, 1997). The starting composition of water used in these experiments was effectively the same as that of water from Keewatin well #2, with near neutral pH and chemistry relatively typical of groundwaters in the region (Cotter *et al.*, 1965). Because groundwater composition changes rapidly when exposed to air (due to CO_2 degassing and O_2 entrainment) a special procedure was used to prevent contamination from the atmosphere. The groundwater was collected using apparatus designed to permit continuous purging of the solution with a gas containing 1% CO_2 and 99% N_2. This procedure effectively kept unwanted oxygen from entering the fluid and maintained CO_2 levels at values typical for groundwaters in the Biwabik Iron Formation (P_{CO2}=0.01 atm, see below). The groundwater was injected into the columns from the base port so that it would displace the existing pore fluids from below and eliminate possible entrainment of oxygen and loss of CO_2 during the transfer process.

Because the columns are quite large (15 feet), sufficient sample could be injected into the columns to provide adequate fluid for full evaluation of groundwater/tailings interaction over the entire period of the study. Because of the low permeability of tailings, however, the injection process was very slow and required several weeks to complete. The fluid was purged with the CO_2/N_2 mixture throughout the injection period. Samples were taken periodically thereafter.

Rainwater infiltration experiments

Three additional columns from process water experiments (with tailings from National, Inland, and LTV) were used to simulate infiltration of previously aged tailings by rainwater or local surface runoff. In contrast to the groundwater penetration scenario, it was important for water in these experiments to be introduced into the tailings in a fully oxygenated state (saturated with air). This was accomplished by replacing the water existing above the tailings/water interface (at the top of the columns) with deionized water, and opening the sampling valve at the base of the column to permit downward flow. In this manner, fluid removed at the base of the column, was replaced by oxygenated "rainwater" at the top of the column.

Flow systematics were varied in this case to simulate rapid and slow movement of water through a tailings-filled pit. The first eight weeks of the experiments were characterized by flow of deionized water through the columns until a little over four liters of water had been collected at the base (flow rate equals approximately 500 mls/week). Since the pore volume for each of the columns is approximately 1.5 to 2 liters, this amount of flow was more than adequate to displace all of the pore fluid existing in the column. After this, the fluid was allowed to equilibrate with minerals in the column for a period of approximately 12 weeks. The flow rate was then increased again to approximately 500 mls/week to evaluate water chemistry associated with flow of large amounts of dilute water through the tailings. This process was continued until a total of nearly 11 to 12 liters of dilute water had passed through the column. Approximately nine months later, a final sample was collected from the base of the column and used to estimate the final equilibrium chemistry and to measure carbon isotope composition.

Small scale fluoride leach study

Tailings have on the order of 200 mg/kg fluoride, but the majority of this fluoride is probably contained in silicate minerals (clays and/or amphiboles) and/or in the mineral fluorapatite (Zhu and Sverjensky, 1991). Although none of these minerals are easily altered at low temperatures, some F was found to leach from tailings in the rainwater experiments. A series of separate experiments was designed to characterize and quantify extractable F in tailings. Columns used for this purpose were constructed of glass and measured approximately 40 cm in height and had an internal volume of 22.5 mls. A slurried mixture of freshly collected tailings and process waters were introduced into the columns. After allowing the tailings to settle out of solution, the remaining pore fluid was decanted from the top of the column and replaced by deionized water. Flow was then initiated and allowed to continue freely for a period of two weeks with samples collected daily for the first week and every two to three days, thereafter. The concentration of mobile F in tailings could then be calculated by integrating flow volume and F concentration.

Large scale field experiments

In addition to the laboratory column experiments, four relatively large scale experiments were performed in large in-ground tanks at the field experimental facility, DNR, Hibbing. As opposed to the laboratory experiments, which were performed under more controlled conditions, these field experiments were designed to simulate deposition of tailings in a pit-like environment under field conditions. The "pit", in this case, was simulated using a 4 ft diameter x 10 ft tall plastic tank, open to the air at the surface. The results of these experiments will not be addressed here but preliminary results are available in Jakel et al. (1998). A final report for these experiments was also being generated at the time this document went to press.

Computer modeling

Fluid speciation, mineral saturation, and reaction path calculations were performed using "The Geochemist's Workbench, vs. 2.0" (Bethke, 1994). Thermodynamic data used in this program are predominantly from Johnson et al. (1992) and Dzomback and Morel (1990). The data was expanded to include modeling of MoO_4^- and F^- adsorption effects using adsorption constants estimated by Dzomback and Morel (1990) who derived them using correlation algorithms. Calculations were performed on an SGI work-station at the University of Minnesota.

The carbonate minerals in tailings are complex solid solutions of Fe, Mn, Mg, and Ca carbonates which are not easily modeled using computer applications. In addition, the silicate minerals minnesotaite, talc, and stilpnomelane are complex solid solutions as they exist in the taconite tailings environment. Carbonate reactions were modeled in our simulations using stoichiometric siderite ($FeCO_3$), dolomite ($CaMg(CO_3)_2$), and rhodochrosite ($MnCO_3$). Reaction of fluid with stilpnomelane and silicates was not considered explicitly, although such minerals provide important functions by controlling the concentrations of Si, Na, and K (cation exchange). The current version of Geochemist's Workbench does not permit modeling of cation exchange reactions. Our primary aim in this case was to identify chemical processes affecting redox and pH which affect strongly the adsorption and desorption of anions, and solubility of $MnCO_3$. Developing a means to assess pH and redox also gives us a means to assess mobilities of Mn, F, Mo, As, and B in a variety of geochemical settings.

Geochemical Concepts

Chemical measurements made at one time and place can be used to predict what can be expected in another setting or at a different time provided the primary processes that govern chemical composition of water are understood and provided the key variables that affect chemistry are known. While factors related to water mass balance and mineral processing may change from day to day in an unpredictable fashion at each operation, the key chemical reactions that occur at each site will remain relatively fixed through time. Thus, some prediction on what to expect if in-pit disposal is initiated can be made. A general understanding of taconite mineralogy and of simple oxidation and acid/base chemistry related to groundwater composition are required for the most accurate interpretation of results to be made.

Taconite minerals: effect on solution chemistry

Carbonate minerals are quite common throughout the Biwabik Iron Formation, primarily as ankerite and siderite. The presence of ankerite in taconite tailings is important from a geochemical point of view, because calcium rich carbonate minerals tend to react rapidly with fluids to neutralize acid. Siderite, meanwhile, is a reduced iron source, that upon oxidation may result in formation of Fe-oxides and carbonic acid. The relative amounts of siderite and ankerite in any particular ore horizon may vary considerably as both minerals are likely secondary, having formed during diagenesis of sediments rich in organic matter (Perry et al., 1973; Thode and Goodwin, 1983; Bauer et al, 1985).

The other major reactants commonly found in taconite tailings are the non-magnetic Fe-oxides (hematite and goethite). The presence of these minerals in tailings has an important influence on the mobility of F, Mo, and As which are present as negative anions (F^-) or oxyanions ($As(OH)_4^-$, MoO_4^-). Negatively charged species such as these tend to adsorb to Fe-oxides over a wide range of pH conditions, covering the spectrum of most natural groundwaters.

Sulfide minerals (pyrite) are minor constituents in most iron ore, but they are locally important in some areas of the Biwabik Iron Formation. Waters contacting pyrite that has been oxidized can become highly acidic if no other reactions are available to neutralize the acid.

Silicate minerals in tailings are typically dominated by quartz, stilpnomelane, minnesotaite, and talc. Although silicates may be quite abundant in comparison with carbonate minerals, they are generally much slower to react with aqueous fluids and may or may not impact solution chemistry. However, stilpnomelane has exchange sites which can affect the relative concentrations of cations such as Ca^{++}, Mg^{++}, Na^+, and K^+.

Because taconite tailings are derived from the Biwabik Iron Formation, reaction of water with tailings might be expected to produce water with a chemistry similar to that of water in tailings basins. However, there are numerous reasons why this might not be the case. In particular, water in the Biwabik Iron Formation circulates through fractures that may have existed for thousands, if not millions, of years. More reactive constituents in the walls of fractures would tend to be depleted over the many years of contact with the water. Tailings, meanwhile, are composed of minerals that have recently been ground to a fine grain size and exposed to oxidizing conditions. The increased surface area associated with grinding would be expected to increase mineral reaction rates and adsorptive capacity of tailings compared to the Biwabik Iron Formation. Oxidation that accompanies the grinding process may also initiate a series of reactions as described below.

Oxidation, acid generation, and acid neutralization

Particular attention in this study is paid to the sources and sinks for dissolved oxygen and carbon dioxide (Table 3). It has long been known that these two gases play a key role in controlling both the extent and rates of reactions between minerals and water. A chain of events is usually required to generate groundwater chemistry, typically beginning with reaction of O_2 and organic matter to generate carbon dioxide and ending with dissolution of minerals to yield dissolved constituents like Ca, Mg, and HCO_3^- (see reactions 1 to 4 in Table 3). If this is the type of reaction sequence that takes place during interaction of tailings and water, then the resulting solutions should have relatively high alkalinity, neutral to slightly alkaline pH, and relatively limited ability to mobilize trace metals such as Mn, Fe, and As. If, on the other hand, CO2 is generated, but carbonate minerals are not present in the tailings, the solutions may become mildly acidic owing to conversion of some of the carbonic acid to bicarbonate ion (HCO_3^-) and H^+ (reaction 5 in Table 3).

Combining reactions 2 and 5 in Table 3 establishes an important link between solution pH and P_{CO2} (partial pressure of CO_2). As shown in Fig. 2, high P_{CO2} promotes low pH at a given HCO_3^- activity. Air has a P_{CO2} of 0.000316 atm, while soils and other media characterized by degradation of organic matter may generate P_{CO2} between 0.01 and 1 atmosphere and pH values less than neutral. Groundwaters commonly have P_{CO2} on the order of 0.01 atmospheres, and resulting pH values that are close to neutral. As shown in Fig. 2, these conditions lead to several meq/kg of HCO_3^-. Thus, by establishing P_{CO2} and alkalinity for a particular environment, we can estimate pH, which is, in turn, a master variable that controls the mobility and solubility of many anions and cations, including Mn, F, Mo, As, and B. .

Although the processes represented by equations 1 through 5 in Table 3 are probably the most important in a majority of situations involving water infiltration, there are several other reactions important in special situations. For example, in places where organic matter is buried, relatively high CO_2 partial pressures can still be generated in the absence of O_2 (anaerobically) as shown in reaction 6. Another series of reactions entirely can occur if sulfide minerals such as pyrite are present. Reaction of pyrite with oxygen generates sulfuric acid (H_2SO_4) rather than carbonic acid (see reactions 7 to 9 in Table 3). In either case, carbonate minerals, if present, will consume the acid (see reactions 8 and 9 for the sulfuric acid case) and the resulting solution may not be highly acidic. If carbonate minerals are absent, however, sulfuric acid can dissociate to form a highly corrosive solution (reaction 10 in Table 3), and lead to acid mine drainage problems.

Finally, siderite is a common carbonate mineral in banded iron formations that creates special problems in terms of geochemical interpretation. Much like reaction 1 in Table 3, siderite oxidation (reaction 11 in Table 3) consumes oxygen and releases CO_2. Unlike reaction 1, however, the amount of CO_2 generated is four times the amount of O_2 consumed and the process potentially occurs in the absence of organic matter. Whether or not siderite oxidation is an important process during reaction of taconite tailings or in the Biwabik Iron Formation depends upon mineral reaction rates which are largely unknown.

One of the goals of the current study, therefore, is to evaluate occurrence and relative importance of reactions shown in Table 3. Although these reactions have been well studied in a number of other environments, they had not previously been studied in reference to taconite tailings and groundwater in the Biwabik Iron Formation.

Carbon isotopes

HCO_3^- is the predominant anion in many waters analyzed in this study, including Biwabik groundwaters, taconite processing waters, and waters in tailings basins. Many studies have shown that most HCO_3^- in natural waters is derived either from decomposition of plant matter (either oxidative or anaerobic) or from dissolution of carbonate minerals (Deines and Langmuir, 1974, Deines, 1980; Reardon et al., 1980; Clark and Fritz, 1997). In many cases carbon isotope measurements can be used to distinguish the relative amounts of HCO_3^- in groundwaters that were derived from each of these sources.

Most plants that grow in northern and temperate regions have $\delta^{13}C$ between –24 and –30 per mil. Degradation of this material under *aerobic* conditions results in little fractionation of carbon isotopes, but there can be a 4-5 per mil isotopic fractionation associated with diffusion of CO_2 along the intense chemical gradients that exist within soil horizons. Thus, CO_2 in soil from northern regions generally has $\delta^{13}C$ of approximately –19 to –30 per mil. There is another carbon cycle that some plants utilize which results in $\delta^{13}C$ values about 10 per mil higher than this range, but these plants usually only dominate in special agricultural settings (corn, sorgham, sugar cane) and in hotter climates (tropical and temperate grass lands). CO_2 generated during *anaerobic* decay of plants has $\delta^{13}C$ that is somewhat heavier than that produced by *aerobic* decay owing to fractionation of the lighter isotope (^{12}C) into more reduced carbon species such as methane and organic acids that form in the absence of an O_2 source. Carbonate minerals such as calcite and dolomite often have $\delta^{13}C$ close to zero because most carbonates in glacial tills and soils are derived ultimately from marine limestones with $\delta^{13}C$ close to this.

Dissolved carbon in groundwaters is almost always isotopically intermediate to plant and carbonate derived carbon owing to the well known reaction:

$$CO_2(\text{plant decay}) + CaCO_3 = Ca^{++} + 2HCO_3^{-}. \qquad (1)$$

Waters percolating into the groundwater system are exposed first to high CO_2 levels in soil horizons owing to respiration and oxidation of organic matter (Deines and Langmuir, 1974; Reardon et al., 1980), but when carbonate minerals are dissolved, the CO_2 from plants and the $CO_3^{=}$ from the minerals are combined to form HCO_3^{-} ions of mixed heritage (Clark and Fritz, 1997). A similar relation for CO_2 and $CO_3^{=}$ holds for dissolution of $(Ca,Mg)CO_3$ and other carbonates (ankerite). Alexander and Alexander (unpublished) have found that most Minnesota groundwaters in limestone dominated regions have $\delta^{13}C$ values between −9 and −13 which suggests approximately half of the dissolved HCO_3^{-} was derived from decay of plants and the other half from limestone as predicted by the stoichiometry of reaction 1 above.

A survey of the literature reveals that carbon isotope ratios in banded iron formations are quite distinct from marine carbonates (Perry et al., 1973; Thode and Goodwin, 1983; Bauer *et al.*, 1985). The chief sources of carbon in banded iron formations are the carbonate minerals ankerite and siderite. The $\delta^{13}C$ values for carbonate minerals found in banded iron formations are highly variable, ranging from approximately −3 to −17, but the variability exists at a fine scale and an average value of approximately −10 can be used to represent $\delta^{13}C$ of the carbonates as a whole. The negative values are almost certainly related to the involvement of organic matter in the early diagenesis of the iron formation sediments. Degradation of organics promoted the reducing conditions needed to convert ferric iron in the original sediments to ferrous iron common in the taconite ore (e.g., in magnetite, siderite, and stilpnomelane). Thus, siderite ($FeCO_3$) has somewhat lower $\delta^{13}C$ than ankerites in banded iron formations. Perry et al (1973) also observed a small but significant organic carbon component in the whole rock specimens from the Biwabik Iron Formation with narrowly ranging $\delta^{13}C$ values of approximately −33.

Groundwaters evolving according to reaction 1 above, and involving carbonate minerals from the Biwabik Iron Formation, would be expected to have $\delta^{13}C$ in the approximate range -14 to −20 (assuming an average value of −10 for $\delta^{13}C$ of Biwabik carbonates and −19 to −30 for CO_2 from decay of local plants). To our knowledge, $\delta^{13}C$ for inorganic carbon in Biwabik groundwaters has only been measured once and in that case water from the Scranton well in Hibbing was found to have a $\delta^{13}C$ value of −15.1 per mil (Alexander and Alexander, 1988). This $\delta^{13}C$ value suggests that HCO_3^{-} in these well waters could have been derived approximately half from a mixture of plant-derived CO_2 and half from Biwabik formation carbonate minerals.

Hydrogen and oxygen isotopes

Hydrogen has two stable isotopes (^1H and ^2H or Deuterium (D)) and one radioactive isotope (^3H or tritium) that can be measured in conjunction with oxygen isotopes to evaluate the age and source of groundwaters (Turner et al, 1984; 1987; Clark and Fritz, 1997).

Abundant tritium, is indicative of water infiltration after 1950's nuclear testing while a lack of tritium suggests the waters infiltrated prior to this period.

When stable isotopes of hydrogen are measured along with oxygen isotopes in water that falls as snow or rain, a linear correlation emerges which has been come to be known as the meteoric water line. The isotopic compositions of water and oxygen can then be affected by such processes as evaporation and mineral/fluid interaction. Alexander and Alexander (1997) determined that rainfall and evaporation play dominant roles in controlling the hydrogen and oxygen isotopic characteristics of water in pits and groundwaters near Virginia, Minnesota. Hydrogen and oxygen isotopes were analyzed in the present study to help determine the general relationships between precipitation, storage, and infiltration in the Biwabik Iron Formation regions west of Virginia, Minnesota.

Water Quality Limits

A number of water methods exist to analyze water quality including but not limited to HRL's (Human Risk Limits) and MCL's (Maximum Contaminant Levels). HRL's for Mo, As, and B are 30, 50, and 600 µg/kg, respectively. No HRL was found for F. MCL for F is 4 mg/kg, and a secondary standard for F, relating to yellowing of teeth, is 2 mg/kg. The Minnesota Department of Health suggests that water with 1.3 mg/kg Mn can be safely consumed on a regular basis (MDOH, 1998). Mn concentrations above approximately 50 µg/kg can be problematic for non-health related reasons.

Results and Discussion

Biwabik Iron Formation groundwater

Compositional trends

The chemical composition of waters in the Biwabik Iron Formation are shown in Table 4 and plotted in Fig. 3. Alkalinity (HCO_3^-) in these groundwaters ranges from approximately 3 to 4 meq/kg and is balanced mostly by Ca and Mg. Na, K, and Cl concentrations are usually low. SO_4 is locally present at concentrations ranging up to 1 mmol/kg. Measured pH values are near neutral to slightly alkaline. Geochemically, these waters can be interpreted as having been derived by a combination of oxidation and dissolution processes whereby CO_2 is generated and carbonate minerals are dissolved by reactions similar to those shown in Table 3. SO_4 is likely added during oxidation of sulfide minerals which are present in small amounts in some parts of the iron formation (e.g., Morey, 1992).

Water source

Abundant tritium was found in 8 of the 11 wells analyzed (Table 4), suggesting that much of the infiltration of water took place after the 1950's. The recent recharge for these wells suggests hydraulic communication to surface waters in the area is relatively direct. Low or undetectable tritium concentrations were found in three of the wells. Water from these wells (Keewatin well #1 and from both of the Calumet wells) must have infiltrated the Biwabik Iron Formation more than 45 years ago.

δD and $\delta^{18}O$ for wells sampled in this study are presented in Table 4 and plotted in Fig. 4. δD values we report are not consistent with past measurements obtained for these and other wells in the area (Walsh, 1999). Because of this, we have refrained from interpreting the δD values in our study, but we report the values for completeness. $\delta^{18}O$ values for many of the wells are close to those of local rainfall (meteoric water) which typically range between −11 and −12 ‰ in this part of Minnesota (Alexander and Alexander, 1997; Walsh, 1999). Waters with $\delta^{18}O$ above this value include those from Keewatin #2, Nashwauk #4, and Hibbing's Scranton well, and also possibly water from Mt. Iron and Kinney #2 wells. Waters with elevated $\delta^{18}O$ relative to local meteoric values may have experienced evaporation prior to infiltration as the evaporation process is one of the best ways of enriching ^{18}O (and D) in low temperature/meteoric systems (Turner *et al.*1984, 1987). None of the waters that infiltrated the ground prior to nuclear bomb testing appear to have been affected by an evaporation process as their waters have the lowest $\delta^{18}O$ values we found.

Alexander and Alexander (1997) defined an evaporation trend for water in pits and lakes in the area around Virginia, Minnesota (Fig. 4). Their data form an evaporation trend revealing increasing $\delta^{18}O$ and δD with increasing evaporation. The largest amount of evaporation in the Virginia, Minnesota area occurred in shallow waters from the Minorca Pit and resulted in a $\delta^{18}O$ shift of approximately +2.5 ‰. Our data suggest comparable shifts in $\delta^{18}O$ values for Nashwauk 4, and smaller shifts for the other well waters. Thus, much of the more recent recharge to municipal water supplies in the Biwabik Iron Formation in this region appears to occur through pits. Qualitatively at least, wells located closest to pits (Keewatin #2, Nashwauk #4, and Hibbing's Scranton well, Mt. Iron, and Kinney #2) produce waters that appear most directly affected by evaporation processes. Waters from wells located far from pits probably infiltrated before the current extensive mine-pit system existed and these waters, were more likely to have penetrated the ground directly without first being stored in a pit.

Major elements

The reactive minerals present in rock contacted by water in the Biwabik aquifer are similar to those in tailings. Consequently, the same reactions that can be shown to affect groundwater chemistry will likely affect the chemistry of water entering the aquifer from pits filled with taconite tailings. Geochemical speciation calculations were performed on groundwaters we sampled in order to determine saturation levels for minerals present in the formation (Fig. 5) and to evaluate the approximate P_{CO2} range that prevails within the Biwabik Iron Formation (Fig. 6).

Saturation level is represented here in units of "Log Q/K" which is zero for waters at saturation with respect to a mineral, positive if supersaturated, and negative if undersaturated. The further Log Q/K is from zero, the more undersaturated or supersaturated the water is with respect to that mineral. Gross undersaturation suggests that the mineral is either not present or slow to dissolve, while gross supersaturation is an indication that a mineral is slow to precipitate.

Most Biwabik groundwaters studied here are relatively close to saturation with respect to Ca and Mg carbonate minerals (calcite and dolomite). This is not particularly surprising because ankerite[(Ca,Fe,Mg)CO_3] is a common mineral in the Biwabik Iron Formation and Ca and Mg concentrations are both high in Biwabik formation groundwaters. A little more puzzling is the fact that most of the waters appear to be distinctly undersaturated with respect to siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$). If siderite or rhodochroiste were present and reacting with waters in the Biwabik Iron Formation, these waters should have Fe and Mn concentrations significantly higher than observed. Only the waters from Kinney well #2, and waters that infiltrated prior to bomb testing (from wells in Calumet and Keewatin #1) appear to be close to saturation with respect to siderite. Most of the waters are highly undersaturated with respect to Fe-silicate minerals (minnesotaite and greenalite) even though these minerals are abundant in the Biwabik Iron Formation. This suggests that these minerals are either slow to react or not present in the fractures where the water is flowing.

Most of the waters in the Biwabik Iron Formation have P_{CO2} close to 0.01 atm, which is quite similar to that found in soil and groundwaters in many other regions of the US (See Drever, 1997; Stumm and Morgan, 1996; or Langmuir, 1997). Of potential significance are the lower P_{CO2} levels (between 0.001 and 0.01 atm) for waters from the three wells that lack tritium. Although the dataset is small, it suggests that P_{CO2} decreases gradually from a high of 0.01 atm upon infiltration, to a low of 0.001 atm during long term exposure of groundwater to minerals in the Biwabik Iron Formation. Regardless, the high Ca, Mg, and HCO_3^- in these fluids demonstrates water chemistry is dominated by CO_2 generation and ankerite dissolution (reactions 1 and 4 in Table 3).

Si concentrations are consistent with dissolution of fine grained silica which is also abundant in the formation. All of the groundwaters are supersaturated with respect to the more crystalline forms of silica (e.g., quartz and tridymite). The waters are also supersaturated with fine-grained silica (chalcedony). Although the solutions are close to saturation with respect to cristobalite, this high temperature phase is likely not present in the Biwabik Iron Formation. It is more likely that the solutions are controlled by saturation with respect to a SiO_2 phase whose crystallinity is intermediate to chalcedony and amorphous silica.

Trace elements (Mn, F, Mo, As, B)

Trace element data for waters in the Biwabik Iron Formation are presented in Table 4 along with the other major element data.

Manganese concentrations for Biwabik groundwaters that we sampled ranged from 0.0 to 0.69 mg/kg. The highest values approach those required for saturation with respect to rhodochrosite. This is a good indication that rhodochrosite saturation can be used to approximate maximum Mn concentrations in Biwabik aquifers (see Mn section below).

F concentrations average 0.28 mg/kg. Waters from Nashwauk appear to contain anomalously high concentrations of this element (0.78), but even this value is far below what would be considered normal for fluorite saturation. The source of the anomalously high F, in this case, is unknown.

Mo and As concentrations are all very low, approaching the limits of detection for the ICP-MS. B concentrations are also relatively low, but appear to be measurably higher in Calumet wells than in the other wells. These values are only 100 μg/kg, which are far below any drinking water standard values.

Tailings basins

Major elements

The averaged major element chemistry of water in tailings basins is plotted in Figs. 7 and 8 and reported in Table 5. A number of trends are apparent.

First, a comparison of the chemistry plotted in Figs. 7 and 8 to that plotted in Fig. 3 reveals that waters in tailings basins have significantly higher concentrations of Cl, SO_4, HCO_3, Mg, and Na than Biwabik groundwater. This is not surprising as the grinding and oxidation of iron ore leads to significant dissolution of minerals and can increase the concentrations of dissolved constituents.

Second, it is apparent in Fig. 7 and 8 that waters discharged into tailings basins have generally higher concentrations for nearly all elements when compared to water stored within the tailings basin. This is a clear indication that dilution by rainfall, snowmelt, or surface runoff dominates evaporation during storage of water in tailings basins. This dilution is most pronounced at National and Inland and less evident at LTV. The amount of dilution at a given tailings basin depends on the ratio of nonplant basin inputs to the plant discharge. Nonplant basin inputs include the product of the net precipitation (precipitation-evaporation) and the total catchment area draining to the basin plus any other make-up water input (e.g., due to pumping from wells or surface reservoirs). Large amounts of dilution at Inland Steel's tailings basin results from the relatively large catchment area at this site (Jakel and Lapakko, 1999).

The final general trend that is shown in Figs. 7 and 8 and in Table 5 is that the concentrations of many of the major elements found in basin waters; HCO_3, Ca, and Mg, in particular, increase during seepage of the water from the basin (compare "basin" and "reacted" waters). This indicates that fluids react with minerals during seepage from the basin. The chemical changes occurring at each basin, however, are quite variable and depend on site-specific conditions. At National, for example, Ca and HCO_3^- increase during seepage of water from the basin, while Fe and Mn increase at Inland. At LTV, where oxidized sulfidic waste rock was deposited in the tailings basin, large gains in $SO_4^=$ accompany similarly large increases in HCO_3^-, Ca, and Mg.

Trace elements (Mn, F, Mo, As, B)

Manganese concentrations of waters discharged to and stored in tailings basins are relatively low (Fig. 9) owing to limited solubility of Mn minerals under oxidizing conditions. However, Mn concentrations up to 7 mg/kg were observed in waters collected from wells at the toe of Inland's tailings basin dike and over 1 mg/kg Mn was observed in water collected from a similar location relative to National's tailings basin dike. The 7 mg/kg values are much higher than the 0 to 0.3 mg/kg typically observed for tailings pore fluids in experiments. We will show later, in the carbon isotope section of this paper, that high Mn (and Fe) concentrations in wells and seeps at Inland are almost certainly related to reactions occurring in the substrate beneath the basin. In particular, we found that anaerobic decay of vegetation beneath the basins is supplying CO_2 and generating reducing conditions (see carbon isotope section below).

Fluoride concentrations are elevated to high levels in some tailings basins, exceeding 10 mg/kg in a few of the samples collected from the tailings discharge pipe at LTV steel (Fig. 10). For each site studied, water within the basins has less F then water discharged from the plant. That changes in F are similar to the relative changes in Cl suggests that most of the change in F is the result of dilution within the basin. Reactions occurring in waters seeping from LTV and National's basin result in decreases in F concentration, while little change was observed in waters seeping from Inland's tailings basin. Computer calculations reveal that this element adsorbs to the surfaces of Fe-oxides more readily at near neutral pH than it does at mildly alkaline pH. The lower pH and higher Ca in waters seeping from basins promote both adsorption on to oxides and precipitation of CaF_2 when water reacts with tailings. The F/Cl and F/Br ratios of waters stored in Inland's tailings basin are less than water discharged to the tailings basin, suggesting a mechanism exists to remove F within this particular basin. Water flows through an interior dike in this basin, and some of the F may be removed during interaction with minerals in this dike.

Molybdenum concentrations in tailings basins are highest at the plant discharge sites (Fig. 11). As is the case for most elements, Mo concentrations are diluted by precipitation and local runoff during storage in the basin Mo concentrations are further decreased in waters seeping through the tailings basins. $MoO_4^=$ is adsorbed more effectively at near neutral pH levels than it is at the mildly alkaline pH of raw taconite processing waters (8.5 to 9). Thus, the near neutral pH that evolves in waters seeping through tailings basins accounts for the observed low Mo concentrations.

Arsenic concentrations are highest at LTV and Inland (Fig. 12). Unlike other elements, arsenic concentrations do not decrease significantly during storage of water in the basin and in one case, arsenic actually increased during storage. At LTV, the time-averaged concentration of arsenic in waters stored in the basin was 11 µg/kg while that of waters discharging from the plant into the basin was only 4 µg/kg. The specific reason for this is unclear, but may be related to oxidation of minor sulfides within the basin. Despite the fact that concentrations of conservative elements like Cl and Br decreased by 10% owing to dilution from precipitation, $SO_4^=$ concentrations actually increased from 116 to 120 mg/kg within the basin.

Boron concentrations in waters discharging to tailings basins ranged from values under 100 µg/kg at National to an average of 349 µg/kg at LTV (Fig. 13). This element is diluted by rainfall occurring with the basin. There is a slight decrease in B that takes place in waters seeping from tailings basins at Inland and National, but a conspicuous increase in waters seeping from LTV's tailings basin. The increase at LTV indicates a source for B is present in LTV's tailings.

Carbon isotopes in tailings basins

The HCO_3^- in water in tailings basins has $\delta^{13}C$ ranging from –5.82 at National to –8.62 at LTV. These values bracket the value for atmospheric CO_2 (-7) although it is likely the HCO_3^- in the basins was derived from a complex mixture of carbon derived from a variety of sources including HCO_3^- in makeup water, CO_2 in air, CO_2 derived from oxidation of organic reagents used in mineral processing, and $CO_3^=$ derived from dissolution of carbonate minerals. Of primary interest to the present study is that the water from seeps and wells at the edge of tailings basins has chemistry and isotope composition distinct from that of water held in the basins. This indicates that significant reaction takes place as water migrates from the inner water reservoir to the sampling location at the outer edge of the basin.

The isotopic and chemical changes in the dissolved carbon can be used to determine the predominant types of reactions that affected the overall chemistry of waters seeping from the basins. However, because some HCO_3^- is already present in water as it flows into tailings, this component must be subtracted from the carbon inventory of the reacted fluid in order to determine the isotopic composition of the added carbon. Detailed discussion of equations and calculations needed for this are provided in Appendix I and results are provided in Table 6. Water seeping from the basins experienced 35 to 52% increases in the total inorganic carbon concentrations, and the carbon that was added had a bulk $\delta^{13}C$ value ranging between –10.8 and –17.6, depending on which basin was studied. Because reactions occurring at each basin were found to be unique, however, systematics for each system are discussed individually.

Inland: Water seeping through the tailings basin impoundment at Inland had the smallest percentage change in total carbon and the largest change in $\delta^{13}C$. The addition of carbon in

Inland's case was not accompanied by a significant change in alkalinity (HCO_3^-), indicating that most of the carbon was added as CO_2 rather than as $CO_3^=$. Furthermore, the $\delta^{13}C$ of the added carbon at Inland was approximately -18 which suggests this CO_2 could have been supplied from decay of plants under partially anaerobic conditions.

One clue to a possible source of these fluids is provided by hydrologic observations at the W-5 and W-6 well sites. Although these wells were developed very close to each other, water in the casing from the deeper of the two wells (12 ft deep) stood approximately two feet higher than water in the casing from the shallower well (7 ft deep). This indicated a strong vertical pressure gradient which would prevent water from flowing downward in the area of the wells. Water from the basin was apparently moving laterally beneath the dike, and possibly leaking back into the tailings (upward) at the toe of the dike.

Another possible clue is provided by the conspicuous lack of Ca and Mg increases in the seeps and wells compared to water stored in the basin at Inland. Ankerite is a common mineral in tailings, and was found to be present in the tailings collected near the well locations (Scanning Electron Microscopy). This mineral reacting with waters having a high influx of CO_2 from plants should result in elevated alkalinity and induce high Ca and Mg concentrations in the resulting fluid. This is the type of reaction observed at all other sites and in experiments performed with taconite tailings in the present study. That there was little or no increase in alkalinity in waters flowing from the tailings basin at this site suggests that the water in these wells did not react with the tailings after CO_2 was added to the water. If it had, we would have expected high Ca and Mg concentrations to be found in the well waters.

Taken together, the carbon isotope, hydrologic, and chemical data suggest that the anomalous Mn in Inland's well waters may be a local phenomena related to burial of organic carbon during tailings basin construction and also to an absence of Ca and Mg carbonates in the underlying strata. High partial pressures for CO_2 are encountered during seepage of tailings water into organic rich zones and the later dissolution of Mn- and Fe-oxides that are so common in most environments, results in high Mn and Fe concentrations in the well waters at the edge of the basin.

National: HCO_3^- in well 12 waters at National has a $\delta^{13}C$ value that is also significantly lower than the value for HCO_3^- in the basin, but the carbon that was added, in this case, has an isotope ratio of −12.8. This is much "heavier" than the −18 value of carbon added to water seeping from Inland's tailings basin. Furthermore, chemical data reveal, that much (36.4%) of the CO_2 at National must have been added originally as the carbonate species ($CO_3^=$) rather than as molecular CO_2. It is not entirely surprising, therefore, that isotopic data suggest a mixture of carbon sources for the added carbon at National. Fig. 14 shows how the carbon isotope signature of the carbon added at National could be interpreted as a mixture of carbon from marine carbonates and from the decay of plants.

As was the case for Inland, the well sampled at National was developed within the sediments (tills) that underlie the tailings basins. This till may have been overlain by plant material prior to construction of the tailings impoundment, but plant material is commonly incorporated into the till itself (Keller, 1991; Keller et al., 1991; Simpkins and Parkin, 1993). The carbonate minerals that dissolved in the process have $\delta^{13}C$ values more consistent with marine limestones than with Biwabik Iron Formation carbonate minerals. The Ca concentrations increased in the solution much more than Mg concentrations did. This suggests calcium carbonate was reacting with the water seeping from the basin, rather than the more magnesium rich carbonate minerals that dominate in the Biwabik Iron

Formation. Waters reacting in experiments with tailings or in the Biwabik Iron Formation usually exhibit near equi-molar increases in Ca and Mg concentrations.

Thus, as was the case at Inland, water seeping from National's tailings basin also appears to be influenced strongly by reactions taking place in material beneath the tailings basin. In National's case, however, there appears to be sufficient limestone present in the glacial till material to limit the leaching of Mn and Fe that were observed at Inland.

<u>LTV:</u> The case at LTV is unique owing to the apparent presence of sulfide minerals in the tailings at this site. Any oxygen penetrating the tailings at LTV potential reacts with sulfide minerals to produce sulfuric acid which can react immediately with carbonate minerals in tailings to generate high alkalinity, Ca, and Mg concentrations. Because $SO_4^=$ concentrations increased to high levels in these waters, and because both Ca and Mg increased, rather than just Ca, the chemical data are strongly indicative of reactions having taken place within the tailings at this particular site. That the −10.8 per mil value for $\delta^{13}C$ of the added carbon is similar to the average $\delta^{13}C$ of carbonates in the Biwabik Iron Formation, supports this interpretation.

Snively Pit pore fluids

Chemistry of water from the Snively Pit is presented in the appendix VII. Both pore (well) and surface (sump) water are of similar types with very high SO_4 and high alkalinity. Both waters have, therefore, apparently been exposed to oxidized sulfide minerals, and are most similar, in this regard, to water from the USX tailings basin (Lapakko and Jagunich, 1991; Berndt and Lapakko, 1997a,b). The dissolved concentrations of trace concern elements (As, Mo, B, and F) are extremely low, while Mn concentrations are close to 2 mg/kg.

Several chemical indicators suggest that the pore fluid is composed of surface water that has infiltrated the tailings. In particular, differences that do exist in the surface and pore waters in the Snively Pit are consistent with reactions that generally take place within tailings. For example, $SO_4^=$, HCO_3^-, Ca, and Mg concentrations are all higher in the pore fluid compared to water at the surface, while K, Na, Rb, and Cs, are all less. These chemical changes are exactly what would be predicted if the surface water from the pit were to react with tailings in a closed environment (see above, and Berndt and Lapakko, 1997a).

However, fluids currently reacting with tailings in the Snively Pit are atypical of any waters that we collected from Biwabik Iron Formation aquifers or of waters that result from tailings/water interaction (except at USX, see Lapakko and Jagunich, 1991 and Berndt and Lapakko, 1997a). We believe that the unusual chemistry is a local by-product of the extensive mining and mineral processing activities that have occurred in the vicinity of the Snively Pit. Since the area around the Snively pit has been actively mined for many years, the precise source of the high $SO_4^=$ fluids is not known, but probably related to sulfide oxidation effects.

Column experiments

Process water/tailings interaction

The results from the initial one-year experiments with process waters were presented by Berndt and Lapakko (1997 a,b), but the chemical data for those experiments are included in the appendix. During this time period, alkalinity and concentrations of Mg and Ca increased substantially in the process water/pore fluids, while the concentrations of

Na and K decreased. F, Mo, and As concentrations generally decreased, while B and Mn concentrations increased. Reduction in pH lead to adsorption of F, Mo, and As from the process waters, dissolution of Mn-carbonate and ankerite, and release of minor B from the tailings. The increased Ca from dissolution of ankerite may have helped to precipitate F as CaF_2 in tailings from LTV. The full results are discussed in detail by Berndt and Lapakko (1997).

The mineralogic and chemical compositions of the tailings used in experiments are presented in Tables 7 and 8, respectively. Quartz dominates, but clay minerals (stilpnomelane, minnesotaite, talc), and carbonates (siderite, ankerite) are also abundant. Non-magnetic oxides are far more abundant in the tailings from Inland (18% hematite and goethite) and National (11%) than in tailings from LTV (3%). LTV ore which is derived partly from metamorphosed Biwabik Fe-formation, contains the metamorphic minerals cummingtonite and Fe-hornblende. The grain size of tailings from LTV (33 wt% passing through a 500 mesh sieve) is significantly greater than that of tailings from the other two companies (55 wt% passing through the same sieve).

Groundwater/tailings interaction

Major element chemistry

In these experiments, oxygen-free groundwater with a P_{CO2} of 0.01 atm was injected into tailings that had been previously aged with the original process waters as a pore fluid for a period of one year. In each case, the pre-existing pore fluid had much higher total dissolved solids than the groundwater being injected. The most conspicuous differences between the groundwater and initial pore fluids were in concentrations of dissolved HCO_3^-, Cl^-, Mg^{++}, and Na^+. The major element composition of water that existed before and after injection, and during the groundwater experiments is shown in Figs. 15 through 17.

Although the chemistry of water changed gradually throughout the experiments, the chemical trends suggested that the most important process was a gradual mixing between the injected groundwater and the initial pore fluid. Even a generally non-reactive component such as Cl, for example, decreased to low levels upon injection and rebounded to values approaching the original Cl concentrations during the course of each experiment. This type of result was not entirely unexpected because the permeability of tailings is heterogeneous and some "streaming" (short circuiting) could not be avoided during the injection of the groundwater. In effect, the groundwater that was injected would seek the routes of highest permeability through the column and avoid the least permeable zones. After injection of groundwater was stopped, water remaining in the low-permeability zones was free to exchange diffusionally with water in the high-permeability zones. This resulted in the apparent mixing of dissolved constituents. Because flow rates in these experiments were very slow (e.g., <50 mls/wk), the amount of water passing through the column during the entire experiment was less then one pore volume. Thus, the longer the experiment progressed, the more diffusive mixing that took place.

Noticeably lacking during the intrusion of groundwater into our columns, however, is any significant reaction between the tailings as would be indicated by increases in HCO_3, Ca, or Mg above values found in the original pore fluid. This lack of reaction is believed to be related to the lack of dissolved O_2 in the injected groundwater. As shown in the series of reactions provided in Table 3, oxidation of organic carbon and sulfide minerals leads, respectively, to production of carbonic and sulfuric acids which lead, in turn, to increased dissolution of Ca and Mg carbonates.

Trace elements (Mn, F, Mo, As, B)

Mn concentrations for water in equilibrium with $MnCO_3$ are inversely proportional to HCO_3^- and directly proportional to P_{CO2} (see *Relevance to In-Pit Taconite Tailings Disposal: Manganese* section below). Manganese concentrations in groundwater experiments (Fig. 18) quickly reached high concentrations, up to 0.8 mg/kg in experiments, most likely as a response to the high P_{CO2} and relatively low alkalinity of the injected groundwater ($P_{CO2}=0.01$). As experiments progressed, however, the concentrations of Mn decreased owing to the higher alkalinity and lower P_{CO2} induced by mixing with the initial pore fluid.

F concentration in the groundwater experiments (Fig. 19) quickly decreased during injection of the groundwater, but then rebounded gradually with time. As was the case for major elements, this pattern is related to mixing of the two pore fluids rather than to reaction with minerals. The higher the F concentration in the initial pore fluid, the higher the concentration of F in the mixed fluid later.

Mo concentrations dropped immediately to low values during injection of the groundwater (Fig. 20), but the concentration of this element rebounded quickly to values intermediate to the initial and injected pore fluid compositions. The mixing and/or slight mobilization that occurred resulted in Mo concentrations below 10 μg/kg in all experiments. This indicates that groundwater penetration into tailings does not cause large release of adsorbed Mo from tailings.

Arsenic concentrations in experiments also remained very low throughout groundwater experiments (Fig. 21) indicating that conditions never approached the $As(OH)_3$ stability field. $As(OH)_3$ is a dissolved aqueous species that can form under moderately reducing conditions and near neutral pH. The neutral charge of this species causes it to bond less strongly to Fe-oxide surfaces than other arsenic species (which are all charged). Prior to this experiment, it was thought that conditions needed to mobilize arsenic might be met if groundwater intruded into tailings, but this is apparently not the case.

Boron concentrations in experiments (Fig. 22) also appear to reflect a gradual mixing between the injected ground water and the initial pore fluid.

Rainwater/tailings interaction

Major element chemistry

In the rainwater/tailings experiments, reacted process waters were replaced by deionized water to simulate infiltration from local runoff. Detailed flow records are shown in Fig. 23. Perhaps the most remarkable aspect of the results from these experiments (Figs. 24 through 27) is the demonstrated ability of minerals in tailings to maintain high concentrations of dissolved salts in fluids they react with. Conductivity of the water passing through the columns decreased gradually through time, but not nearly as fast as would be expected for simple rinsing. Even after six pore volumes of fluid had passed through the columns, the conductivity of the waters remaining in the column were close to 300 μmho and this was long after non-reactive elements like Cl and Br^- had decreased to concentrations below detection levels.

The major reason for the elevated conductivity throughout these experiments is that Ca, Mg, and HCO_3 were being mobilized (Figs. 25 through 27). More Mg was generated in the early portions of the experiments than Ca, but the ratio of Ca to Mg increased as time evolved. Na was also important early in the experiments. The high HCO_3^- concentrations in these experiments and predominance of Ca and Mg as the major dissolved ions indicates that carbonate minerals are the most reactive components in tailings. The changing distribution of Ca/Mg/Na throughout the experiments indicates that cation exchange processes are also important. Mg and Na are elevated compared to Ca, early in the experiments, probably reflecting the fact that these elements were disproportionately represented among the cation exchange sites in clay minerals. Ca and Mg released from carbonate dissolution dominate later when excess Mg and Na are rinsed from the system .

The alkalinity in each case was appreciable. When National's tailings were exposed to the oxygenated rainwater, for example, the alkalinity of water penetrating the column increased from 0 to 4 meq while that in experiments involving tailings from Inland and LTV increased from 0 up to 7 meq. The low Cl concentrations in the reactant fluids from these experiments rule out mixing to account for the large increase in alkalinity and dissolved cations. It is clear, therefore, that much reaction takes place when taconite tailings interact with oxygenated water. This is in distinct contrast to what was observed during interaction of tailings with groundwater. Reaction with rainwater gradually decreased with the passage of more water through the column, but considerable Ca, Mg, and HCO_3 concentrations were generated even at the end of the experiment. The reduced rate of reaction may reflect depletion in the amounts or reactive surface areas of one or more of the primary reactants.

Trace elements (Mn, F, Mo, As, B)

Manganese concentration that evolved during rainwater/tailings experiments (Fig. 28) ranged between 0.200 and 0.300 mg/kg, close to the levels that evolved in groundwater experiments. The similarity in values suggests similar mineral buffering reactions occur in both cases. One possibility is that a Mn-carbonate mineral (rhodochrosite) controls the solubility of Mn in these experiments. The similar values for Mn concentrations would then be related to the fact that P_{CO2} and alkalinity are similar in the two types of experiments.

F concentrations remained somewhat elevated during the initial portions of experiments, long after Cl had rinsed from the column (Fig. 29). If F behaved conservatively, like Cl and SO_4, in these experiments, one would expect high levels to be limited to the first one or two pore volumes when Cl and SO_4 were still present. That elevated F concentrations persisted late into the experiments suggests that a source of mobile F existed in the tailings. Two possibilities include fluorite (CaF_2) and adsorbed F^- ions. This will be discussed in more detail later in a separate section on F mobility.

Mo concentrations increased rapidly up to 60 µg/kg in experiments with tailings from LTV, and remained elevated above 10 µg/kg throughout the rest of the experiment (Fig. 30). Thus, this element which is generally adsorbed to the tailings during reaction with process waters (Berndt and Lapakko, 1997a,b), is released during infiltration by dilute water. Computer simulations of the dilution process reveal that Mo is liberated more readily than either As or F when a concentrated fluid in equilibrium with the mineral surfaces is replaced by dilute water. This is consistent with what happened in the present experiments and suggests that some remobilization of Mo can be expected when a pit filled with tailings is infiltrated by dilute water.

Arsenic is not mobilized significantly by infiltration of dilute water (Fig. 31). This is also consistent with computer simulations which indicate relatively specific Eh and pH conditions are required to mobilize As.

Like F, B does not rinse as effectively as either Cl or $SO_4^=$ from the columns during infiltration by dilute water (Fig. 32). Measurable concentrations of B were always found in experiments, but the highest B concentrations involved reaction with tailings from LTV. We suspect that B is also adsorbed to tailings, but could not simulate the desorption process using computer models.

Carbonic acid source

In rainwater experiments there is no decaying plant source for carbon, so possible HCO_3^- sources are limited to carbonate minerals and organic carbon already present in the Biwabik Iron Formation and possibly to oxidation of recalcitrant organic reagents that may have been adsorbed to mineral surfaces during mineral processing. The −21 to −22 values measured for $\delta^{13}C$ of HCO_3^- in these experiments are consistent with approximately half of the HCO_3^- having been generated from oxidation of organic carbon present in the Biwabik Iron Formation and half from dissolution of coexisting carbonate minerals (Eq. 1, Fig. 14).

Because the isotopic composition of the organic chemicals used in mineral processing are unknown, we cannot fully eliminate such compounds as sources for some of the HCO_3^- in these waters. In this case, however, the tailings were rinsed gradually with approximately 6 to 7 pore volumes of oxygenated water over a period of two years prior to the carbon isotope measurements. It is expected that any organic compounds would have degraded to CO_2 during this time and been removed as dissolved HCO_3^-. The fact that $\delta^{13}C$ values for dissolved HCO_3^- are similar in all experiments even though a different series of processing chemicals were used in each plant, suggests to us that the synthetic compounds are not involved in the reactions occurring in these experiments, at least during the interval when the carbon isotope samples were collected. A further isotope study, involving measurement of carbon isotope values of reagents and of HCO_3^- earlier in the experiments might help to determine exactly when organic reagents degrade to CO_2..

Relevance to in-pit tailings disposal

Manganese

A large amount of experimental and field data collected in this study now suggest that manganese concentrations in the Biwabik Iron Formation ground waters and in tailings pore fluids are limited by saturation with respect to $MnCO_3$ (Berndt and Lapakko, 1997 a,b). Alkalinity of waters in taconite tailings basins and in Biwabik Iron Formation aquifers, provided in the appendices at the end of this report, can therefore, be combined with estimates of P_{CO2} to place upper limits on the levels of dissolved Mn that can be expected for tailings pore fluids in a variety of environments.

The procedure involves first calculating the equilibrium constant for the reaction:

$$H_2O + MnCO_3 + CO_2 = Mn^{++} + 2HCO_3^- \qquad (2)$$

and then substituting appropriate values for CO_2 and HCO_3^- (alkalinity). Results for the calculations are displayed graphically in Fig. 33. Alkalinity of water in the Biwabik Iron Formation is typically between 150 and 250 mg/kg $CaCO_3$ and P_{CO2} is buffered at levels between 0.01 and 0.001 atmospheres. Thus, Mn concentrations greater than 1 mg/kg are not expected to be found in waters in the Biwabik Iron Formation.

High Mn levels can be found, however, when another process is involved that increases P_{CO2} without increasing alkalinity. Anomalous Mn at Inland's tailings basin are a result of locally elevated CO_2 levels resulting from decay of buried plant matter. Mn levels in the well at the Snively pit tailings disposal site ranged between 1 and 2 mg/kg. High

SO_4 in these waters suggests sulfide oxidation may have played a role in generating slightly elevated CO_2 levels and Mn in those pore fluids.

Fluoride

From a geochemical perspective, the behavior of fluoride in process waters has been particularly difficult to quantify. A number of thermodynamic constants have been reported in the literature for fluorite solubility (Brown and Roberson, 1977; Hem, 1985; Wolery, 1992; Johnson et al, 1991), and water in LTV's basin can be calculated to be either supersaturated or undersaturated with respect to CaF_2 depending on which thermodynamic constant is used (Fig. 34). It appears, however, that fluorite must be precipitating from water seeping through some tailings, as very high Ca seeps from LTV's tailings basins have much lower F concentrations then the lower Ca waters stored in the basin. Similar observations of high F in a basin and high Ca and low F in associated seeps were found previously by Berndt and Lapakko (1997a,b) at USX-Minntac. Ca added to water from carbonate dissolution during tailings/process water interaction, combines with F in the water to make CaF_2.

The data from LTV (the site with the highest F concentrations) all appear to fall intermediate to literature values for fluorite solubility. In the basin, where Ca concentration is high, the samples plot closer to the highest solubility limits available in the literature. In LTV seeps, however, where Ca concentrations are relatively high, the samples plot closer to the lower solubility limits. Thus, no one value can be applied to predict F solubility in all settings.

An empirical fitting of our own data for LTV samples with Ca concentrations less than 80 mg/kg suggest that the following calculation might be applied as a reasonable maximum estimate for fluorite solubility in taconite tailings disposal sites:

$$[M_{Ca++}][M_{F-}]^2=8.91 \times 10^{-11} \qquad (3)$$

where $[M_{Ca++}]$ and $[M_{F-}]$ are the concentrations (in mol/kg) of Ca and F, respectively. If Ca concentrations are greater that 80 mg/kg, the F concentrations will be less than predicted by this equation.

Application of equation 3 to predict fluoride mobility required a means to assess $[M_{Ca++}]$. One approach might be to assume stoichiometric dissolution of fluorite, whereby $[M_{Ca++}]$ would then be equal to $2x[M_{F-}]$. Under these conditions, F concentrations would be 8.5 ppm. Alternatively, one could use empirical or calculated data to estimate $[M_{Ca++}]$, and apply equation 3 directly.

Although equation 3 can be applied to operations that have high Ca and F levels or even to evaluate fluorite precipitation in processing lines where Ca and F are elevated (see Berndt and Lapakko (1997a)), it is not well suited to predicting the long term low level release of F from tailings deposited in a pit. At Inland and National, for example, the concentrations of Ca and F in basin waters fall well below the fluorite saturation values implied by equation 3. It seems reasonable to conclude, therefore that most of the F in these basins is present as adsorbed F, rather than as the mineral fluorite. Even at taconite processing sites like LTV, where fluorite is apparently precipitating in pore fluids within the tailings, the concentrations of F will remain high long after fluorite is dissolved due to desorption of F from the tailings. In such cases, it is more appropriate to use desorption criteria to estimate F release from tailings.

Results from the rainwater experiments suggest that relating fluoride release to the number of pore volumes of fresh water circulated, may provide a reasonable approach for predicting F levels leached from tailings deposited in a pit. As an example, results from fluoride release experiments are depicted in Fig. 35, with F concentrations depicted as a function of the number of pore volumes passed through the column. Concentrations of F, Ca, Mg, and HCO_3 (Fig. 35) in the effluent were detected throughout the experiments even after 8-10 pore volumes of fluid (see Fig. 35) had passed through the column. Desorption, in this case, led to release of F at levels similar to that of F in the initial pore fluid until approximately 2 pore volumes of water passed through the system. Thereafter, the levels decreased gradually to less than one half the initial volume by the time that 3 pore volumes passed through the column. That the concentration of F in our experiments depended solely on the amount of water that passed through the column confirms that an adsorption/desorption process controls F mobility in Inland's tailings rather than a mineral dissolution process.

The experimental data also permit quantification of the total amount of fluoride that can be leached from these particular taconite tailings. In general, it appears that the amount of F adsorbed to tailings is approximately twice that present in the initial pore fluid (e.g., F(adsorbed)/F(dissolved) = 2 in freshly deposited tailings). For Inland, at the time our tailings sample was collected, this amounts to approximately 2 mg/kg leachable F (on a mass basis), or approximately 1% of the total F typically found in taconite tailings (200 mg/kg) (see Berndt and Lapakko, 1997 a,b). A detailed discussion of these calculations are provided in Appendix II.

Fluoride source

An important question that must be asked is, "What factors control the amount of mobile F in taconite tailings?" A partial answer to this question was provided by results of Berndt and Lapakko (1997a) and Jakel et al (1998) who measured F in taconite processing streams at Inland and LTV. It was determined in both studies that the scrubber water was the predominant source of F in taconite processing streams. Engesser (1998) has made similar observations.

A possible mechanism for F mobilization in taconite processing streams is presented schematically in Fig. 36. In general, F in unprocessed ore is immobile because it is bound in relatively insoluble minerals such as fluorapatite, amphibole, and clay minerals (Zhu and Sverjensky, 1991). Support for this notion can be found in the fact that Biwabik Iron Formation waters typically have low F concentrations (Table 4) even though some of the minerals in the formation obviously contain significant F. During mineral processing, most of these F bearing minerals are separated from the ore and disposed along with tailings into the tailings basins. If all of the F-bearing minerals were treated in this fashion, then the concentration of F in mineral processing streams and tailings basins would be expected to be low. However, because no ore separation process is 100% efficient, a small fraction of the F bearing minerals present in ore will always be streamed along with the concentrate and agglomerated into pellets. The pellets are heated there to extremely high temperatures in a process known as induration.

During induration, F in apatite and silicates can be converted quickly to HF (in the presence of H_2O vapor) (Zhu and Sverjensky, 1991) which is highly volatile. Gases containing dust and HF are swept from the indurator into scrubber stacks or, in the case of National, into mechanical collectors. These systems are meant to remove the dust from the system, but if a wet scrubber system is used, HF is also swept from the gases and dissolved into the water. The resulting scrubber waters are mixed back into the process streams, where some may adsorb onto the surfaces of the tailing or combine with Ca and precipitate as fluorite (assuming concentrations exceed values in equation 3).

By this mechanism, the amount of mobile F generated during processing of taconite will depend on the efficiency in which F bearing minerals can be removed from the concentrate. National Steel's process waters have low F because they use a mechanical collector rather than a wet scrubber system.

Molybdenum

Adsorption is a key process that controls the mobility of molybdenum. This element is dissolved predominantly as the oxyanion $MoO_4^=$, which is somewhat similar to sulfate in its behavior. $MoO_4^=$ can combine with Ca and precipitate as the salt $CaMoO_4$ (powellite) if Ca and Mo concentrations become high enough. Thermodynamic calculations suggested the waters are undersaturated with respect to powellite (Berndt and Lapakko, 1997a).

The more important process dictating $MoO_4^=$ behavior in taconite streams is adsorption. In general, waters in taconite processing plants and in tailings basins have elevated pH (≥8.5) while waters reacting with tailings have pH close to or approaching neutrality (7 to 8). At high pH, hydroxide ion (OH^-) competes with negatively charged species such as $MoO_4^=$ for available exchange sites on the surfaces of Fe-oxides. At neutral to low pH, however, where there is little OH^-, $MoO_4^=$ adsorbs.

Results of calculations performed to observe MoO_4 adsorption in tailings basins are shown in Figs. 37 and 38. In this computer simulation, 1 kg water (similar to tailings basin water) was reacted with 6 grams of fine-grained hematite (=3.6e7 cm^2) and the pH of the solution was adjusted from 8.7 to 7.0. Temperature was assumed to be 25°C, and the initial composition of fluid was taken to be F=5 mg/kg, Cl = 43.92 mg/kg, SO4= 123.45 mg/kg, Ca = 26.15, Na = 21.3 mg/kg, K = 8.71 mg/kg, Mo=48 µg/kg, As = 5 µg/kg, Mg=36.6 mg/kg, and HCO3 was constrained by charge balance. These inputs approximate the chemistry of water in a tailings pond, while the pH change represents the range of conditions expected during seepage of water through tailings in a pit environment. It is unlikely that pH values much less than 7.0 will be found, unless special circumstances (sulfide oxidation, burial of plants, lack of Ca and Mg carbonates in the ore) interfere.

In the simulation, it was found that $MoO_4^=$ ion concentrations were highest at the initial pH of 8.7 and decreased continuously with decreasing pH. The calculations also suggested that a significant fraction of $MoO_4^=$ was present on the surfaces of the Fe-oxides at all pH values (Fig. 38). The percentage of Mo adsorbed on mineral surfaces increased from approximately 50% initially to near 100%. By comparison, approximately 20% of the fluoride was initially adsorbed, while 70% was adsorbed when the pH decreased to 7. The low degree of adsorption for these elements accounts for their accumulation in process waters that are recycled between the plant and tailings basin.

Arsenic

Arsenic dissolves in water may in a variety of forms, including $As(OH)_4^-$, $As(OH)_3$, and $HAsO_4^=$. $As(OH)_4^-$ is the dominant species under relatively high pH and mildly reducing conditions, $HAsO_4^=$ dominates under near neutral to mildly alkaline pH levels under more oxidizing conditions, and $As(OH)_3$ dominates under mildly acidic and slightly reducing conditions. The uncharged $As(OH)_3$ species is not as readily adsorbed to Fe-oxides as either of the charged species $As(OH)_4^-$ or $HAsO_4^=$. Thus, arsenic concentrations can become elevated in some environments characterized by near neutral, mildly reducing conditions.

Under the conditions of mineral processing, where pH is high (8.7), Arsenic is nearly quantitatively adsorbed (Fig. 38). This accounts for the fact, that unlike Mo and F, As does not accumulate in tailings basins upon recycling of water between the plant in the basin. Furthermore, any new As that might be released during production and storage of taconite tailings should also be nearly quantitatively removed from solution by adsorption to the Fe-oxides that are abundant in taconite tailings. Conditions required to generate $As(OH)_3$ were not found in this study.

Boron

Calculations suggested that the amount of B adsorbed to Fe-oxides was insignificant over the pH interval studied. The minor B release observed in our experiments is probably not related, therefore, to desorption from Fe-oxides. B mobility may, instead, be related to desorption from clay minerals. Keren and Mezuman (1982), for example, noted a considerable tendency for clay minerals to adsorb boron at high pH (e.g., 9 to 10) and release it gradually with decreasing pH (where neutral $B(OH)_3$ species can form). These authors provided a phenomenologically based equation which can be used to predict boron adsorbance on montmorillonite, kaolinite, and illite as a function of pH. This equation probably does not apply to minerals in taconite tailings so will not be discussed here.

Conclusions

A large number of water samples have been collected and analyzed from taconite tailings basins, the Biwabik Iron Formation, and from experiments conducted between water and tailings. Elements of potential regulatory concern include Mn, F, Mo, As, and B. Concentrations of all of these elements are relatively low in Biwabik Iron Formation ground waters but may be elevated at some locations within taconite processing plants, tailings basin reservoirs, or within tailings pore fluids.

Significant intrasite variation was observed for mobilization of Mn, F, Mo, As, and B. Numerous factors account for the differences including water mass balance (recycling/dilution/evaporation), mineral dissolution and precipitation, and adsorption.

Dilution dominates evaporation in tailings basins, an effect that leads to improved water quality during storage. Ideally, process water seeping through tailings reacts in a manner which results in dissolution of carbonate minerals, increased Ca, Mg, and alkalinity, decrease in pH, and adsorption of F and Mo. Infiltration of tailings by groundwater does not induce significant reactions, but infiltration by rainwater leads to renewed dissolution of carbonate minerals, increased Ca, Mg, and alkalinity, and gradual release of F and Mo adsorbed to tailings from pore fluids. Under normal conditions, Mn, As, and B are not mobilized to unacceptable levels during any of these processes.

Special circumstances, however, lead to increased mobilization of some of these elements in certain specific cases:

(1) High Mn in Inland seeps and wells are attributed to anaerobic decay of plant matter beneath the tailings basin in material containing buried plant material with no Ca and Mg carbonates.

(2) High Mn in pore fluids from the Snively pit disposal site and high As in LTV's basin is attributed to sulfide oxidation processes.

(3) High F concentrations can be encountered when taconite processing plants use wet scrubbers to remove particulates and if the waters have low Ca concentrations.

Calculational approaches are provided to evaluate maximum release of Mn and F from tailings based on solubility with respect to rhodochrosite and fluorite, respectively. F release under fluorite undersaturated conditions, and Mo and As release can also be evaluated through use of computer simulations. B release from tailings appears to be specific to reaction with tailings from LTV, but the precise source was not identified in this study.

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Tables

Table 1: Approximate detection limits for analysis by ICP-MS and ion chromatography at the University of Minnesota, Department of Geology and Geophysics.

Detection limit (µg/kg)	ICP-MS	IC
<.1	Ag, As, Ba, Cd, Co, Cr, Cs, Ga, Ge, Mg, Mn, Mo, Ni, Pb, Rb, REE's, Sn, Sr, Th, Tl, U, V, W	
0.1-1.0	Al, Ca, Cu, Si, Zn	
1.0-10.0	Li, K, Fe, Na, Se	Br, Cl, F, NO_2-N, NO_3-N
10-50	B	PO_4-P, SO_4

*REE's = rare earth elements

Table 2: Analytical procedures used in this study.

Element	Method	Preservation/Handling
Cations (see Table 1)	ICP-MS	Filtered, 60 ml, 200 µl HNO_3
Anions (see Table 1)	Ion chromatography	Filtered, Stored at approximately 4°C
Alkalinity	Titration	Filtered, Stored at approximately 4°C

Table 3: Geochemical reactions considered important in our study. Note: $CaMg(CO_3)_2$ is used in this table to represent ankerite. Fe and Mn replace a large percentage of the Mg ion in ankerite.

Reaction:	Importance
(1) $O_2 + C_{organic} = CO_2$	Consumes O_2 Creates reducing redox conditions Increases partial pressure of CO_2
(2) $CO_2 + H_2O = H_2CO_3$	Generates carbonic acid
(3) $H_2CO_3 + CaCO_3 = Ca^{++} + 2HCO_3^-$.	Consumes carbonic acid Generates alkalinity Generates dissolved cations Increases pH
(4) $H_2CO_3 + 1/2CaMg(CO_3)_2 = 1/2Ca^{++} + 1/2Mg{+}{+} + 2HCO_3^-$.	Consumes carbonic acid Generates alkalinity Generates dissolved cations Increases pH
(5) $H_2CO_3 = H^+ + HCO_3^-$	Generates H^+
(6) $C_{org} + 2H_2O = CO_2 + CH_4$	Generates CO_2 in absence of O_2
(7) $15O_2 + 4FeS_2 + 8H_2O = 2Fe_2O_3 + 8H_2SO_4$	Generates sulfuric acid
(8) $H_2SO_4 + 2CaCO_3 = 2Ca{+}{+} + 2HCO_3^- + SO_4^=$	Consumes sulfuric acid Generates alkalinity Generates dissolved cations Increases pH
(9) $H_2SO_4 + CaMg(CO_3)_2 = Ca^{++} + Mg^{++} + 2HCO_3^- + SO_4^=$	Consumes sulfuric acid Generates alkalinity Generates dissolved cations Increases pH
(10) $H_2SO_4 = 2H^+ + SO_4^=$	Generates highly acidic conditions
(11) $2FeCO_3 + 0.5\ O_2 = Fe_2O_3 + 2CO_2$	Consumes O_2 Increases partial pressure of CO_2 in absence of organic matter

Table 4. Biwabik Iron Formation groundwater chemistry.

Loc.	CAL #2	CAL #3	NAS #3	NAS #4	KEE #1	KEE #2	SCR	BUH #1	BUH #2	KIN #2	MI #2	Ave	Std. Dev.	Min.	Max.
Date	5/6/98	5/6/98	5/7/98	5/7/98	5/6/98	5/6/98	5/6/98	5/7/98	5/7/98	5/7/98	5/8/98				
T (C)	9	8	7	7	8	8	7	7.4	7.9	7	7.5	8	1	7	9
pH	7.96	8.14	6.89	7.22	7.57	7.27	7.29	6.73	6.95	7.25	7.31	7.33	0.43	6.73	8.14
mg/kg															
HCO3	161	154	207	167	206	199	198	195	211	158	191	186	22	154	211
F	0.23	0.20	0.78	0.49	0.24	0.17	0.23	0.14	0.20	0.17	0.26	0.28	0.19	0.14	0.78
Cl	2.3	6.4	2.3	1.7	1.5	8.3	15.0	3.7	7.6	1.8	11.4	5.6	4.5	1.5	15.0
Br	<.02	0.025	0.017	<.02	<.02	0.024	0.026	0.018	0.034	<.02	0.049	0.017	0.011	<.02	0.049
NO3-N	0.27	0.11	0.24	0.21	0.51	0.42	0.83	0.97	0.26	0.19	0.46	0.41	0.27	0.11	0.97
SO4	7.8	16.8	13.3	9.5	10.5	106.0	80.1	41.9	35.0	22.3	35.6	34.4	31.7	7.8	106.0
Si	3.7	3.9	4.9	5.7	4.2	5.0	5.0	7.3	7.1	10.7	5.3	5.7	2.0	3.7	10.7
Fe	0.08	0.14	0.07	0.00	0.19	0.10	0.01	0.04	0.16	2.91	0.02	0.34	0.85	0.00	2.91
Mn	0.05	0.09	0.08	0.06	0.69	0.28	0.00	0.00	0.31	0.33	0.11	0.18	0.21	0.00	0.69
Ca	32.7	34.3	47.6	34.7	47.7	69.6	47.7	45.8	47.3	41.3	45.3	44.9	10.1	32.7	69.6
Mg	15.0	16.0	20.2	19.1	17.3	28.5	36.1	25.2	25.5	20.6	24.5	22.5	6.2	15.0	36.1
Na	7.1	7.2	7.2	4.7	7.7	8.5	11.2	8.8	9.6	6.7	12.0	8.2	2.1	4.7	12.0
K	2.4	2.7	2.1	2.1	1.1	1.6	1.9	2.1	2.0	0.5	1.1	1.8	0.7	0.5	2.7
µg/kg															
Li	17.6	21.2	8.4	5.8	7.5	8.7	5.8	7.0	5.3	6.1	4.2	8.9	5.4	4.2	21.2
B	105.7	106.3	27.0	15.4	46.9	68.9	18.7	28.1	16.6	31.1	44.9	46.3	33.4	15.4	106.3
Al	5.2	1.1	0.6	1.5	2.0	3.0	1.7	0.6	0.6	2.1	1.0	1.8	1.3	0.6	5.2
Cr	1.0	2.7	4.5	3.3	3.0	3.5	3.3	3.1	4.0	1.2	2.1	2.9	1.1	1.0	4.5
Co	0.6	0.2	0.1	0.1	0.7	0.6	0.1	0.1	0.7	0.6	0.4	0.4	0.3	0.1	0.7
Ni	1.4	20.8	1.7	1.3	1.6	2.9	4.4	1.5	3.8	1.6	1.6	3.9	5.7	1.3	20.8
Cu	1.1	2.8	2.4	10.1	2.1	1.5	5.3	4.0	0.6	0.3	0.3	2.8	2.9	0.3	10.1
Zn	21	20	19	23	48	19	35	25	28	16	17	25	9	16	48
As	0.7	0.7	0.4	0.3	0.3	0.2	0.2	0.1	0.2	1.9	0.5	0.5	0.5	0.1	1.9
Se	0.0	1.5	0.7	1.0	0.0	2.6	1.5	1.3	0.8	0.0	0.4	0.9	0.8	0.0	2.6
Rb	1.1	1.3	0.9	0.7	0.5	1.0	1.3	3.5	3.7	0.6	2.3	1.6	1.1	0.5	3.7
Sr	356	425	128	85	126	217	104	121	103	82	108	169	116	82	425
Mo	0.72	0.66	0.13	0.05	0.16	0.26	0.13	0.01	0.04	0.28	0.18	0.24	0.24	0.01	0.72
Cd	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Cs	0.04	0.05	0.07	0.05	0.07	0.04	0.13	0.88	0.74	0.07	0.53	0.24	0.32	0.04	0.88
Ba	139.4	135.4	20.0	8.8	160.7	36.1	0.1	1.0	28.5	7.9	36.0	52.2	61.3	0.1	160.7
W	0.10	0.00	0.33	0.08	0.30	0.06	0.32	0.35	0.07	0.30	0.06	0.18	0.14	0.00	0.35
Tl	0.01	0.00	0.02	0.00	0.03	0.01	0.02	0.02	0.01	0.03	0.02	0.02	0.01	0.00	0.03
‰															
δD	-79	-80	-78	-67	-77	-69	-69	-80	-80	-77	-77	-76	5	-80	-67
$\delta^{18}O$	-11.8	-11.9	-11.2	-8.8	-11.8	-9.8	-10.1	-11.4	-11.7	-10.9	-10.8	-10.9	.98	-11.9	-8.8
TU															
^{3}H	0	2	22.2	27.2	2.1	16.9	16.9	25.6	17.9	23.8	13.8	15.31	9.83	0.00	27.20

Table 5: Time averaged (Jun '96 to Feb. '99) concentrations of selected elements in water associated with taconite tailings basins. Full chemistry and statistics are available in the appendices.

	National			Inland			LTV		
	Plant Discharge	Basin	Reacted (W-12)	Plant Discharge	Basin	Reacted (W-6)	Plant Discharge	Basin	Reacted Seep
pH	8.27	8.49	7.16	8.38	8.54	7.07	8.59	8.75	7.32
Eh	312	318	343	283	318	213	278	321	228
majors(ppm)									
Si	16.0	7.7	10.4	11.0	3.6	7.1	8.5	6.2	10.6
Fe	0.01	0.01	0.00	0.03	0.00	7.99	0.00	0.02	1.84
Mn	0.06	0.03	0.02	0.06	0.01	4.26	0.03	0.03	0.99
Sr	0.09	0.07	0.11	0.16	0.11	0.19	0.11	0.13	0.36
Ba	0.01	0.01	0.06	0.01	0.01	0.11	0.01	0.01	0.05
Ca	33.6	24.8	74.1	30.3	28.6	39.5	16.7	20.7	71.5
Mg	37.1	34.1	28.2	46.5	41.4	36.6	31.3	35.7	76.2
Na	38.7	33.5	29.7	43.2	26.2	22.5	130	117	108
K	11.0	7.3	2.3	10.3	9.3	8.1	17.1	13.5	16.6
F	1.30	0.98	0.58	4.57	2.74	2.96	9.8	8.5	3.9
Cl	28.3	22.3	22.2	75.2	51.0	51.6	36.3	33.1	32.4
Br	0.07	0.05	0.07	0.55	0.37	0.39	0.19	0.17	0.16
SO4	61.8	52	46	63.9	48	22	116	119.5	230
HCO3^{-}*	209	191	289	191	183	220	274	275	463
trace (ppb)									
Li	15	9.9	7.6	40	10.6	1.1	85	77	33
B	73	53	41	121	70	51	349	334	457
Mn	57.3	32.0	18.0	61.6	9.9		28.1	27.0	
Fe	6.3	9.3	7.5	60.3	11.8		6.0	23.7	
Zn	16.2	17.3	17.7	20.4	17.8	22	15.1	15.0	17.3
As	2.13	1.6	0.44	3.6	5.1	4.7	4.0	11.1	4.8
Rb	9.13	5.4	1.60	9.2	10.2	6.9	18.1	14	13
Sr	93.50	76	121	168	116	202	120	137	367
Mo	58.1	41	10.3	110	35	6.3	340	279	86
Cs	0.99	0.30	0.01	1.45	0.85	0.57	2.90	1.88	1.11
Ba	5.59	5.13	63	5.67	10.22	113	5.6	5.3	47

*Alkalinity units are mg/kg CaCO$_3$ equivalents.

Table 6: Carbon isotope budget for water seeping from tailings basins.

Site	$d^{13}C_{basin}$	$d^{13}C_{reacted}$	% new C*	$d^{13}C_{new}$	% new C added as:	
					$CO_3^=$	CO_2
Inland Steel	-6.99	-10.7	35	-17.6	4.2	95.8
LTV	-8.62	-9.68	48	-10.8	100	0
National	-5.82	-9.17	52	-12.3	36.4	63.6

*Calculated from change in total carbon concentration.

Table 7: Mineralogy of tailings used in experiments. Modal analysis (wt%) and mineral identifications are based on microscopy, heavy mineral separation, and SEM analysis.

Mineralogy	National	Inland	LTV
Magnetite	1	1	2
Hematite	10	17	3
Goethite	1	1	n.d.
Mn-oxides	n.d.	n.d.	n.d.
Calcite	n.d.	n.d.	1
Siderite	9	7	6
Ankerite	4	4	8
Quartz	51	44	49
Stilpnomelane	11	11	15
Minnesotaite	1	3	6
Talc	12	11	3
Cummingtonite	n.d.	n.d.	4
Fe-Hornblende	n.d.	n.d.	3
Greenalite	tr?	tr?	tr?
Chlorite	tr?	tr?	tr?
Apatite	.2	.2	.2
Pyrite	.03	.01	.04

n.d. = not detected, tr? = possible trace

Table 8 Chemical composition of tailings used in column experiments.

	National	Inland	LTV
Majors (wt%)			
Al2O3	0.59	0.75	0.94
CaO	1.59	1.64	2.99
Cr2O3	.01	<.01	<.01
Fe2O3	21.43	28.72	19.36
K2O	.21	.19	.25
MgO	4.28	3.96	2.93
MnO	.7	.85	.58
Na2O	.05	.07	.11
P2O5	.08	.08	.10
SiO2	63.17	56.9	64.7
TiO2	<.01	.01	.03
LOI	5.78	4.96	6.23
Total	97.89	98.13	98.22
CO2 (wt%)	1.47	3.11	3.66
trace (ppm)			
F	200	240	180
Ag	<.2	<.2	<.2
As	18	18	18
B	<20	<20	<20
Ba	30	20	20
Be	<.5	<.5	<.5
Bi	<2	4	10
Cd	<.5	<.5	<.5
Co	8	15	10
Cr	6	8	27
Cu	9	7	7
Hg	.010	.053	.034
Mo	<1	<1	<1
Ni	3	3	7
Pb	<2	<2	<2
Rb	2	4	6
Sb	<.2	<.2	.2
Se	.2	<.2	<.2
Sr	25	41	41
Tl	<.1	<.1	<.1
V	5	11	9
W	40	40	40
Zn	14	10	10

Figures and Figure Captions

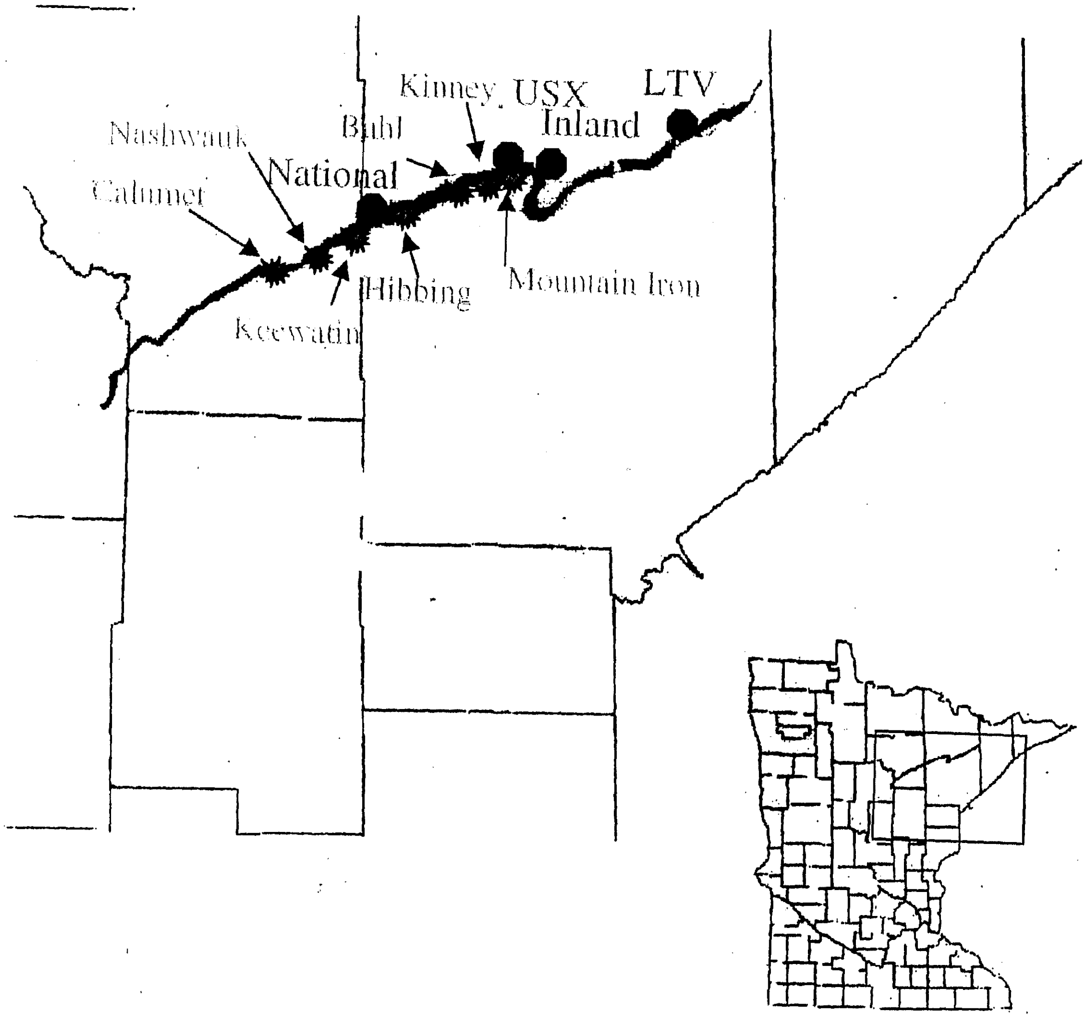

Kinney
USX
LTV
Inland
Buhl
Nashwauk
National
Calumet
Hibbing
Mountain Iron
Keewatin

Figure 1

Figure 1: Location map showing Biwabik Iron Formation and locations of participating mining companies (blue octagons). Cities who's wells in the Biwabik Iron Formation were sampled are also shown (green starbursts).

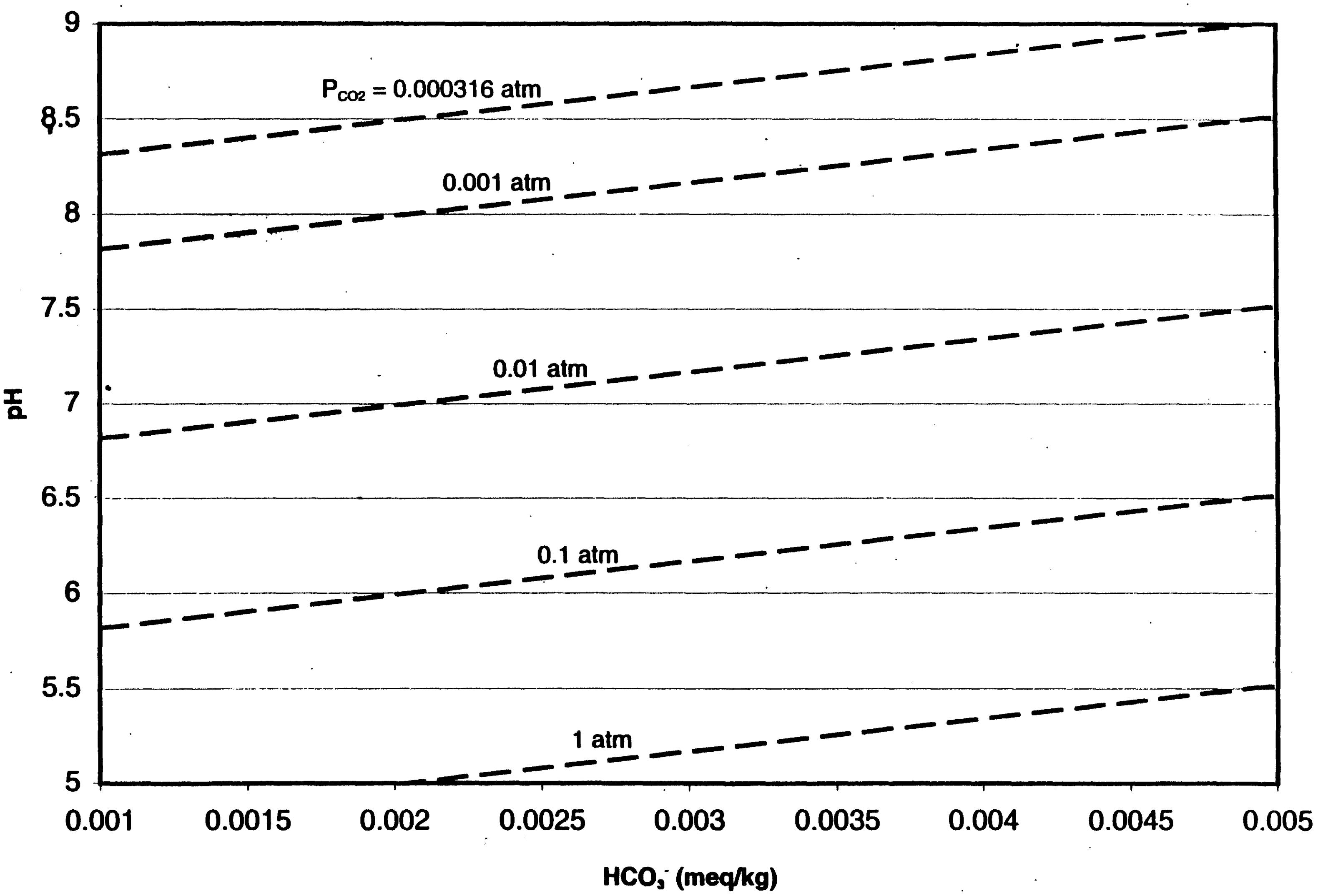

9
8.5
8
7.5
7
6.5
6
5.5
5
pH
P_{CO2} = 0.000316 atm
0.001 atm
0.01 atm
0.1 atm
1 atm
0.001
0.0015
0.002
0.0025
0.003
0.0035
0.004
0.0045
0.005
HCO_3^- (meq/kg)

Figure 2

Figure 2: Relationship between HCO_3^-, pH, and P_{CO2} (the partial pressure of CO_2). Water in equilibrium with the atmosphere (e.g.,taconite processing waters) have P_{CO2} values of 0.000316 atm and should have high pH (≥8.5). Groundwaters typically have P_{CO2} values around 0.01 atmospheres and often have pH values near 7. Additional CO_2 pressure, such as during decomposition of organic matter, can cause solution pH to drop to values below neutral (in absence of reactive carbonate minerals). Thus, one of the primary purposes of the present study was to determine P_{CO2} in waters reacting with tailings and in groundwater from the Biwabik Iron Formation. This diagram assumes a temperature of 25°C, but similar relations hold at temperatures greater or less than this.

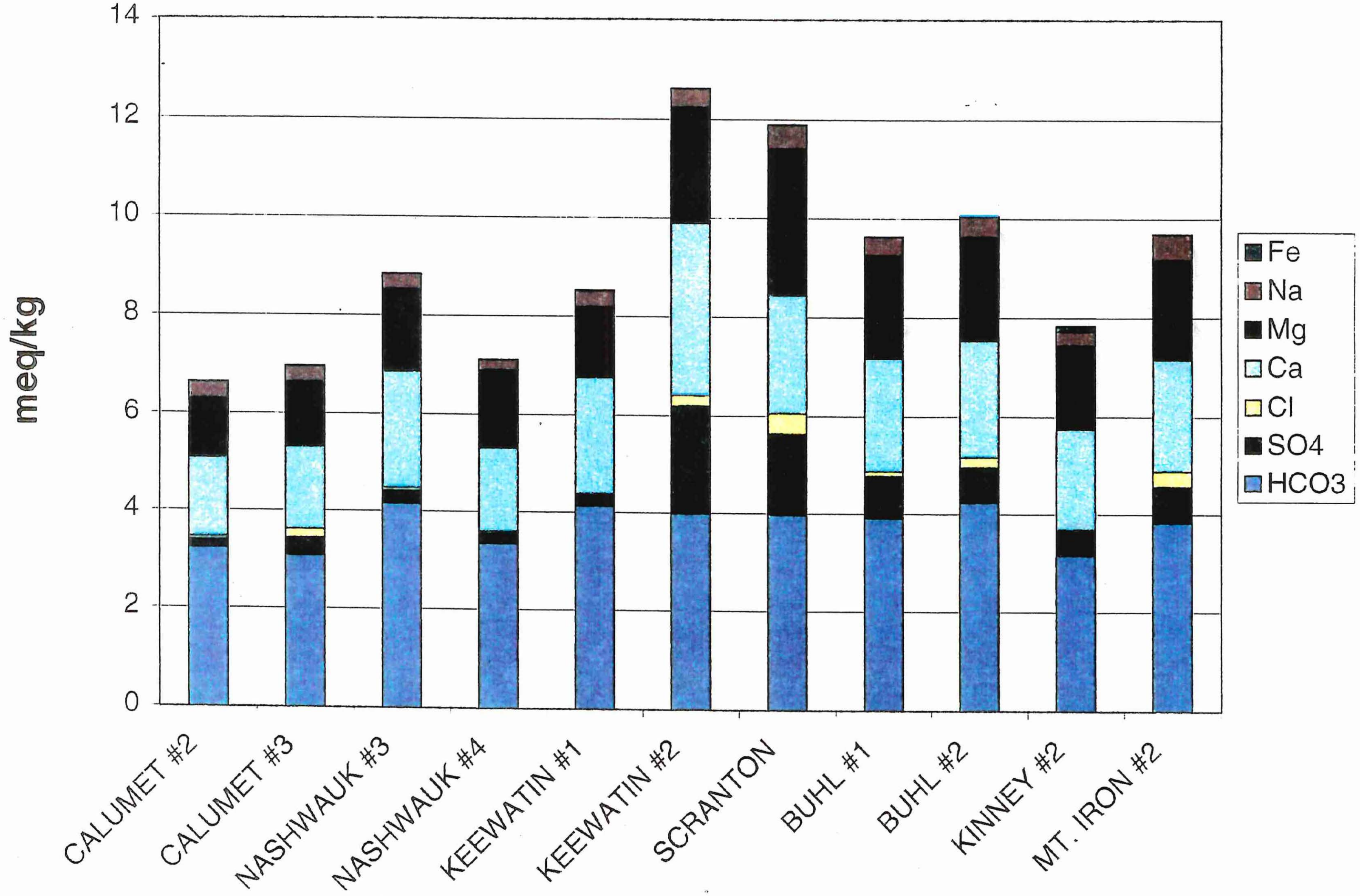
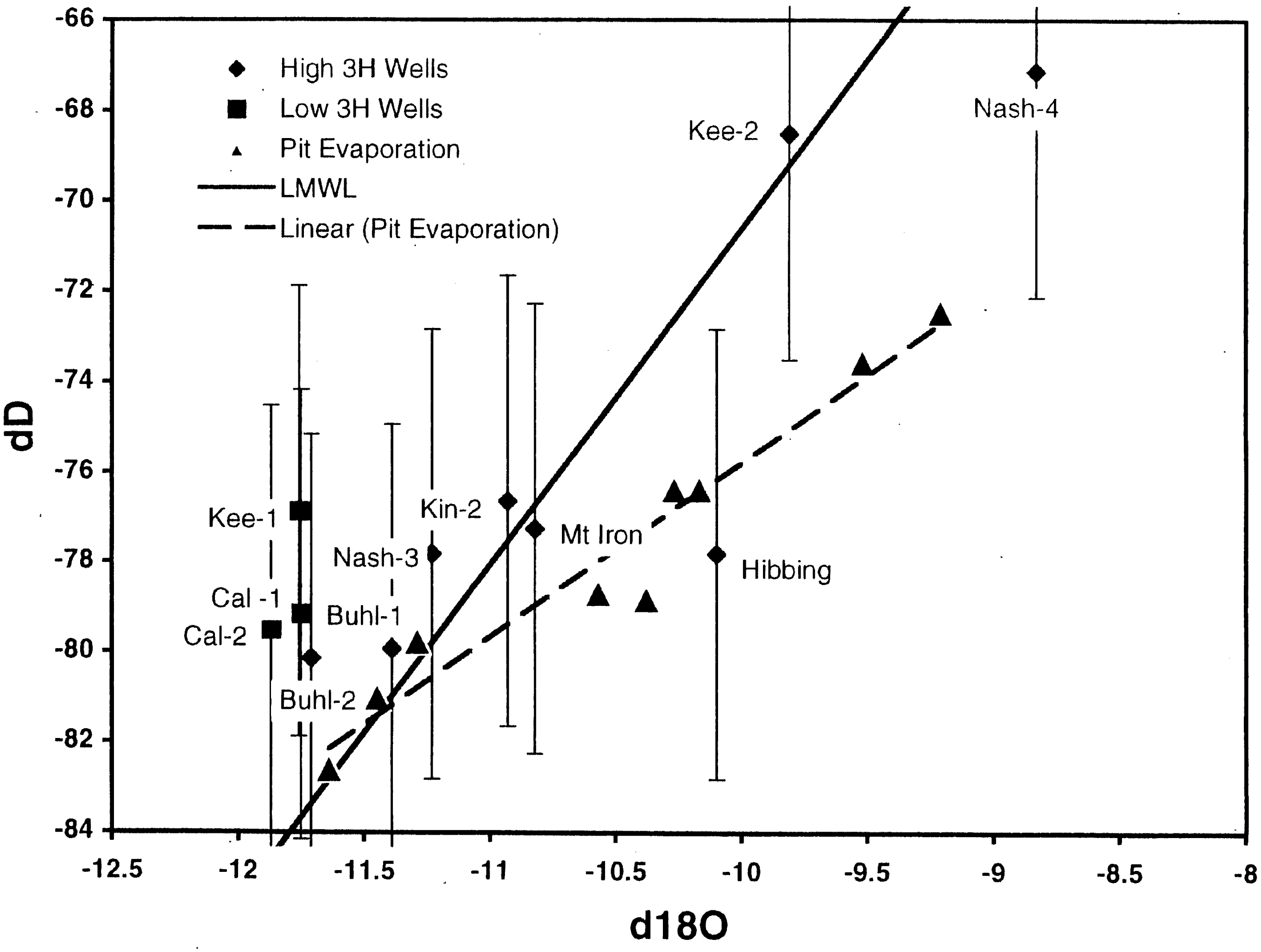

meq/kg
14
12
10
8
6
4
2
0
CALUMET #2
CALUMET #3
NASHWAUK #3
NASHWAUK #4
KEEWATIN #1
KEEWATIN #2
SCRANTON
BUHL #1
BUHL #2
KINNEY #2
MT. IRON #2
Fe
Na
Mg
Ca
Cl
SO4
HCO3

Figure 3

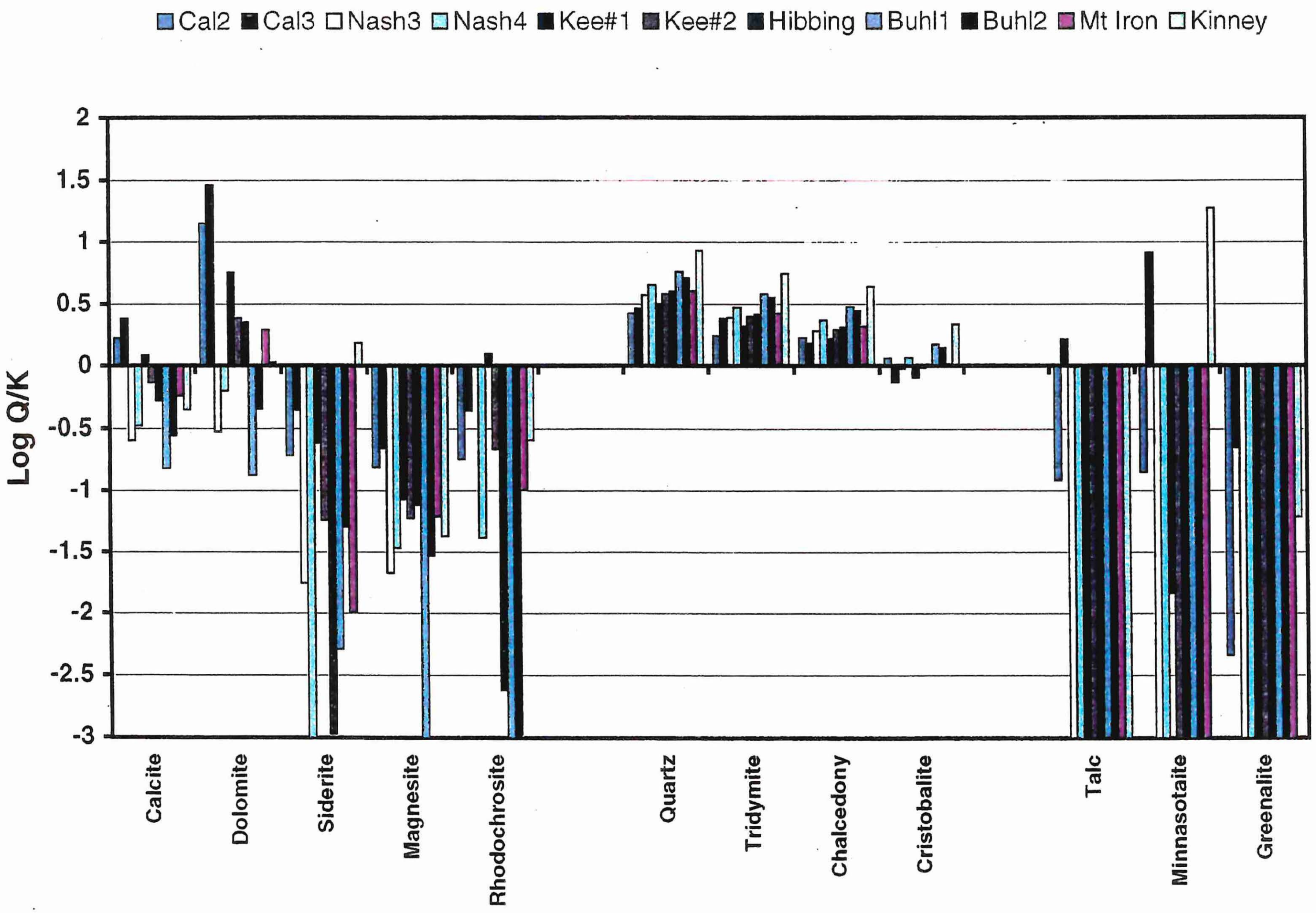
Figure 3: Major element composition of Biwabik Iron Formation groundwaters. All have low Cl and high HCO_3^- concentrations and some of the wells have elevated $SO_4^=$. Ca^{++} and Mg^{++} are the dominant cations.



-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
dD
-12.5
-12
-11.5
-11
-10.5
-10
-9.5
-9
-8.5
-8
d18O
◆ High 3H Wells
■ Low 3H Wells
▲ Pit Evaporation
LMWL
Linear (Pit Evaporation)
Kee-2
Nash-4
Kee-1
Kin-2
Nash-3
Mt Iron
Hibbing
Cal -1
Cal-2
Buhl-1
Buhl-2

Figure 4

Figure 4: Hydrogen and oxygen isotope diagram for Biwabik Iron Formation groundwaters. A 5 ‰ error was assigned to our data for δD based on comparison with previous results (Walsh, 1999). The pit evaporation samples and trend are from Alexander and Alexander (1997). Many of the samples collected in the present study, particularly the younger waters (containing Tritium) also seem to have been derived from waters that once resided in a pit. This indicates that much of the current recharge in the area occurs through the pits.



🟦Cal2 ■Cal3 ☐Nash3 🟦Nash4 ■Kee#1 ■Kee#2 ■Hibbing 🟦Buhl1 ■Buhl2 🟪Mt Iron ☐Kinney
Log Q/K
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
Calcite
Dolomite
Siderite
Magnesite
Rhodochrosite
Quartz
Tridymite
Chalcedony
Cristobalite
Talc
Minnasotaite
Greenalite

Figure 5

Figure 5: Saturation indices for carbonate and silicate minerals common in the Biwabik Iron Formation. Consistent with their high Ca, Mg, HCO_3^- and SiO_2 concentrations, most of the waters are close to saturation with respect to Ca and Mg carbonate minerals and cristobalite. Cal2, Cal3, and Kee#1 waters infiltrated the ground earlier than the other samples and were unaffected by storage in a pit. These three waters and the high Fe waters from Kinney's well (see Fig. 3) are close to saturation with respect to siderite and Fe-silicate minerals (minnesotaite and greenalite).

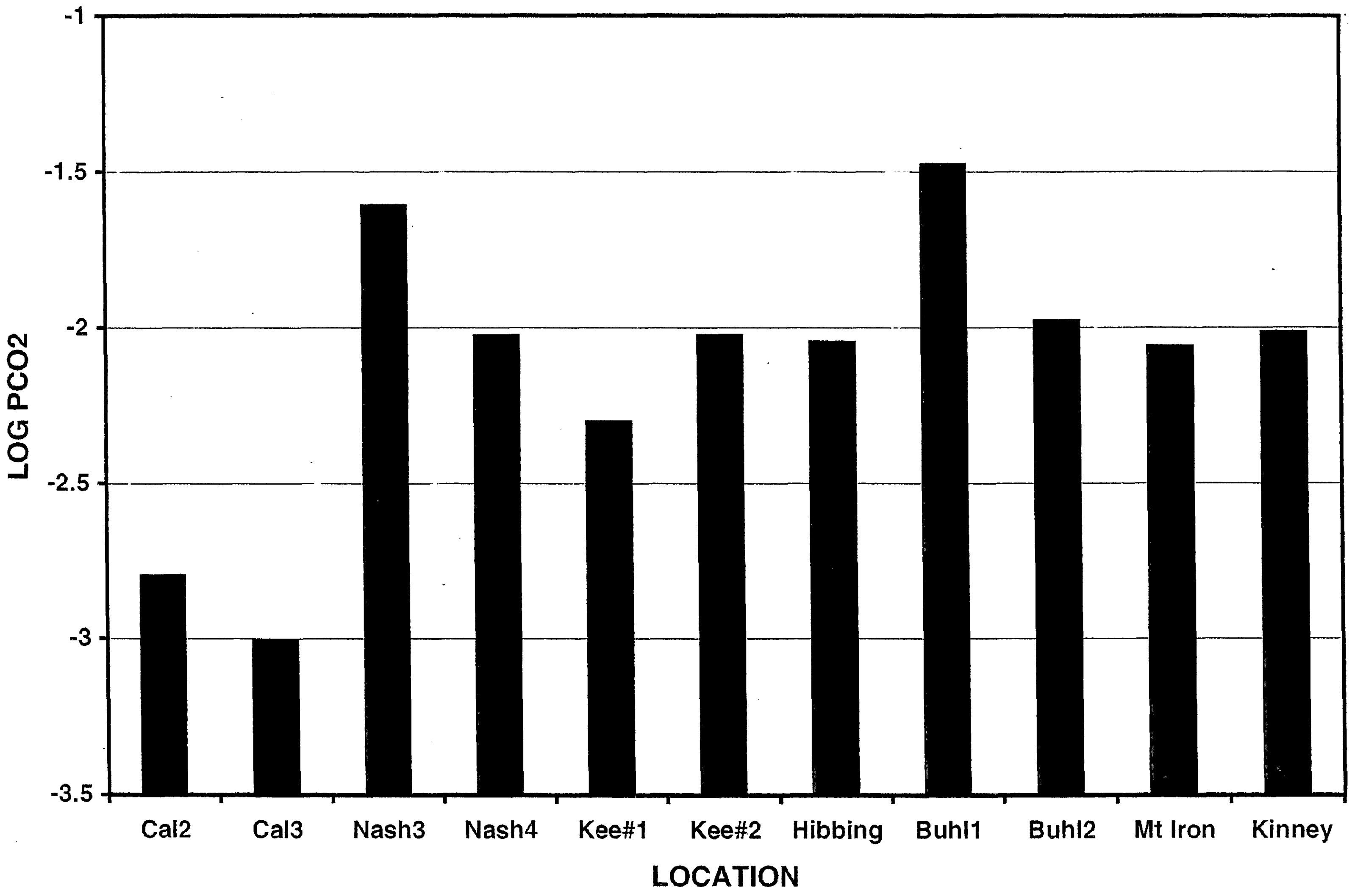
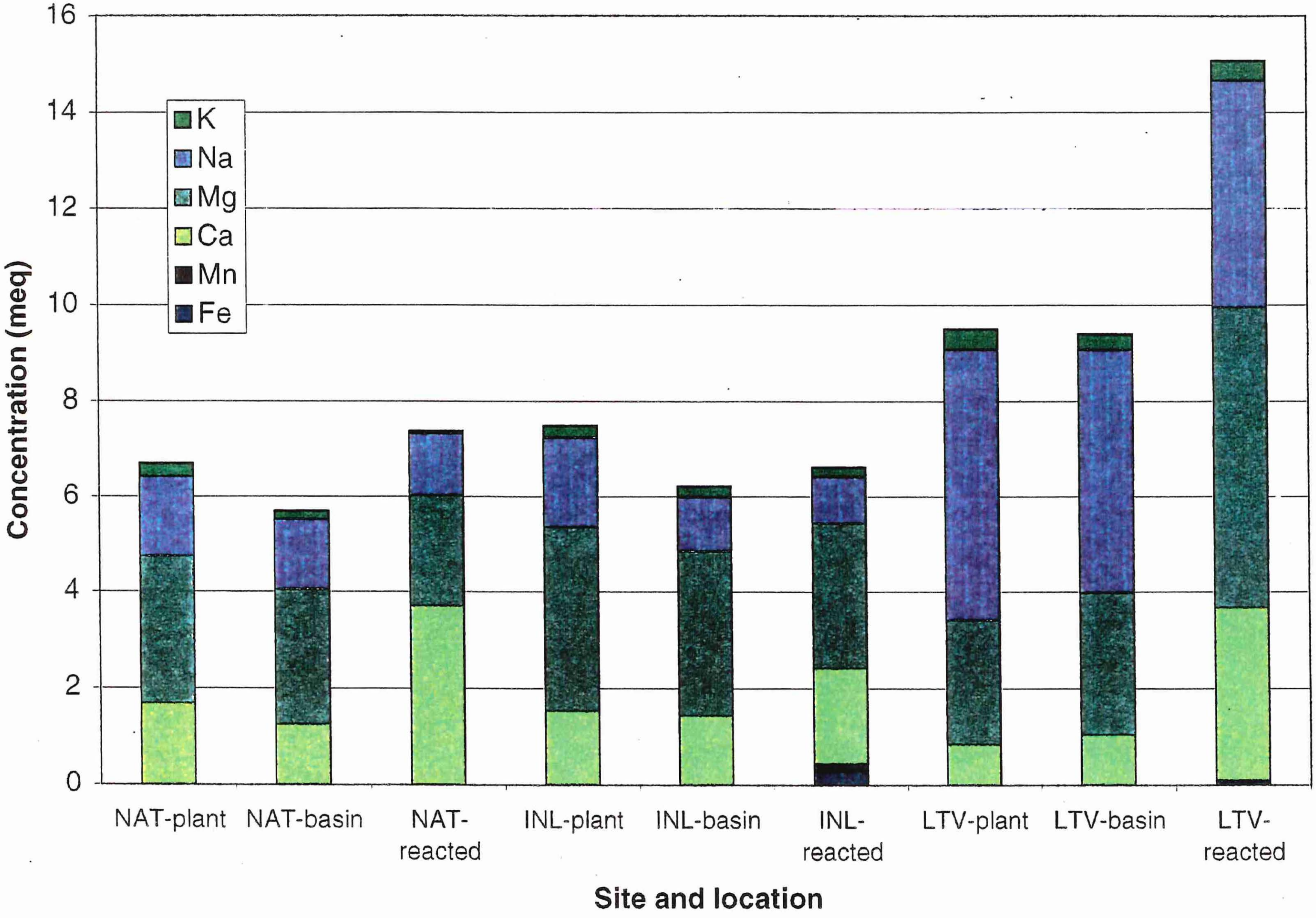

-1
-1.5
-2
-2.5
-3
-3.5
LOG PCO2
Cal2
Cal3
Nash3
Nash4
Kee#1
Kee#2
Hibbing
Buhl1
Buhl2
Mt Iron
Kinney
LOCATION

Figure 6

Figure 6: P_{CO2} of waters in the Biwabik Iron Formation. Low Tritium waters (red) have P_{CO2} values close to 0.001 atmospheres, while the high tritium (younger) waters have P_{CO2} values closer to 0.01 atmospheres. This may suggest that waters penetrating the ground with high P_{CO2} eventually have their P_{CO2} lowered by reaction with Biwabik Iron Formation minerals. P_{CO2} is an important parameter for controlling Mn concentration.



16
14
12
10
8
6
4
2
0
Concentration (meq)
K
Na
Mg
Ca
Mn
Fe
NAT-plant
NAT-basin
NAT-reacted
INL-plant
INL-basin
INL-reacted
LTV-plant
LTV-basin
LTV-reacted
Site and location

Figure 7

Figure 7: Three-year averaged chemistry (major cations) of water discharging into, stored within, or seeping from tailings basins for three mining companies on the Mesabi Iron Range. The waters are shown in sets of three for each basin: plant : basin : reacted water. "Plant" samples were collected at the site where water is discharged in a slurry with tailings into the tailings basin. "Basin" samples were collected at the point where water from the basin is recycled back to the plant. "Reacted water" was collected from either a well or a seep located at the edge of the basin. In each case, major element concentrations are diluted within the basin and increase again in water seeping from the basin. Full data set and statistics are available in the appendix.

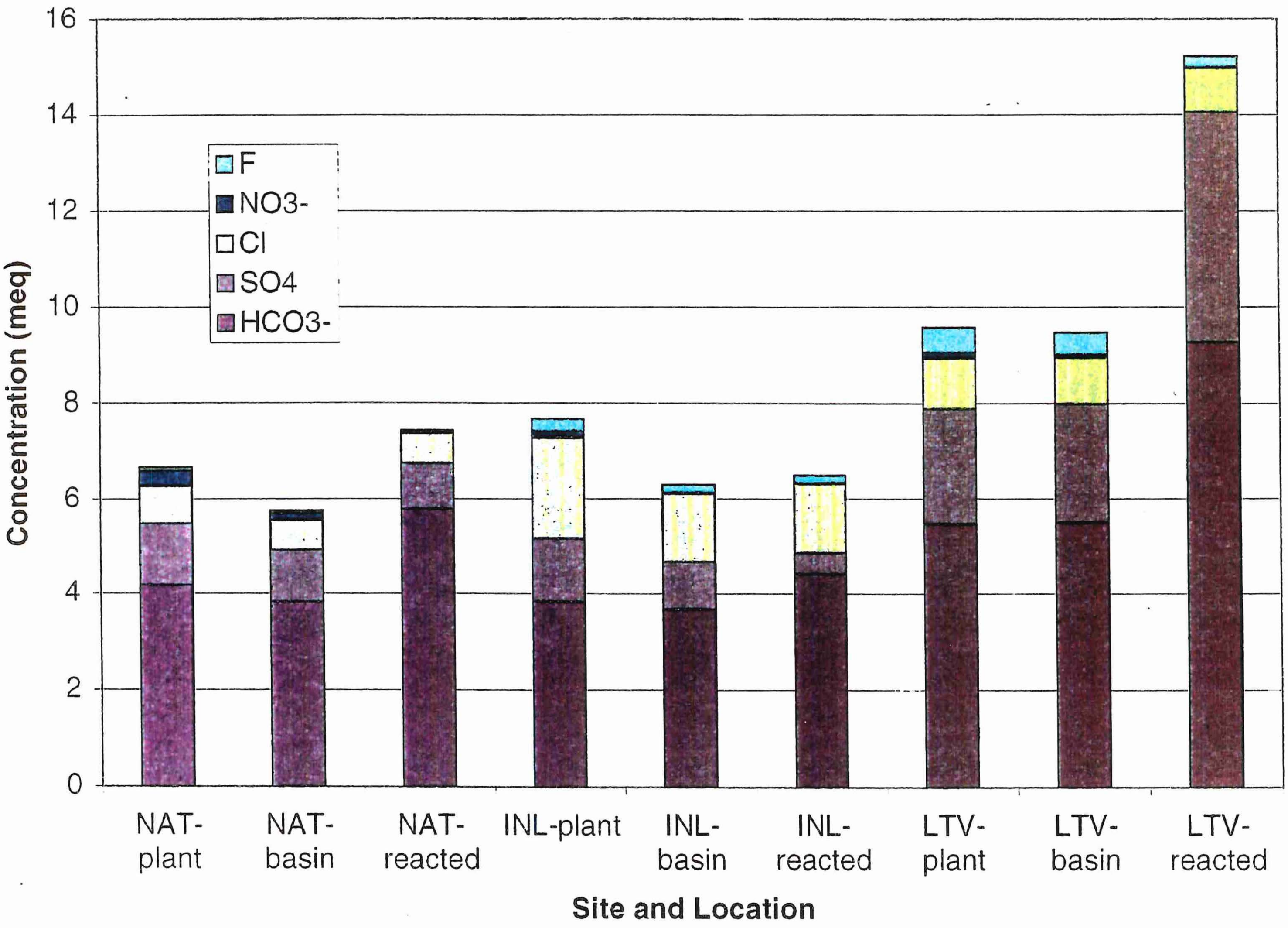
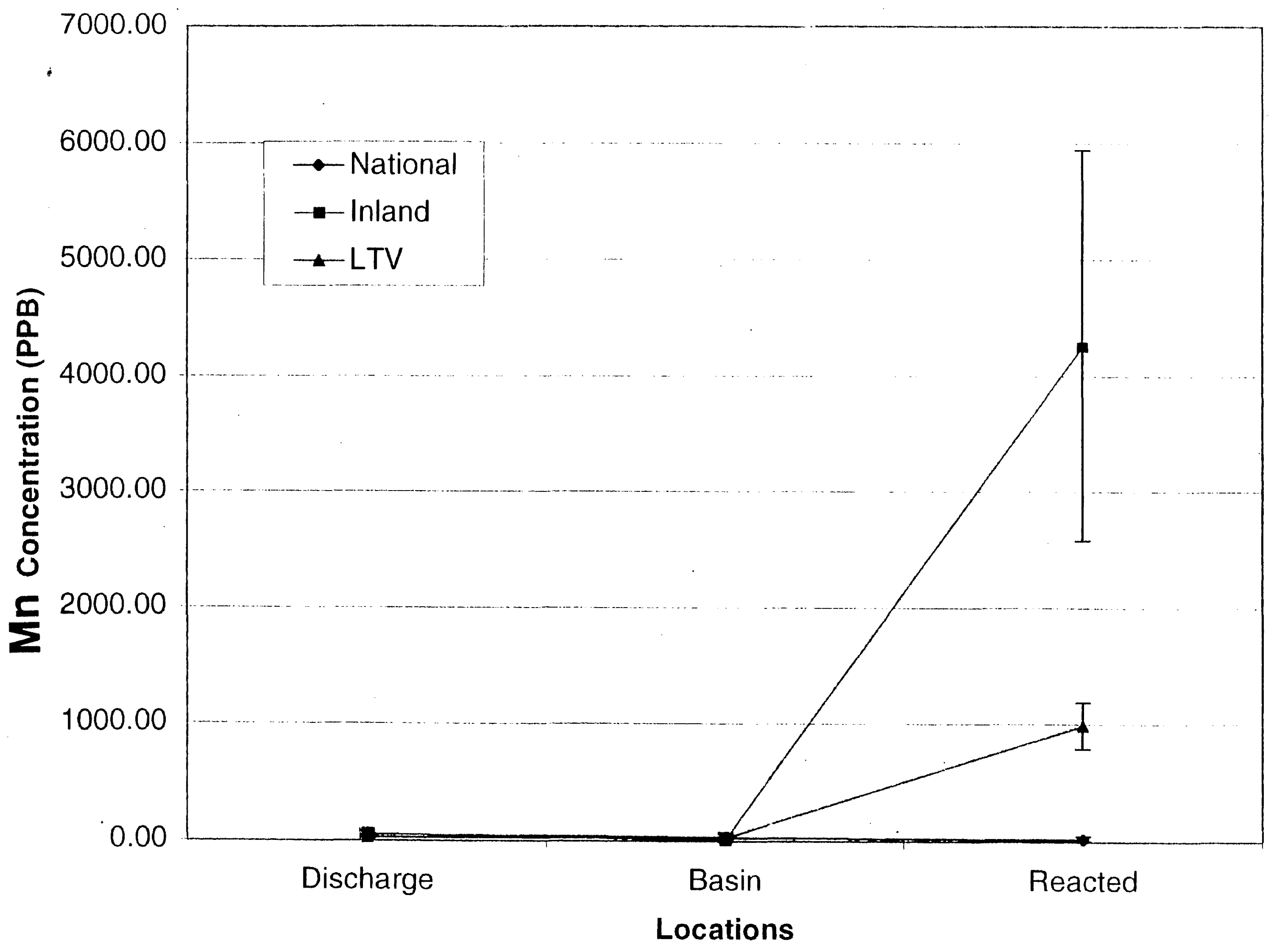

16
14
12
10
8
6
4
2
0
Concentration (meq)
F
NO3-
Cl
SO4
HCO3-
NAT-plant
NAT-basin
NAT-reacted
INL-plant
INL-basin
INL-reacted
LTV-plant
LTV-basin
LTV-reacted
Site and Location

Figure 8

Figure 8: Three-year averaged chemistry (major anions) of water discharging into, stored within, or seeping from tailings basins at National, Inland, and LTV taconite processing sites: Descriptions of samples are given in caption for Fig. 7. Dominant change that occurs during reaction of waters seeping from basins is an increase in HCO_3. Significant sulfide oxidation also occurs in water seeping from LTV's tailings basin as indicated by the increase in $SO_4^=$.



7000.00
6000.00
5000.00
4000.00
3000.00
2000.00
1000.00
0.00
Mn Concentration (PPB)
National
Inland
LTV
Discharge
Basin
Reacted
Locations

Figure 9

Figure 9: Averaged Mn concentrations in water discharging into, stored within, or seeping from tailings basins. Descriptions of samples are given in caption for Fig. 7. Mn concentrations are low under the oxidizing, high pH conditions that prevail in taconite processing plants and in tailings basins. Seeps and wells at the edge of taconite tailings basins can have appreciable Mn concentrations. At Inland, the high Mn appears to be related to reactions occurring beneath the tailings (see carbon isotope section of this manuscript), while at LTV, the high Mn appears to be related to sulfide mineral oxidation taking place within the tailings pile.

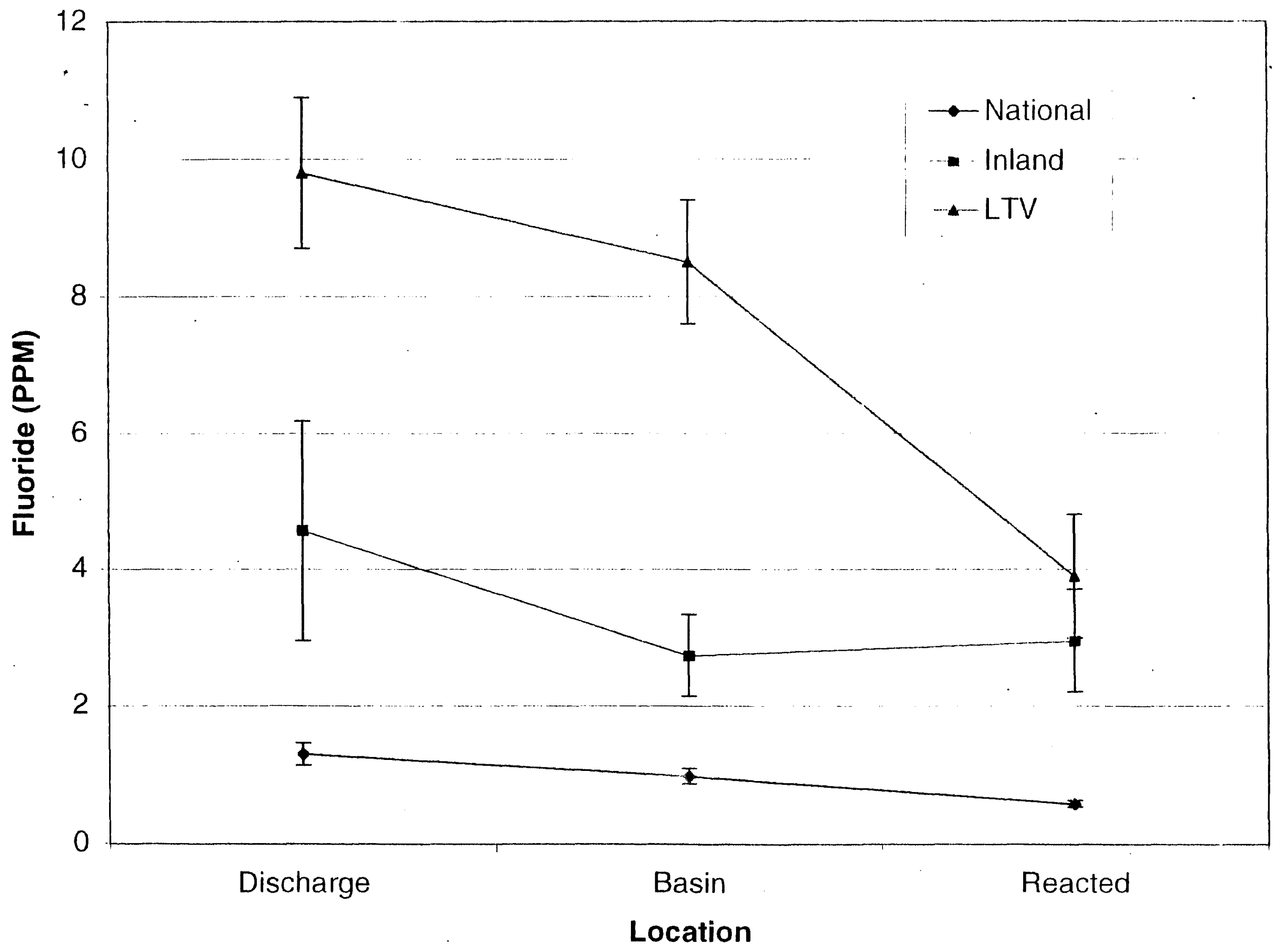

12
10
8
6
4
2
0
Fluoride (PPM)
National
Inland
LTV
Discharge
Basin
Reacted
Location

Figure 10

Figure 10: Averaged F concentrations for water discharging into, stored within, or seeping from tailings basins. Descriptions of samples are given in caption for Fig. 7. F concentrations for water discharging into the tailings basins is highly variable owing to day-to-day variation in ore composition and taconite processing operations. The variation is less in the tailings basin because of the size of the reservoir, but concentrations are lower owing to dilution related to precipitation within the basin. Large increases in Ca^{++} in waters seeping from LTV's basin leads to gross supersaturation and precipitation of CaF_2 within the tailings pile their. F precipitation or adsorption is less conspicuous at the other two sites.

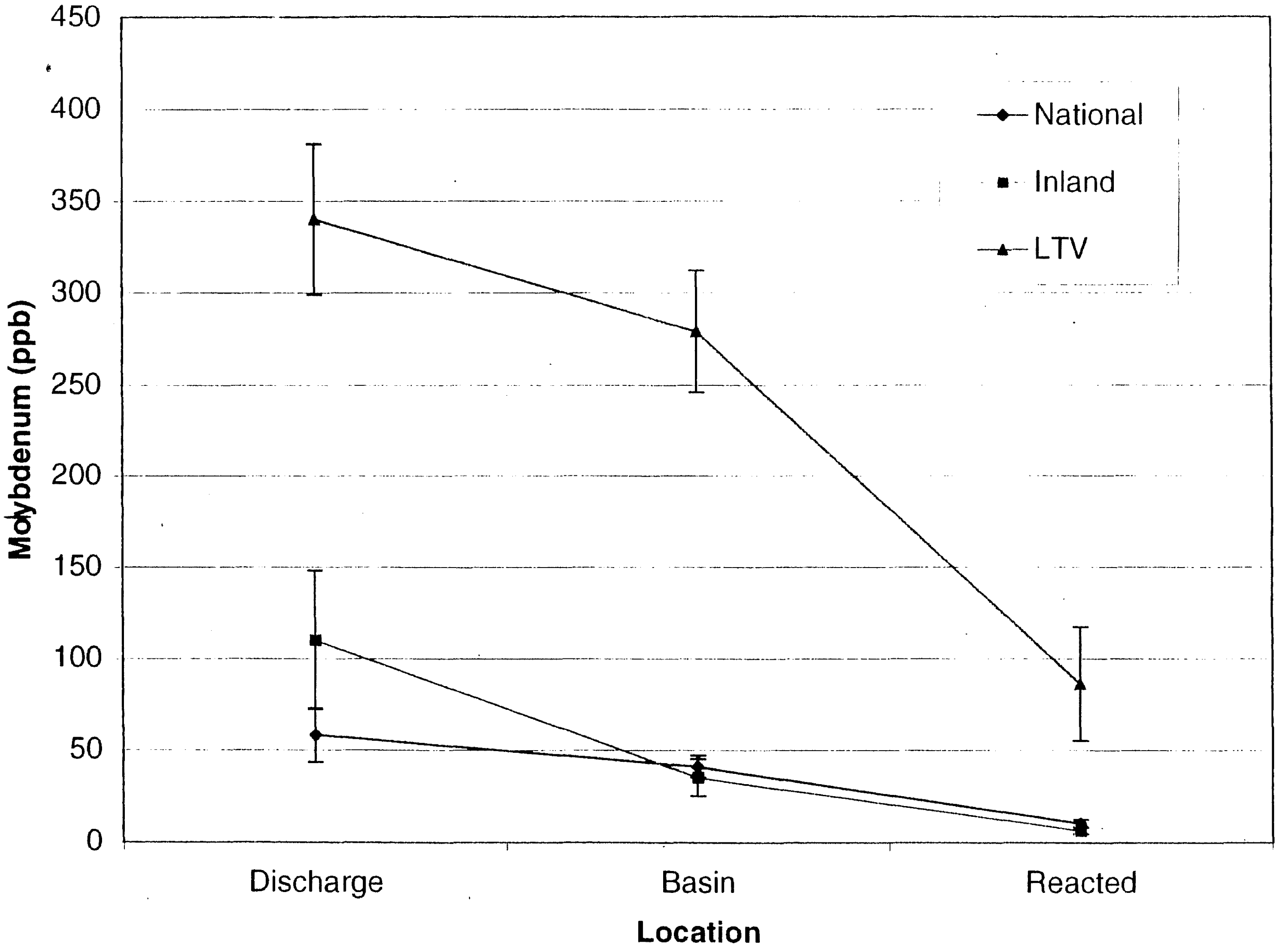

450
400
350
300
250
200
150
100
50
0
Molybdenum (ppb)
National
Inland
LTV
Discharge
Basin
Reacted
Location

Figure 11

Figure 11: Averaged Molybdenum concentration in waters discharging into, stored within, or seeping from tailings basins. Descriptions of samples are given in caption for Fig. 7. Mo is present as soluble $MoO_4^{=}$ species under the high pH conditions present in tailings basins and within mineral processing plants. Dilution accounts for most of the decrease that occurs in the concentration of this element within the tailings basin. This species adsorbs to Fe-oxide minerals under the lower pH of waters reacting with minerals during seepage from tailings basins.

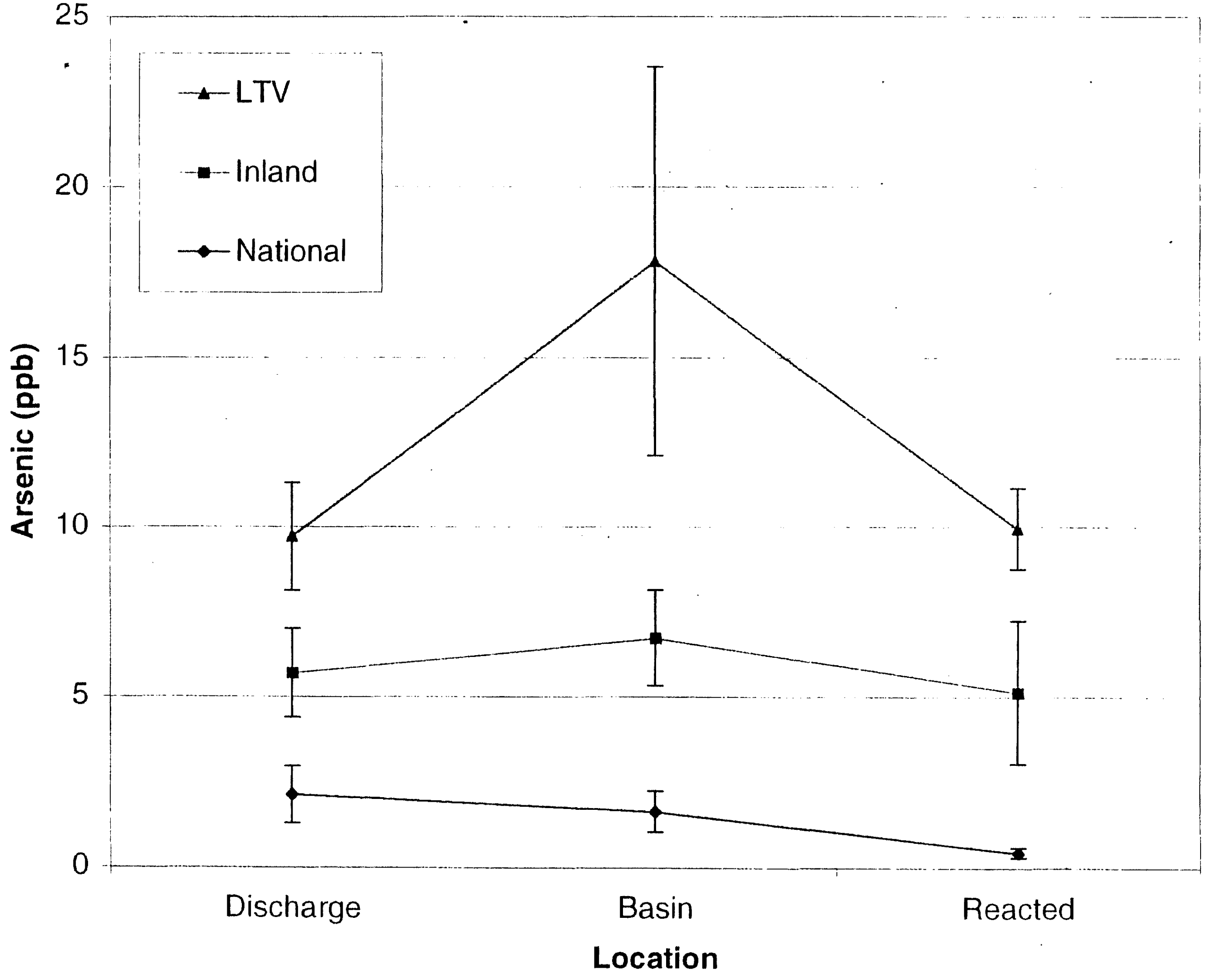

25
20
15
10
5
0
Arsenic (ppb)
LTV
Inland
National
Discharge
Basin
Reacted
Location

Figure 12

Figure 12: Averaged arsenic concentrations in waters discharging into, stored within, or seeping from tailings basins. Descriptions of samples are given in caption for Fig. 7. The increase in Arsenic concentrations in LTV's basin may be related to minor sulfide oxidation within the basin (SO_4 concentrations in the basin increase slightly but should decrease owing to dilution). Arsenic adsorbs readily to the surfaces of Fe oxides at conditions prevailing in taconite processing plants and in waters seeping from tailings basins.

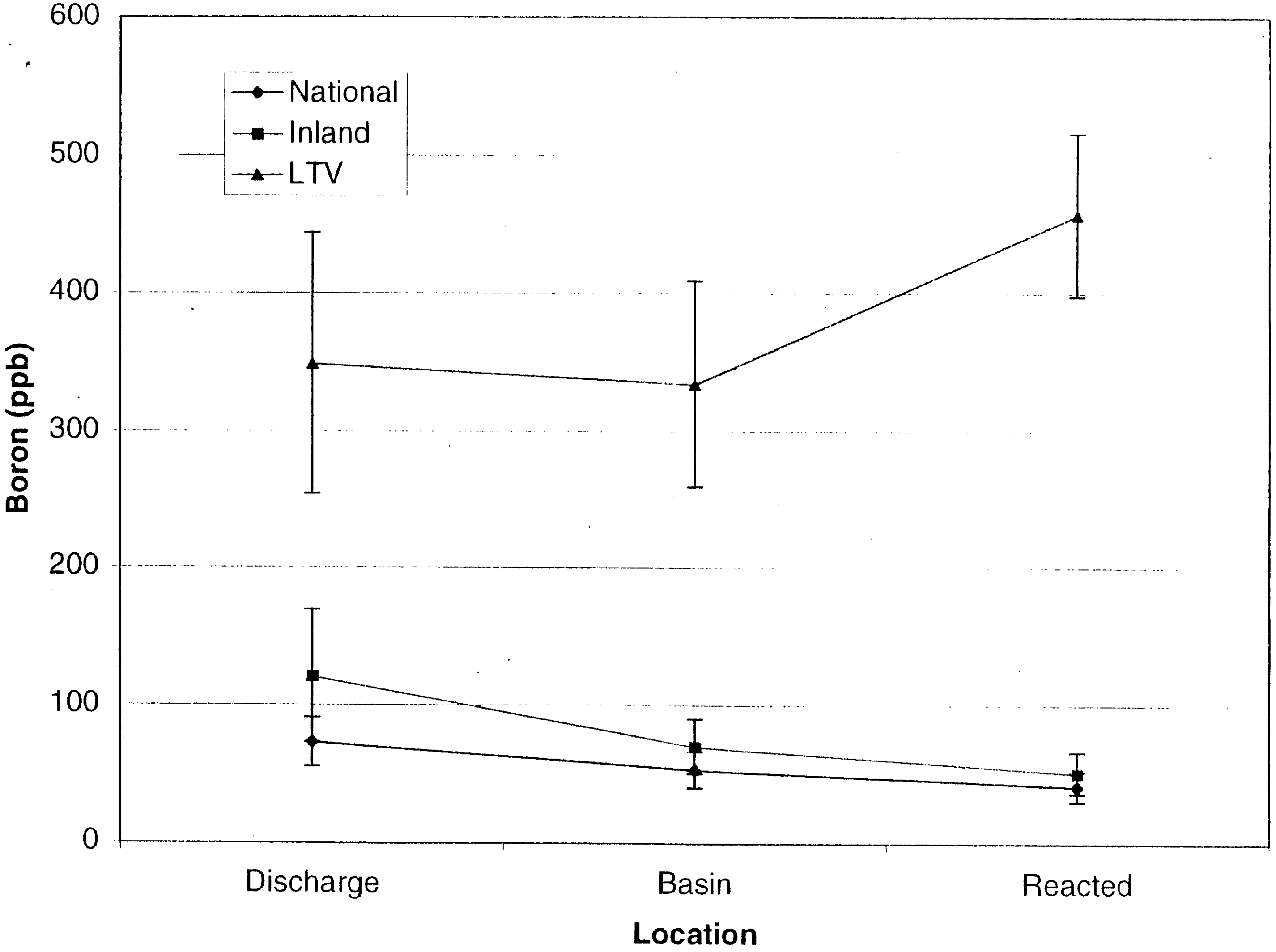

600
500
400
300
200
100
0
Boron (ppb)
National
Inland
LTV
Discharge
Basin
Reacted
Location

Figure 13

Figure 13: Averaged boron concentrations in water discharging into, stored within, or seeping from tailings basins. Descriptions of samples are given in caption for Fig. 7. Relatively high concentrations were only found at LTV. Concentrations for this element are diluted by precipitation within tailings basins. Increases in the concentration of this element were found in waters seeping from LTV's basin suggesting that a source for this element exists within this particular tailings pile.

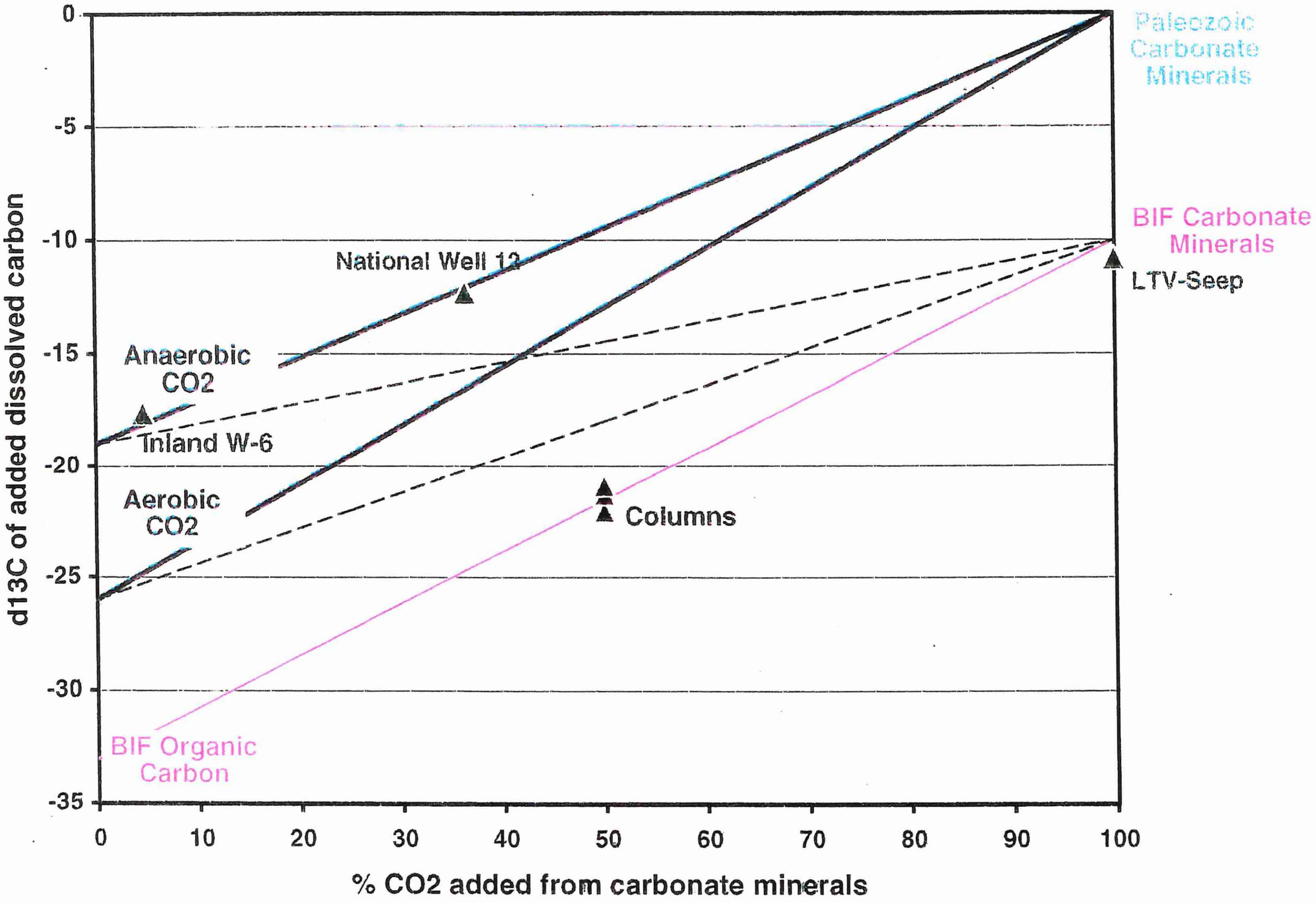
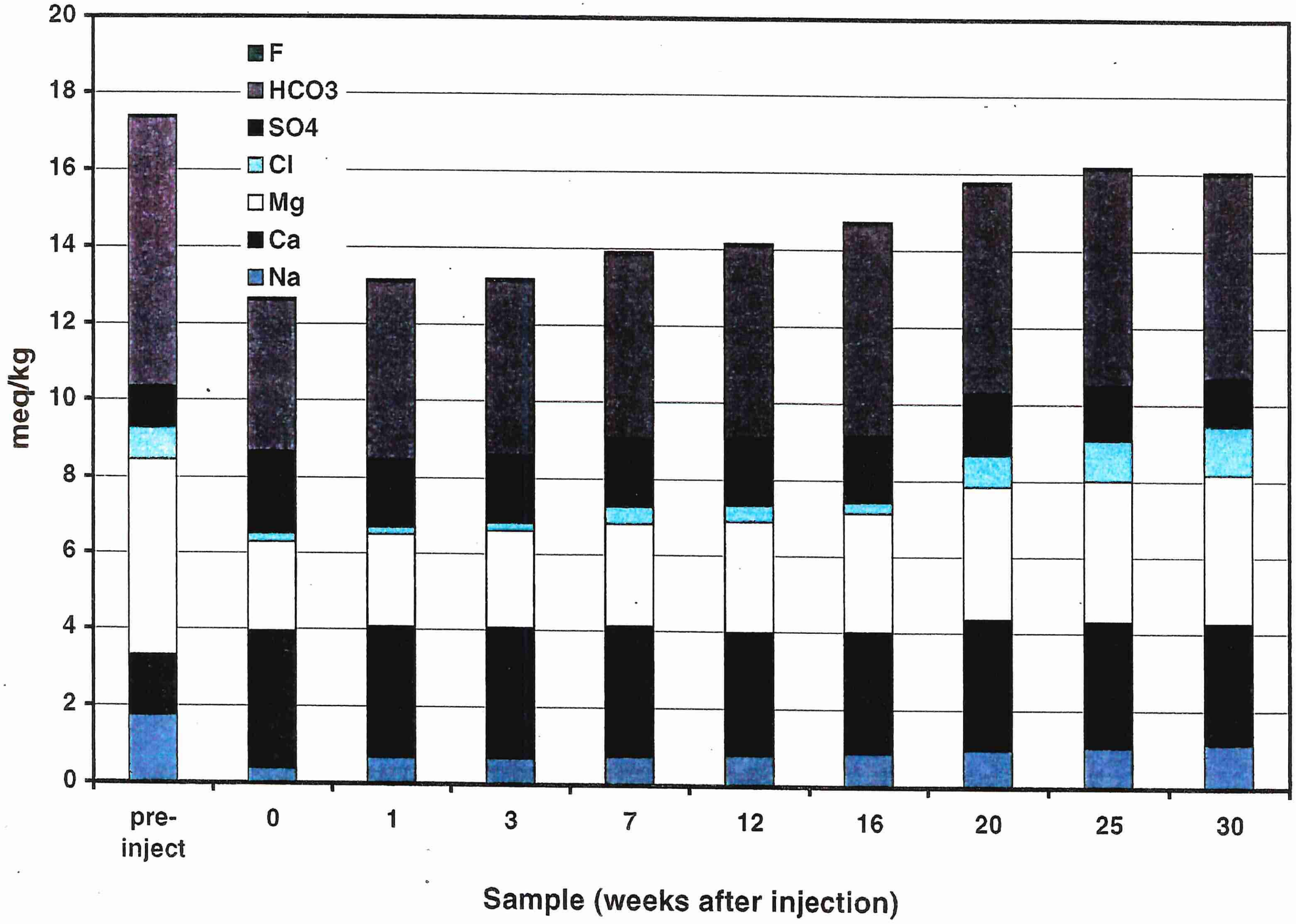

0
-5
-10
-15
-20
-25
-30
-35
d13C of added dissolved carbon
0
10
20
30
40
50
60
70
80
90
100
% CO2 added from carbonate minerals
Paleozoic Carbonate Minerals
BIF Carbonate Minerals
LTV-Seep
National Well 12
Anaerobic CO2
Inland W-6
Aerobic CO2
Columns
BIF Organic Carbon

Figure 14

Figure 14: Carbon isotope plot. Dissolved carbon in groundwaters is a mixture of CO_2 derived by oxidation of organic carbon and $CO_3^{=}$ derived from dissolution of carbonate minerals. CO_2 derived by aerobic decay of plants in this region should have $\delta^{13}C$ between approximately −19 and −26. CO_2 derived by anaerobic decay of plants will be elevated compared to this value. Oxidation of organic carbon present in the Biwabik Iron Formation is expected to have $\delta^{13}C$ close to −33. Marine carbonate minerals have $\delta^{13}C$ close to 0, while Biwabik Iron Formation carbonate minerals have widely ranging $\delta^{13}C$, but averaging approximately −10. Water from Inland and National wells appears to have incorporated CO_2 derived from partial anaerobic decay of plant matter. Marine carbonate material, probably in the glacial tills beneath the basin, also appears to have contributed to the carbon inventory of waters from the well at National. The carbon added to water seeping from LTV's tailings basin was probably derived from dissolution of carbonate minerals within the basin following oxidation of sulfide minerals.

Samples from rainwater column experiments may contain a mixture of carbon derived from oxidation of organic matter and dissolution of Biwabik carbonate minerals.



20
18
16
14
12
10
8
6
4
2
0
meq/kg
F
HCO3
SO4
Cl
Mg
Ca
Na
pre-inject
0
1
3
7
12
16
20
25
30
Sample (weeks after injection)

Figure 15

Figure 15: Chemistry of groundwater interacting with tailings from National Steel and Pellet Company. The tailings were reacted with process waters for a period of one year prior to injection of groundwater (see text). The sample labeled "pre-inject" is the composition of water that existed in the pore fluid prior to injection of the ground water, while the sample labeled with a "0" is the composition of the groundwater before it was injected into the column. All other sample compositions are that of the water at the indicated number of weeks after the injection process was completed. Except for apparent mixing of some of the original pore fluid into the system, their appeared to be limited change in chemistry after the injection process was completed. After 30 weeks, the final major element composition of the pore fluid appears to be a simple mixture of the two starting fluids.

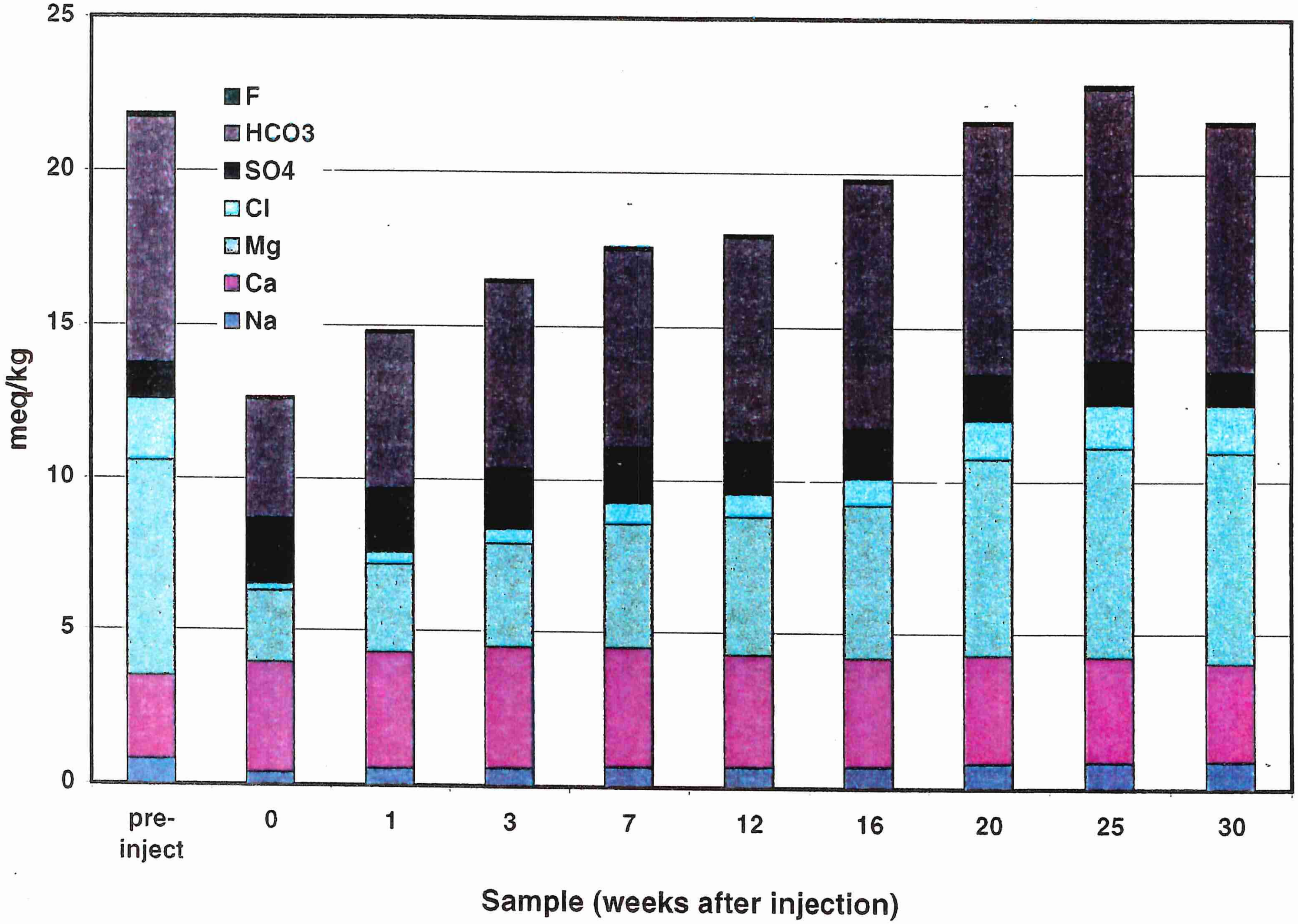

25
20
15
10
5
0
meq/kg
F
HCO3
SO4
Cl
Mg
Ca
Na
pre-inject
0
1
3
7
12
16
20
25
30
Sample (weeks after injection)

Figure 16

Figure 16: Chemistry of groundwater interacting with tailings from Inland Steel. Procedures and description are same as for experiment described in caption of Fig. 15 except that the tailings in this experiment were from Inland Steel. As was the case in groundwater experiments with tailings from National Steel and Pellet, the major element composition of the pore fluids in this experiment appears to be a simple mixture of the two starting fluids. There is little indication of reaction taking place between the groundwater and minerals in the tailings.

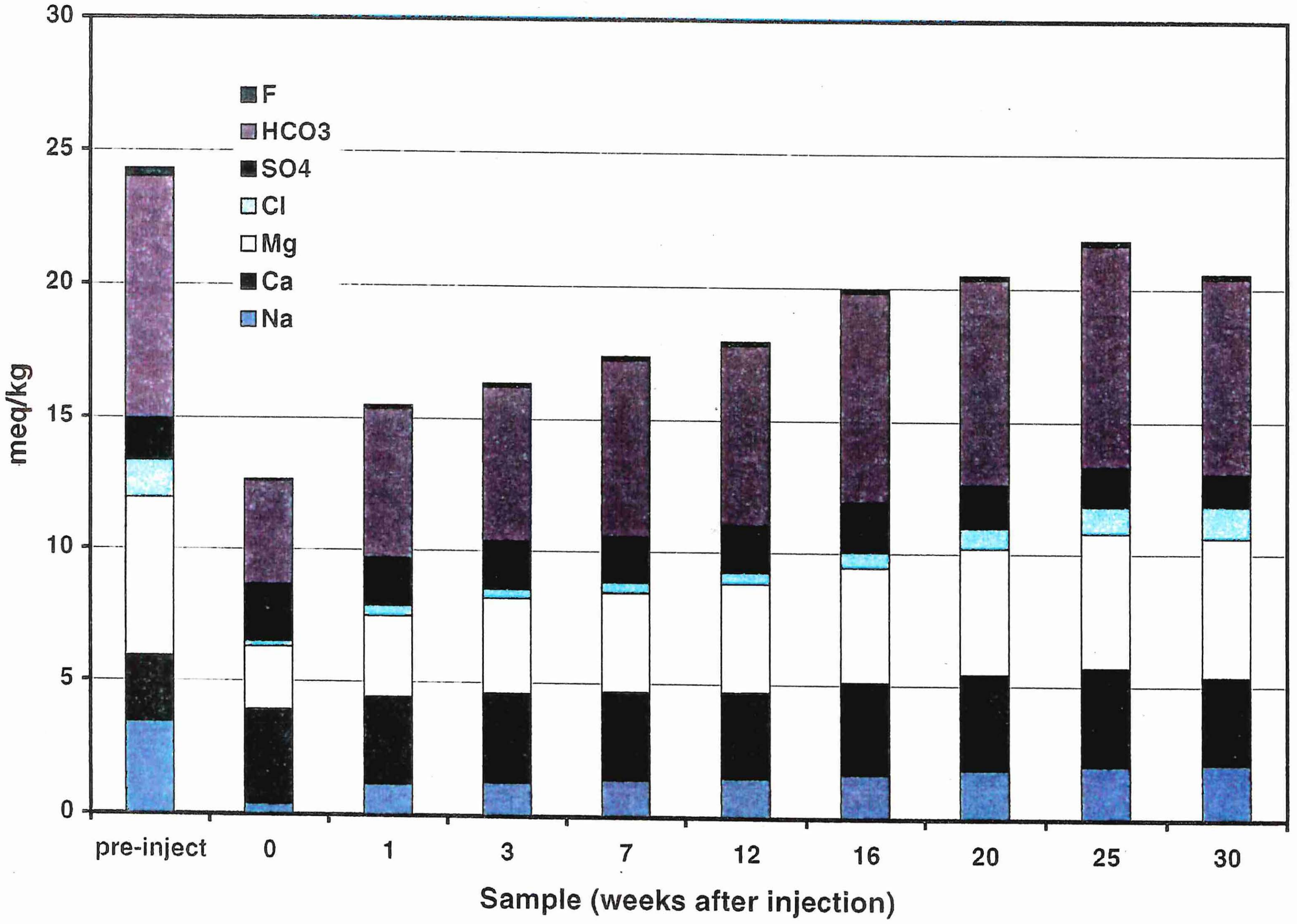

30
25
20
15
10
5
0
meq/kg
F
HCO3
SO4
Cl
Mg
Ca
Na
pre-inject
0
1
3
7
12
16
20
25
30
Sample (weeks after injection)

Figure 17

Figure 17: Chemistry of groundwater interacting with tailings from LTV Steel. Procedures and description are same as for experiment described in caption of Fig. 15 except that the tailings in this experiment were from Inland Steel. As was the case in the other groundwater experiments, the major element composition of the pore fluids in these experiments appears to be a simple mixture of the two starting fluids. There is little indication of reaction taking place between the groundwater and minerals in the tailings.

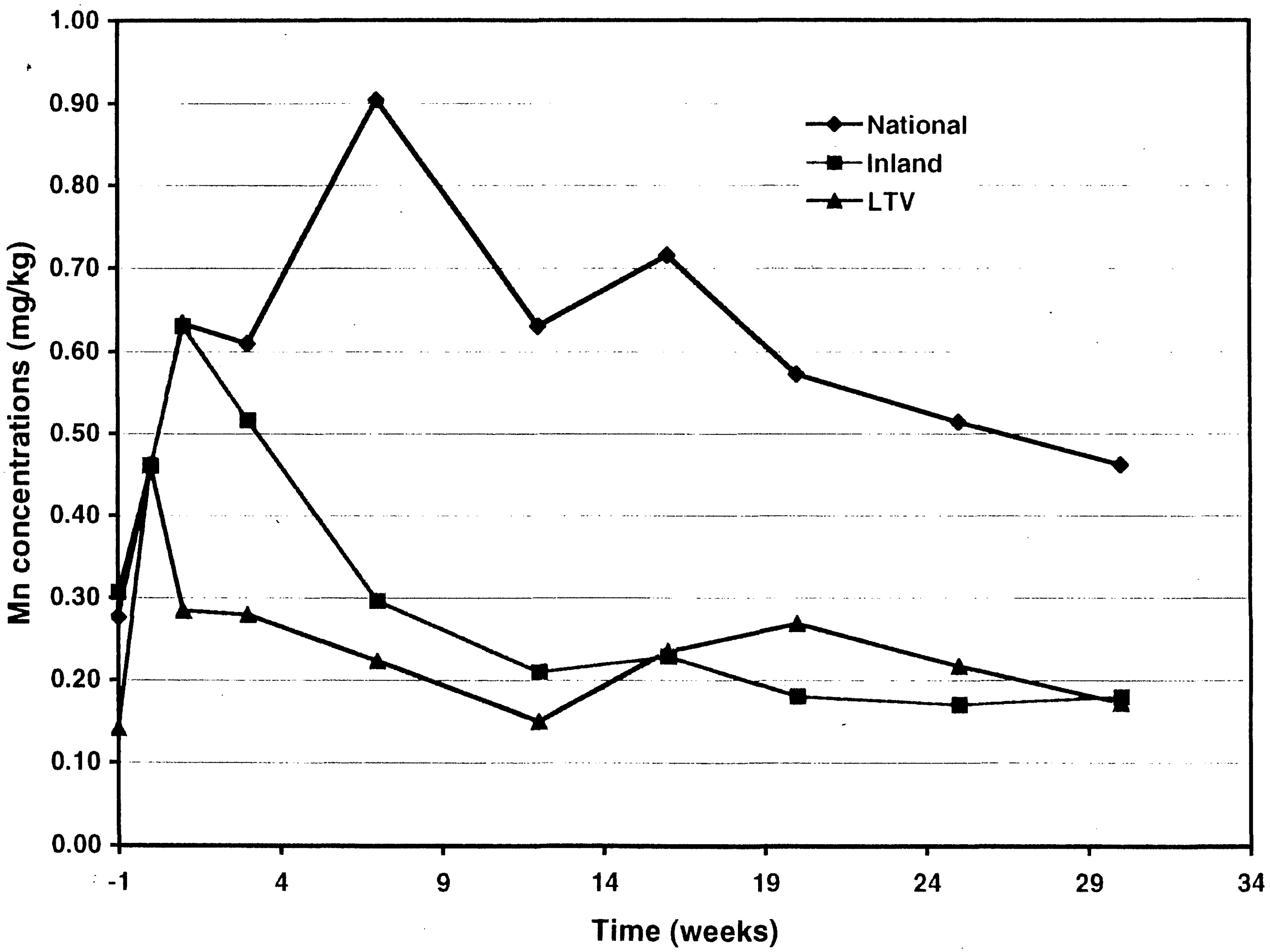

Mn concentrations (mg/kg)
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
-1
4
9
14
19
24
29
34
Time (weeks)
National
Inland
LTV

Figure 18

Figure 18: Mn concentration as a function of time in experiments conducted between groundwater and tailings in long-term column experiments. Concentrations at time=-1 represent those existing in the pore fluid prior to injection of the groundwater while those at time=0 weeks represent the composition of the groundwater before it was injected. Thereafter the concentrations represent the compositions of samples collected at the indicated number of weeks after injection of groundwater was completed. Mn concentrations increased slightly at the beginning of the experiments, but decreased again to values close to those existing in the initial pore fluid by the end of the experiment. Mn concentrations are probably controlled by saturation with respect to $MnCO_3$ (see Mn section).

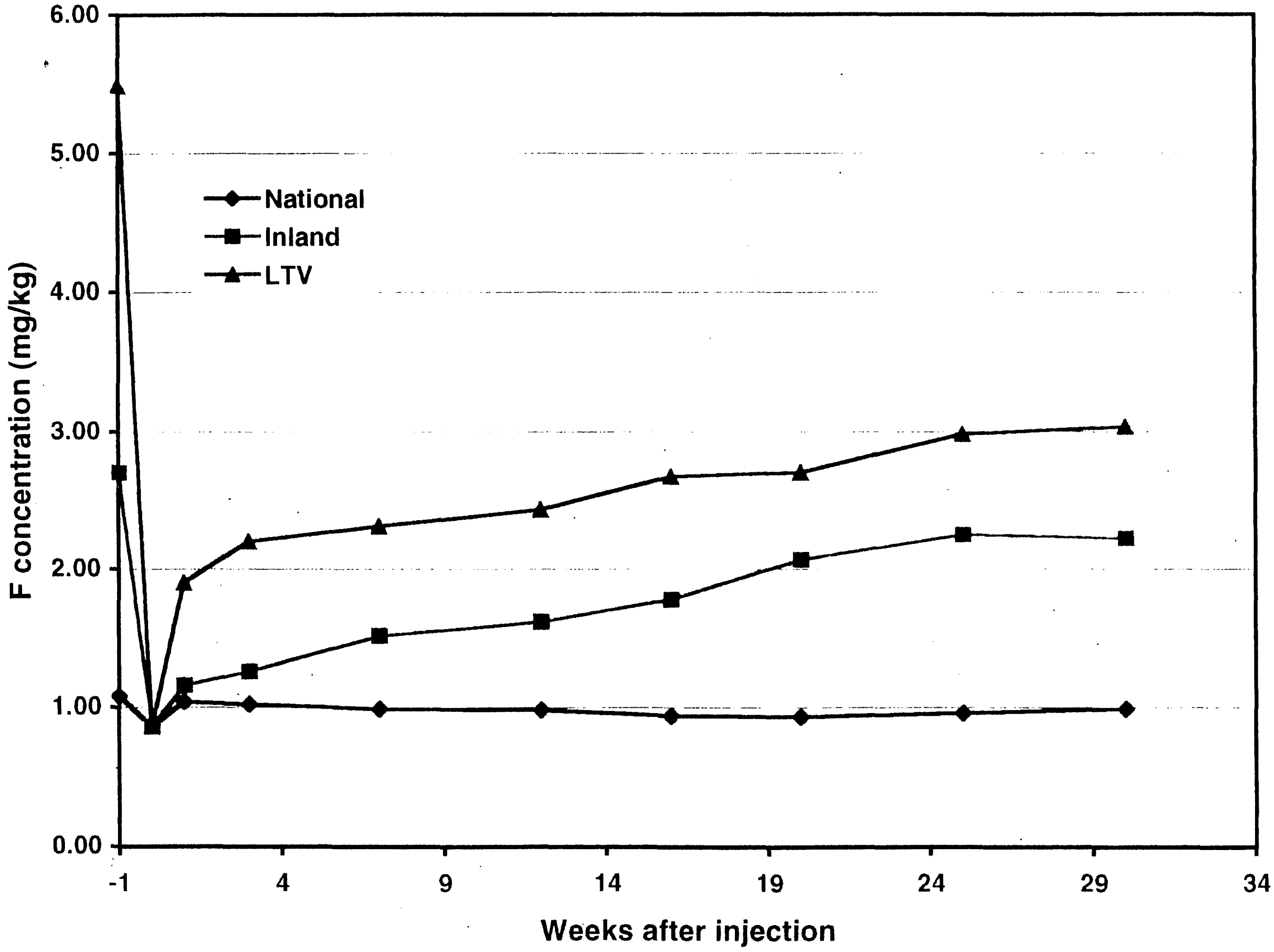

6.00
5.00
4.00
3.00
2.00
1.00
0.00
F concentration (mg/kg)
National
Inland
LTV
-1
4
9
14
19
24
29
34
Weeks after injection

Figure 19

Figure 19: F concentration as a function of time in experiments conducted between groundwater and tailings in long-term column experiments (see caption for Fig. 17). As was the case for the major elements (see Figs. 15-17), the concentrations of F appear to represent a mixture between the initial pore fluid and the injected groundwater.

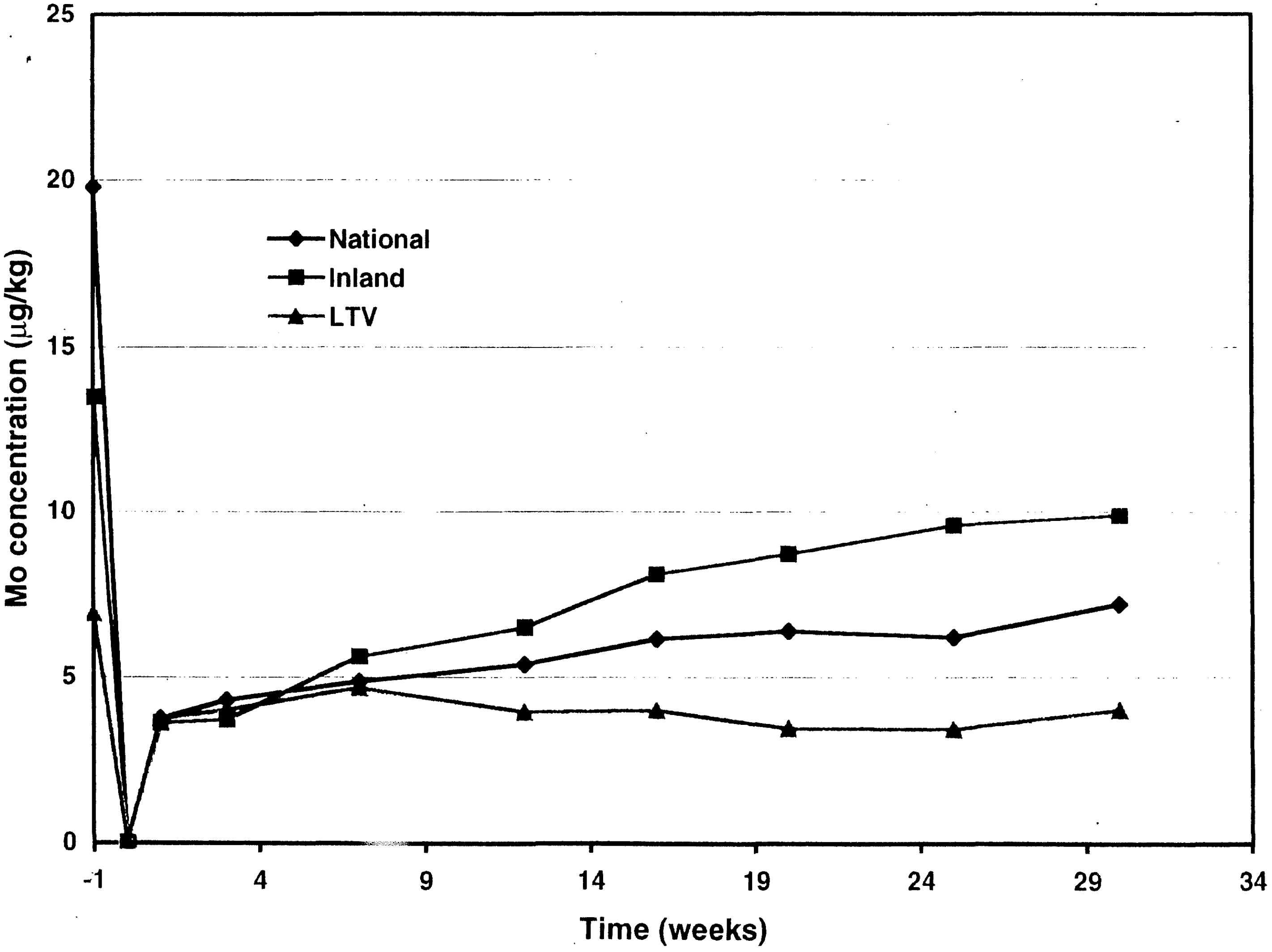
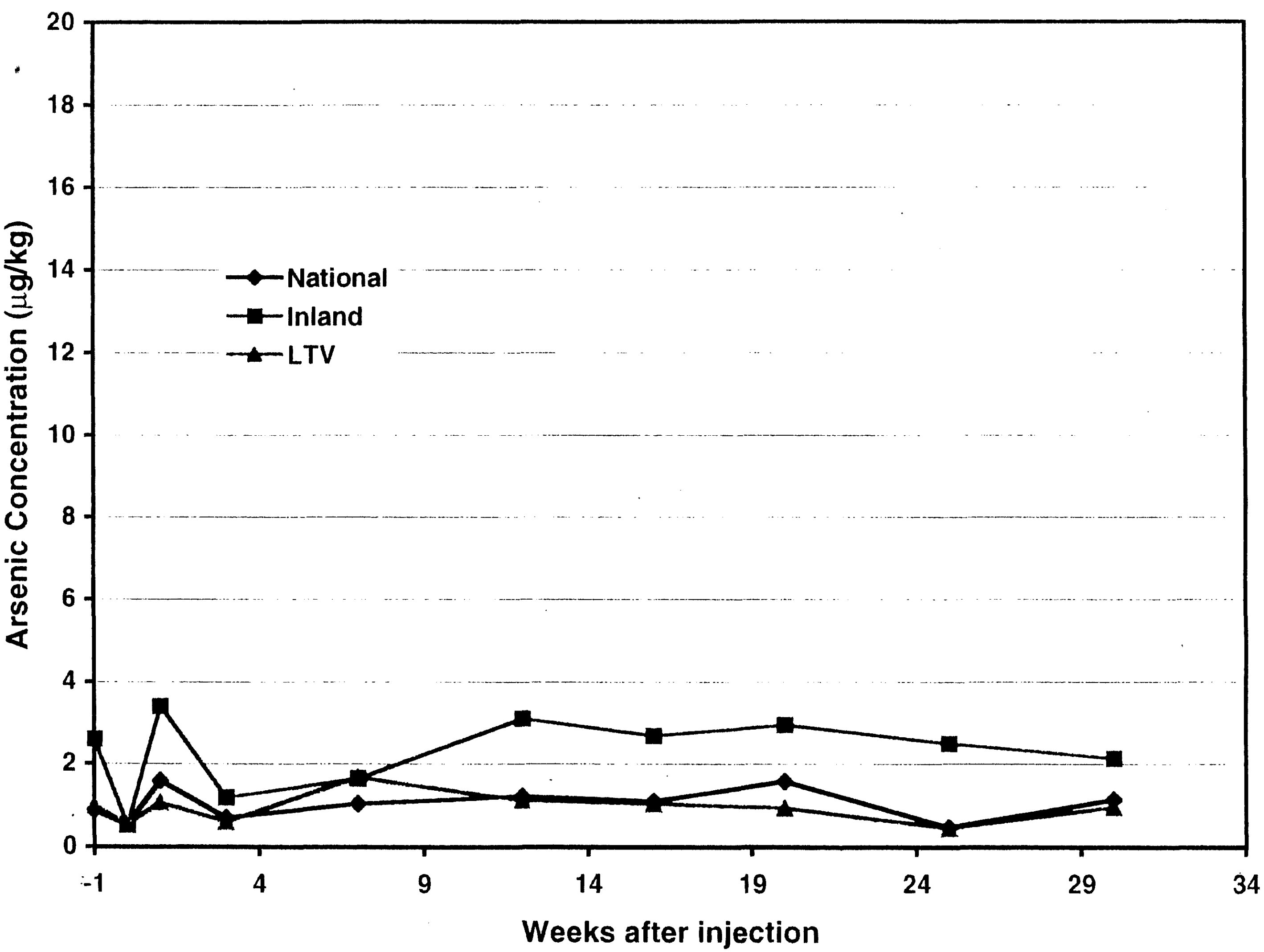

25
20
15
10
5
0
Mo concentration (µg/kg)
National
Inland
LTV
-1
4
9
14
19
24
29
34
Time (weeks)

Figure 20

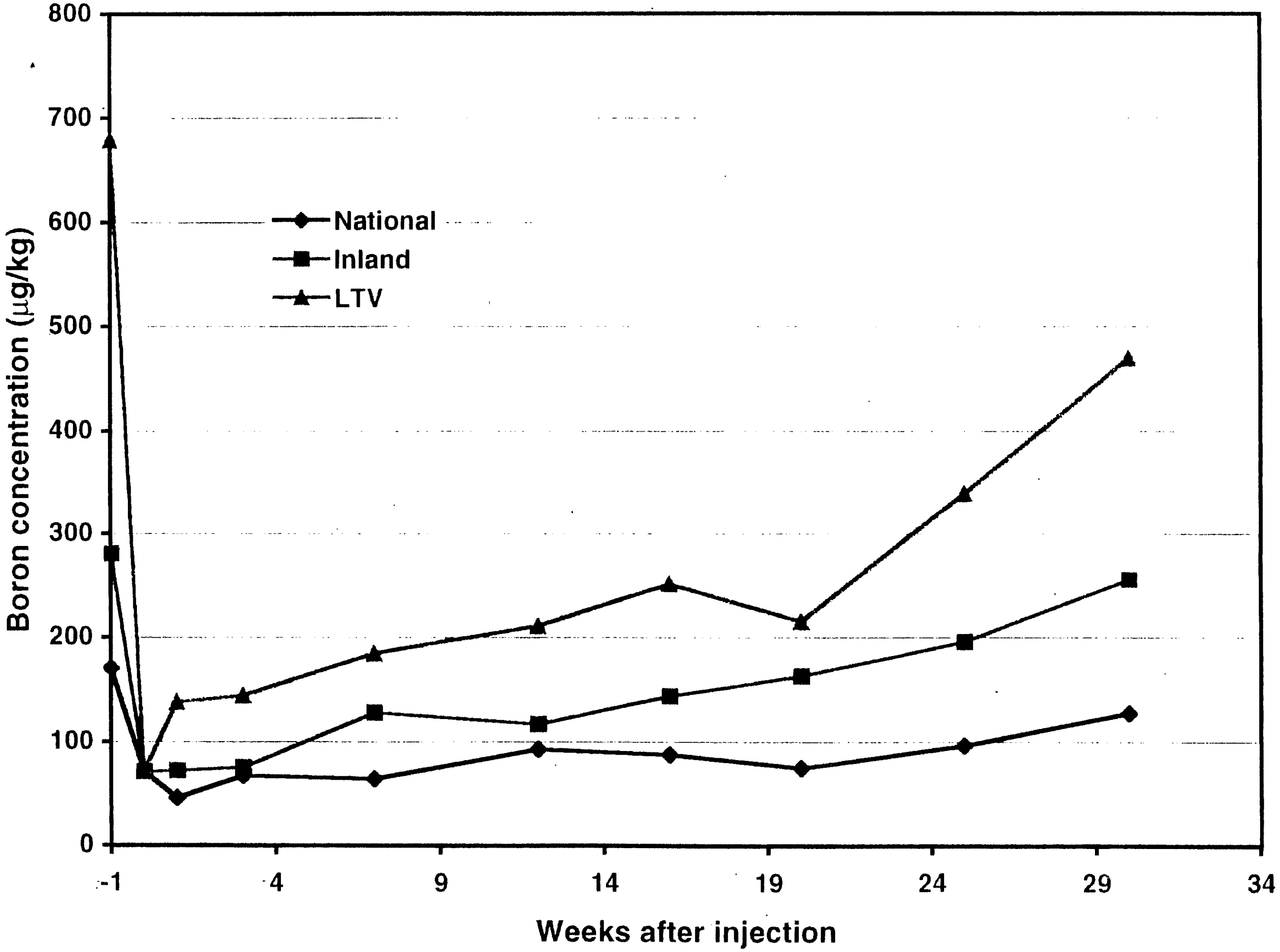
Figure 20: Molybdenum concentration as a function of time in experiments conducted between groundwater and tailings in long-term column experiments (see caption for Fig. 18). Although some Mo was mobilized into the groundwater immediately after injection, Mo concentrations remained low throughout these experiments.



20
18
16
14
12
10
8
6
4
2
0
Arsenic Concentration (μg/kg)
National
Inland
LTV
-1
4
9
14
19
24
29
34
Weeks after injection

Figure 21

Figure 21: Arsenic concentration as a function of time in experiments conducted between groundwater and tailings in long-term column experiments (see caption for Fig. 18). Arsenic concentrations remained very low throughout all groundwater/tailings experiments conducted in this investigation.



800
700
600
500
400
300
200
100
0
Boron concentration (μg/kg)
National
Inland
LTV
-1
4
9
14
19
24
29
34
Weeks after injection

Figure 22

Figure 22: Boron concentration as a function of time in experiments conducted between groundwater and tailings in long-term column experiments (see caption for Fig. 18). As was the case for F and the major elements, the concentrations of Boron in the last sample represents a mixture of B from the two source fluids (ground water and initial pore fluid).

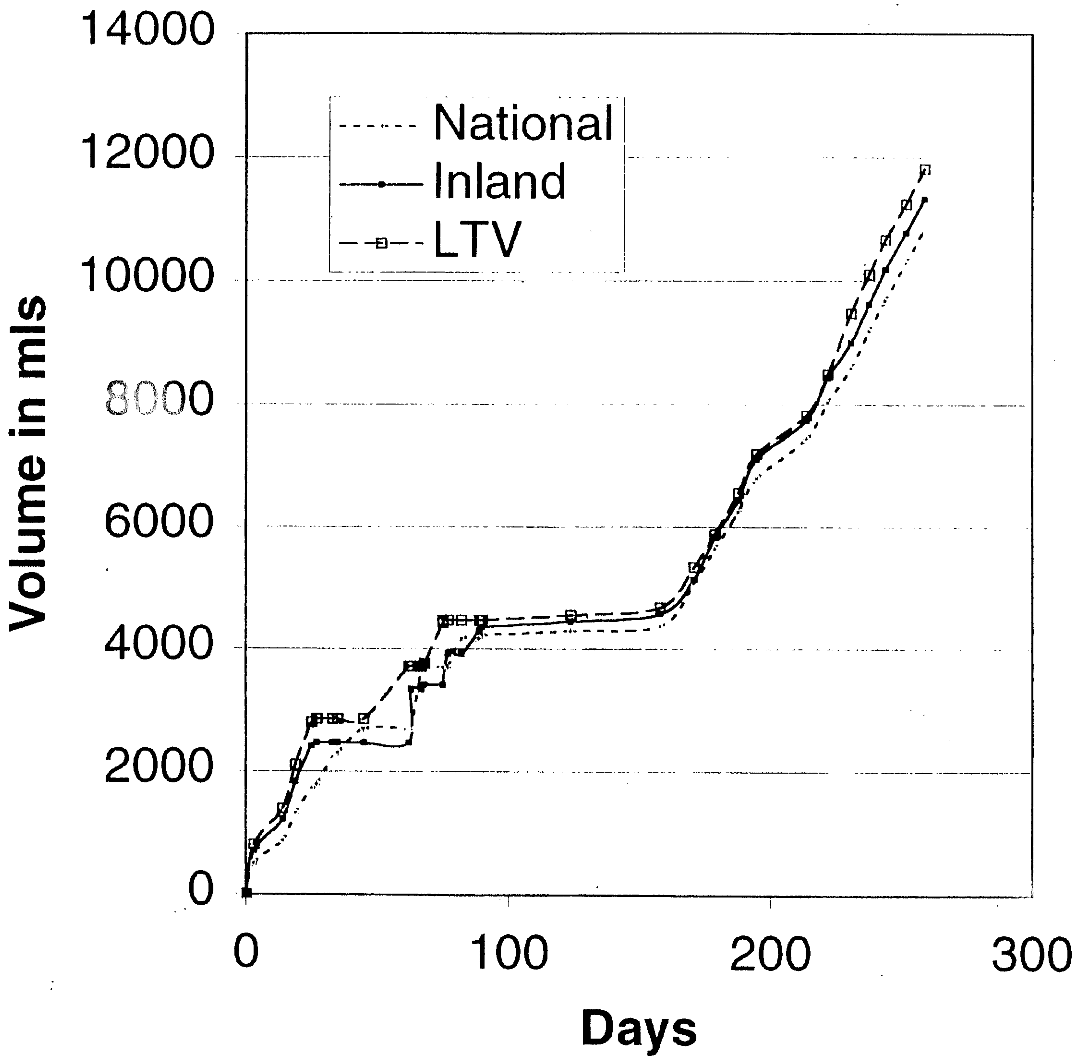

National
Inland
LTV
Volume in mls
14000
12000
10000
8000
6000
4000
2000
0
0
100
200
300
Days

Figure 23

Figure 23: Volume of water as a function of time in experiments reacting taconite tailings with synthetic "rain water". As was the case for the groundwater experiments, tailings were reacted with process waters for a period of one year prior to infiltration with the rainwater. Rainwater used in the experiments was deionized water that was allowed to remain in contact with the atmosphere throughout the experiment. In general, there was an initial period of rapid flow until approximately 4.5 l of water had passed through the column. This was followed by a stagnant period when water was allowed to react with the tailings for approximately three months (12 weeks). After this flow commenced at a rapid rate until 11 to 12 l of water had passed through the column at which time flow was again stopped. In this way we were able to simulate the effects of flow and equilibration on the composition of rainwaters that might infiltrate tailings in a pore fluid environment.

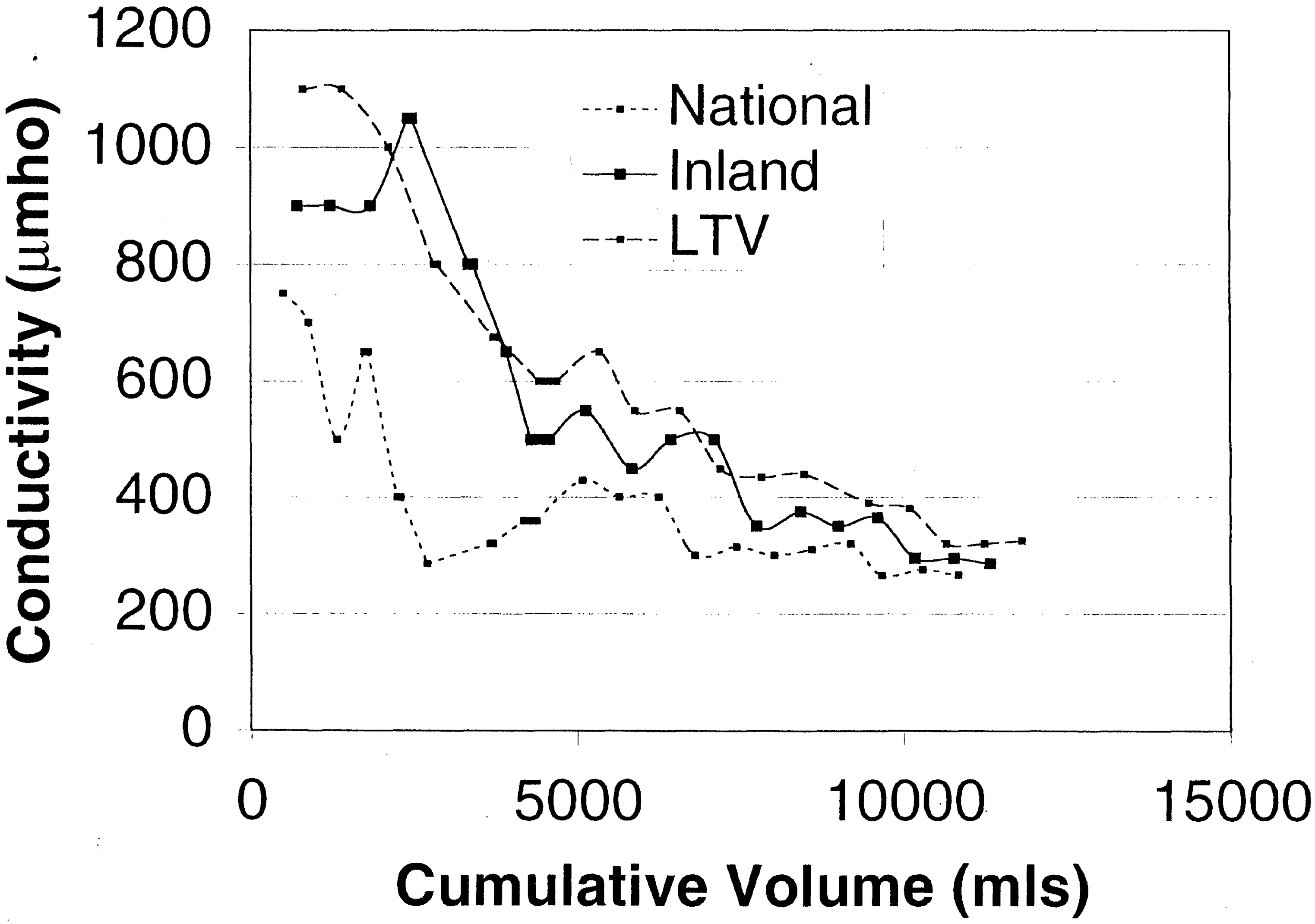
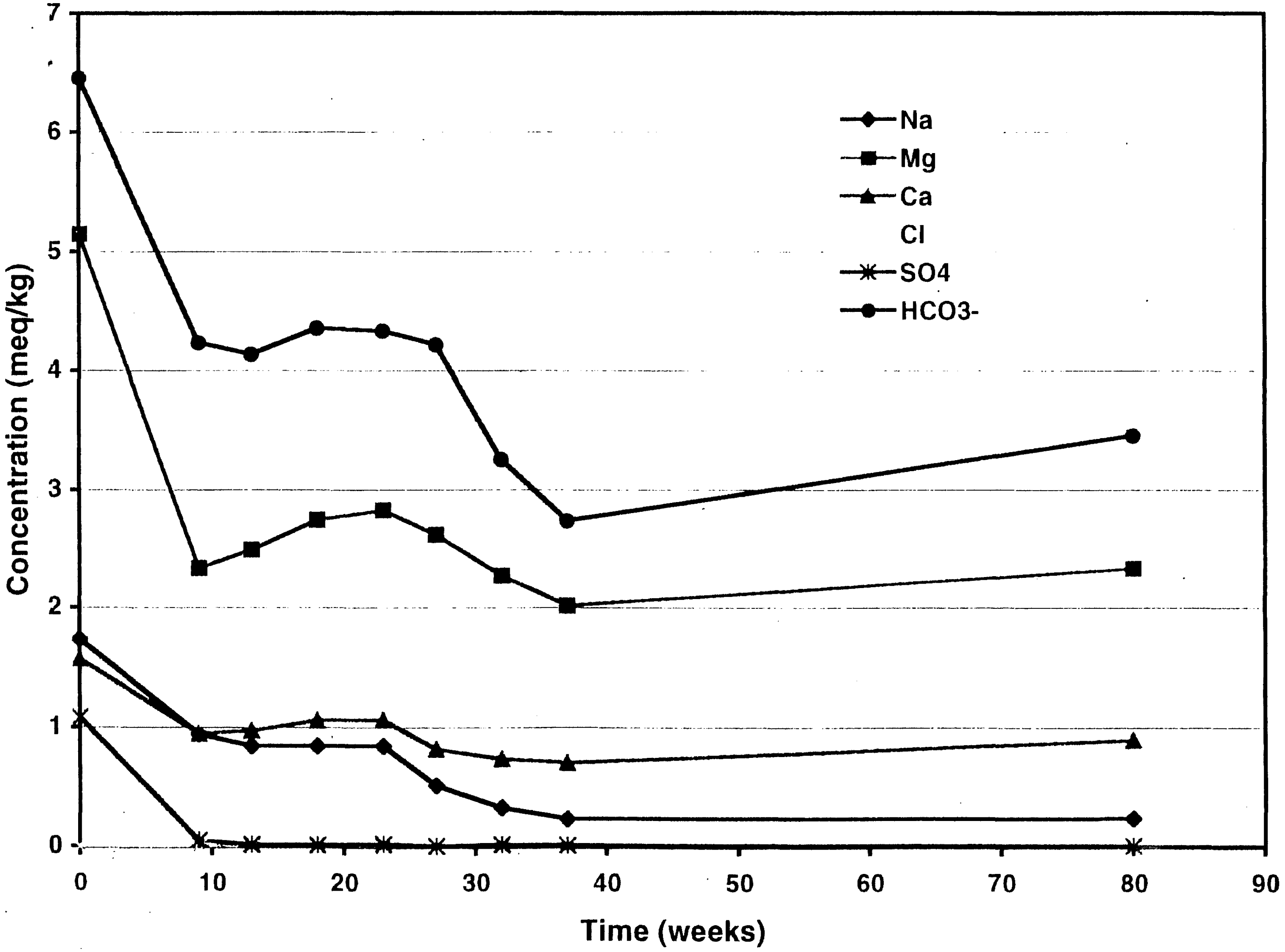

1200
1000
800
600
400
200
0
Conductivity (μmho)
0
5000
10000
15000
Cumulative Volume (mls)
National
Inland
LTV

Figure 24

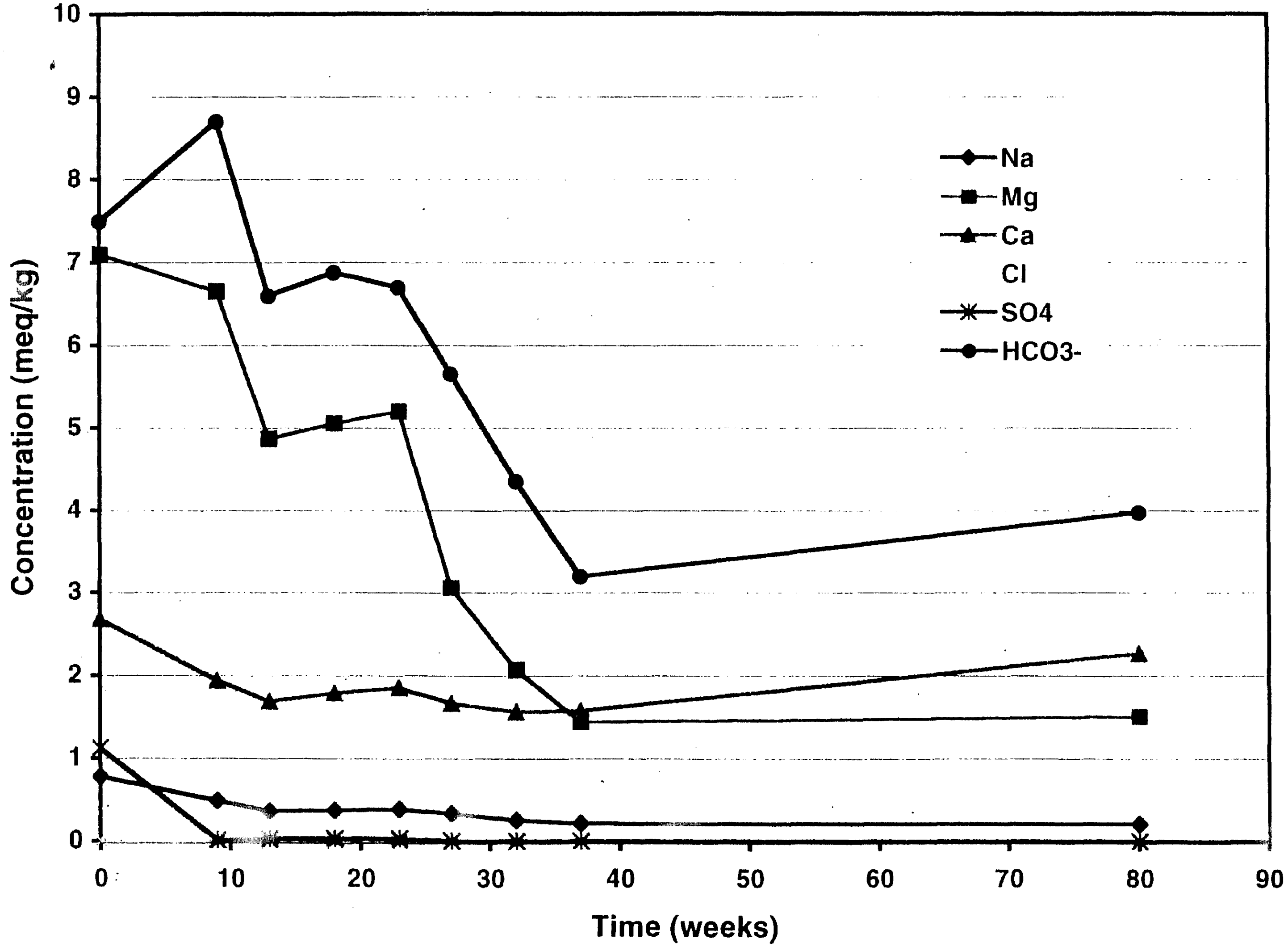
Figure 24. Conductivity as a function of flow volume in experiments between tailings and "rainwater" (see caption for Fig. 23). Pore volumes in these experiments is estimated to be no more than 2000 mls. Thus, conductivity remained high throughout the experiments indicating significant and continuos rapid dissolution of tailings throughout the experiments.



7
6
5
4
3
2
1
0
Concentration (meq/kg)
0
10
20
30
40
50
60
70
80
90
Time (weeks)
Na
Mg
Ca
Cl
SO4
HCO3-

Figure 25

Figure 25: Major element concentrations as a function of time in experiments between "rainwater" and tailings from National Steel and Pellet Company (See Fig. 23). Cl and SO4 were quickly and efficiently rinsed from the system, but HCO_3, Mg, Ca, and Na reached appreciable concentrations throughout the experiment. Isotopic data (see carbon isotope section) suggest that the HCO_3 in these experiments was derived from a mixture $CO_3^=$ derived from dissolution of carbonate minerals and CO_2 derived from oxidation of organic carbon present in the Biwabik Iron Formation. Carbonate mineral dissolution combined with cation exchange processes may account for the relative distributions of Mg, Ca, and Na.



Concentration (meq/kg)
0
1
2
3
4
5
6
7
8
9
10
Time (weeks)
0
10
20
30
40
50
60
70
80
90
Na
Mg
Ca
Cl
SO4
HCO3-

Figure 26

Figure 26: Major element concentrations as a function of time in experiments between "rainwater" and tailings from Inland Steel (See Fig. 23). As was the case in all rainwater experiments, Cl and SO_4 were quickly and efficiently rinsed from the system, but HCO_3, Mg, Ca, and Na maintained appreciable concentrations throughout the experiment. Isotopic data (see carbon isotope section) suggest that the HCO_3 in these experiments was derived from a mixture $CO_3^=$ derived from dissolution of carbonate minerals and CO_2 derived from oxidation of organic carbon present in the Biwabik Iron Formation. Carbonate mineral dissolution combined with cation exchange processes may account for the relative distributions of Mg, Ca, and Na.

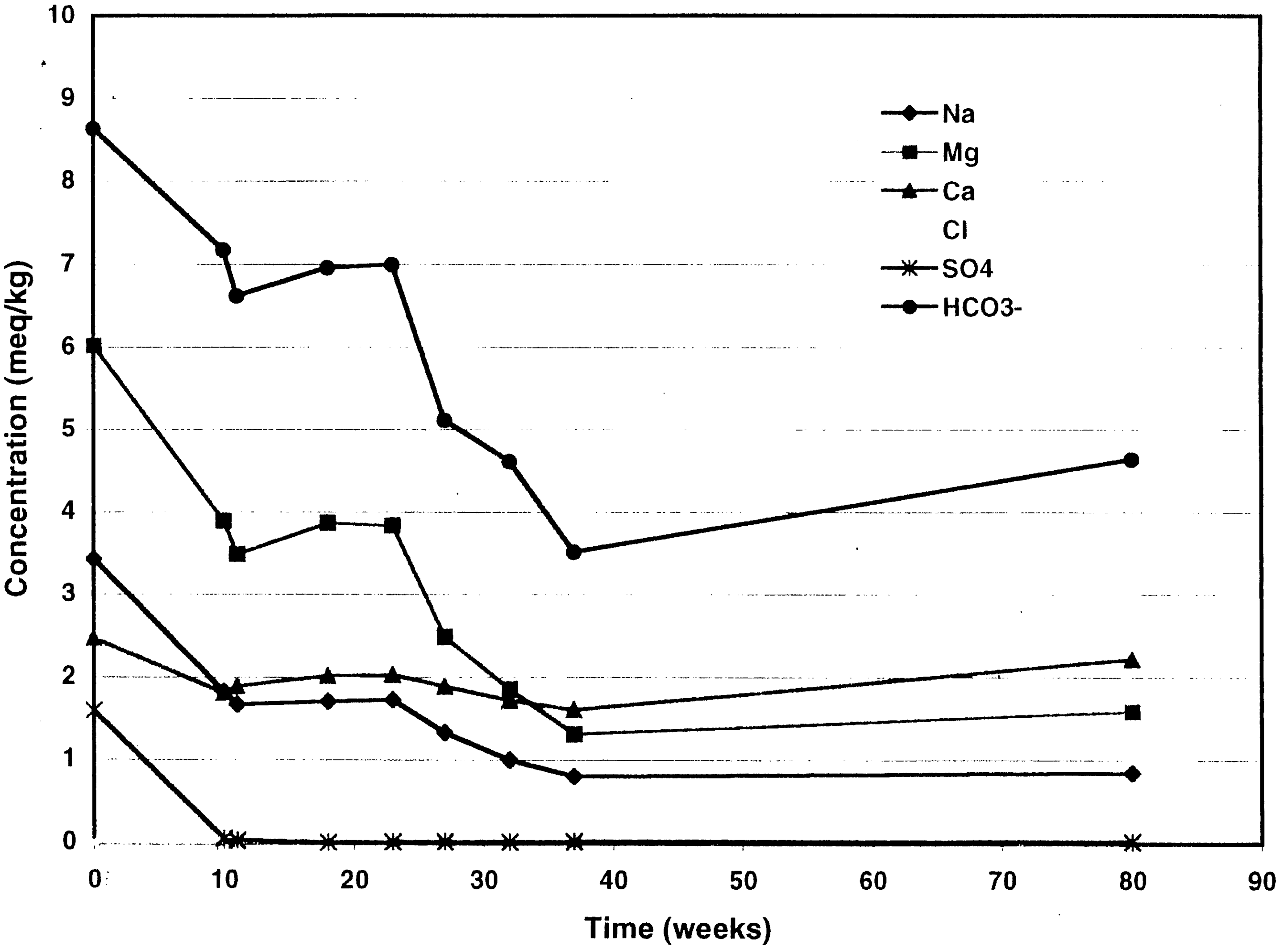

10
9
8
7
6
5
4
3
2
1
0
Concentration (meq/kg)
0
10
20
30
40
50
60
70
80
90
Time (weeks)
Na
Mg
Ca
Cl
SO4
HCO3-

Figure 27

Figure 27: Major element concentrations as a function of time in experiments between "rainwater" and tailings from LTV steel (See Fig. 23). As was the case in all rainwater experiments, Cl and SO_4 were quickly and efficiently rinsed from the system, but HCO_3, Mg, Ca, and Na maintained appreciable concentrations throughout the experiment. Isotopic data (see carbon isotope section) suggest that the HCO_3 in these experiments was derived from a mixture $CO_3^{=}$ derived from dissolution of carbonate minerals and CO_2 derived from oxidation of organic carbon present in the Biwabik Iron Formation. Carbonate mineral dissolution combined with cation exchange processes may account for the relative distributions of Mg, Ca, and Na.

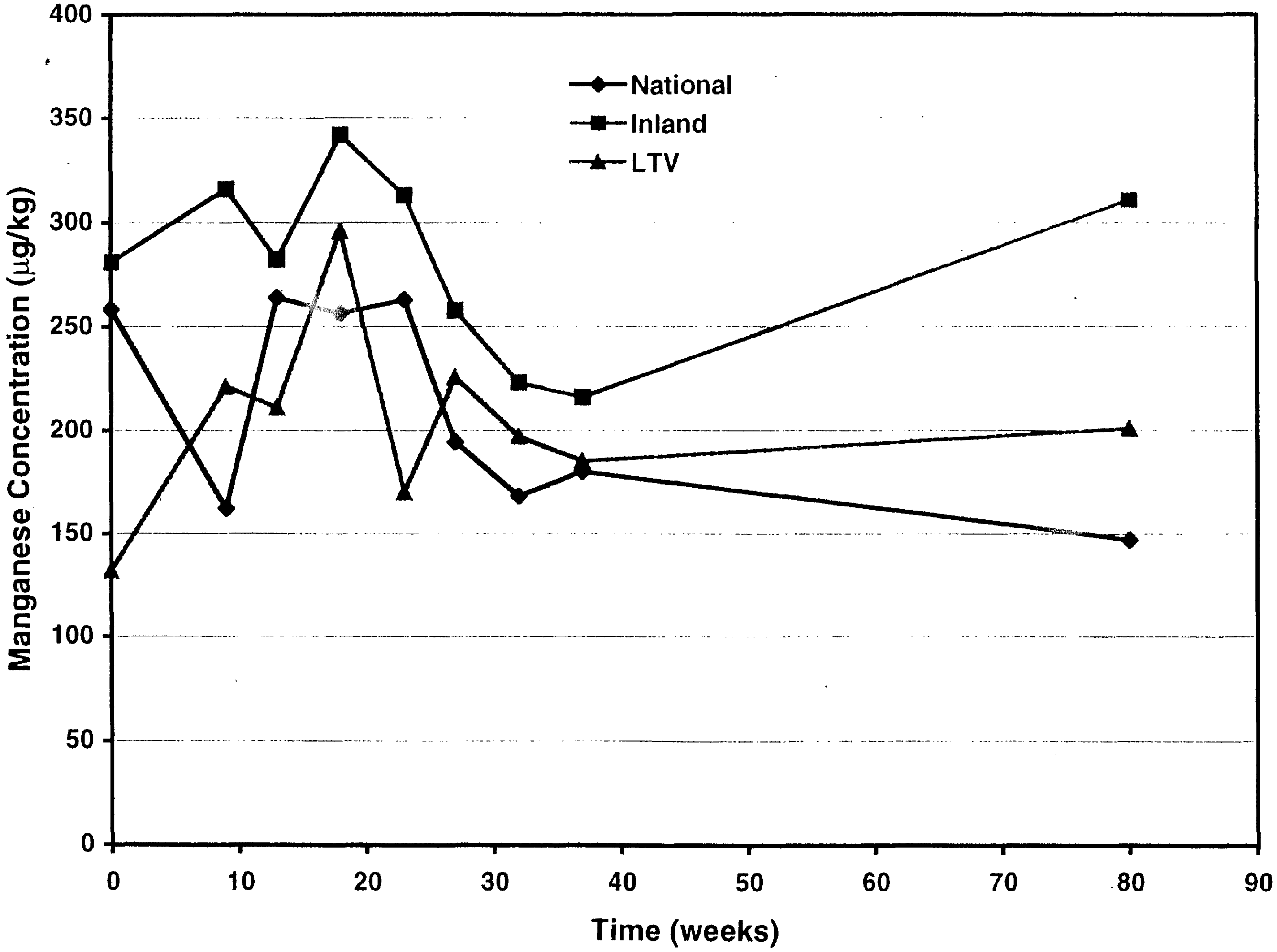

National
Inland
LTV
Manganese Concentration (μg/kg)
400
350
300
250
200
150
100
50
0
0
10
20
30
40
50
60
70
80
90
Time (weeks)

Figure 28

Figure 28: Manganese concentration as a function of time in rainwater experiments (see Fig. 23). Manganese concentrations remained appreciable and nearly constant throughout these experiments indicating a likely solubility control, most likely with respect to $MnCO_3$.

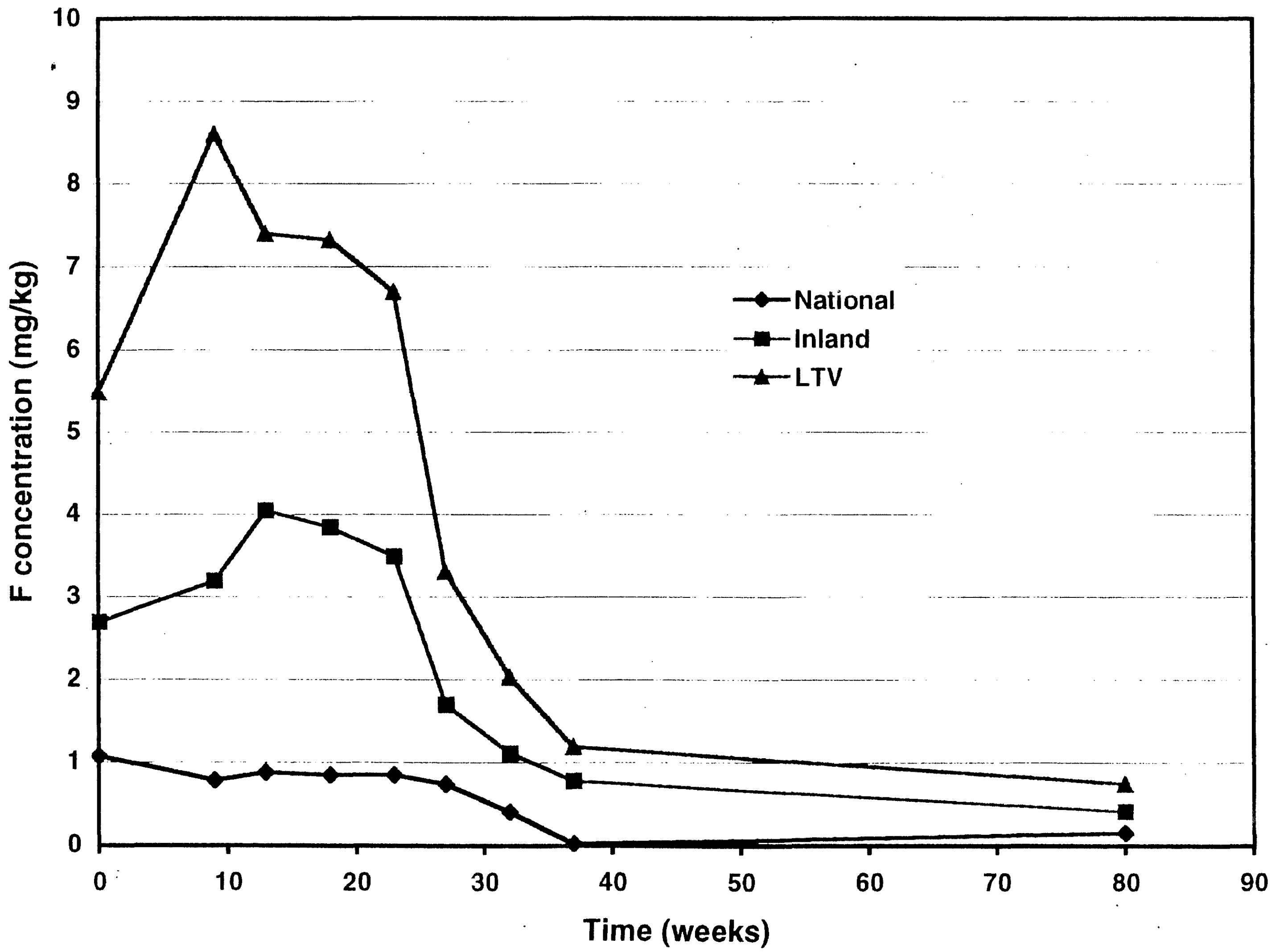

10
9
8
7
6
5
4
3
2
1
0
F concentration (mg/kg)
0
10
20
30
40
50
60
70
80
90
Time (weeks)
National
Inland
LTV

Figure 29

Figure 29: Fluoride concentration as a function of time in rainwater experiments (see Fig. 23). Unlike Cl and SO4 (see Figs. 25-27), fluoride did not rinse easily out of tailings in any of these experiments. Furthermore, its concentrations at any one time in an experiment appeared to be related more to the number of pore volumes that passed through the system (e.g., an adsorption/desorption process) rather than to equilibrium with respect to a mineral (CaF_2).

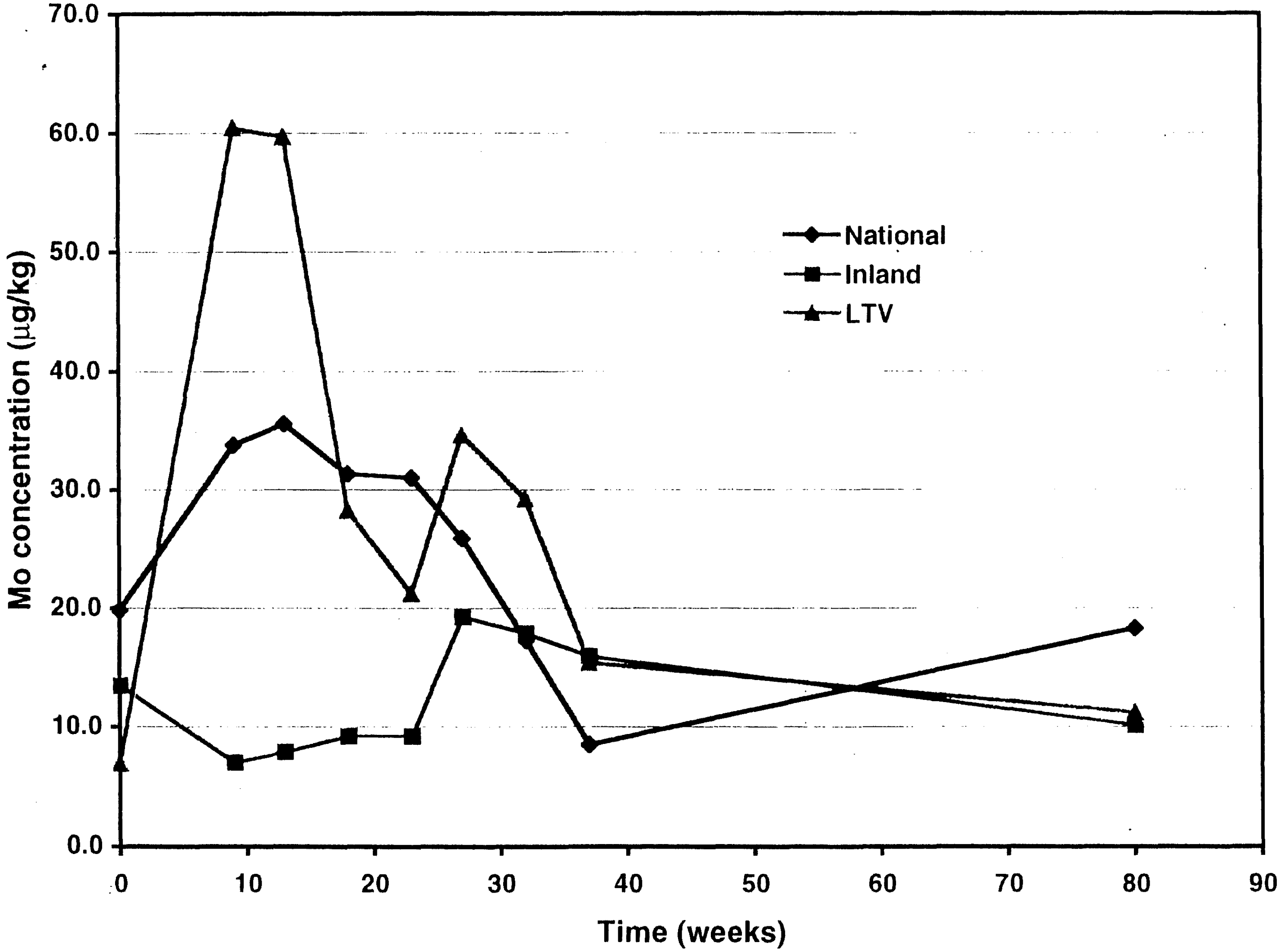
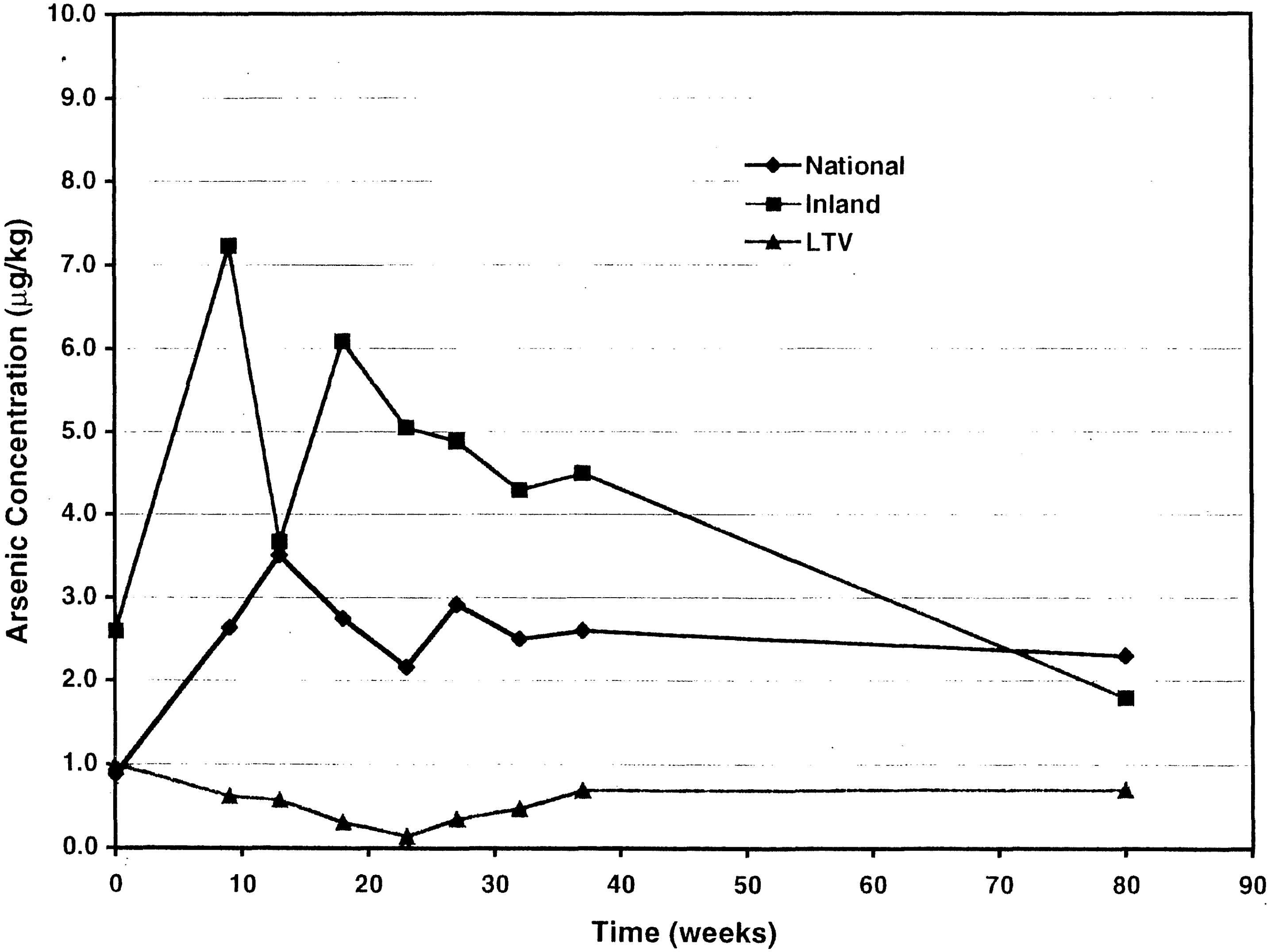

70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Mo concentration (μg/kg)
0
10
20
30
40
50
60
70
80
90
Time (weeks)
National
Inland
LTV

Figure 30

Figure 30: Molybdenum concentrations as a function of time in rainwater experiments (see Fig. 23). Concentrations at time=0 represent those existing in the initial pore fluid prior to infiltration by "rainwater". Mo concentrations increase to relatively high levels indicating conditions became favorable for partial desorption of $MoO_4^=$ ions from the surfaces of Fe-oxide minerals during infiltration of deionized water. Continued flow of water through the columns resulted in gradual rinsing of this species out of the system, but some remained even at the end of the experiment.



10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Arsenic Concentration (μg/kg)
0
10
20
30
40
50
60
70
80
90
Time (weeks)
National
Inland
LTV

Figure 31

Figure 31: Arsenic concentrations as a function of time in rainwater experiments (see Fig. 23). Arsenic concentrations remained relatively low throughout these experiments indicating conditions needed for desorption of arsenic from the surfaces of Fe-oxide minerals were not encountered.

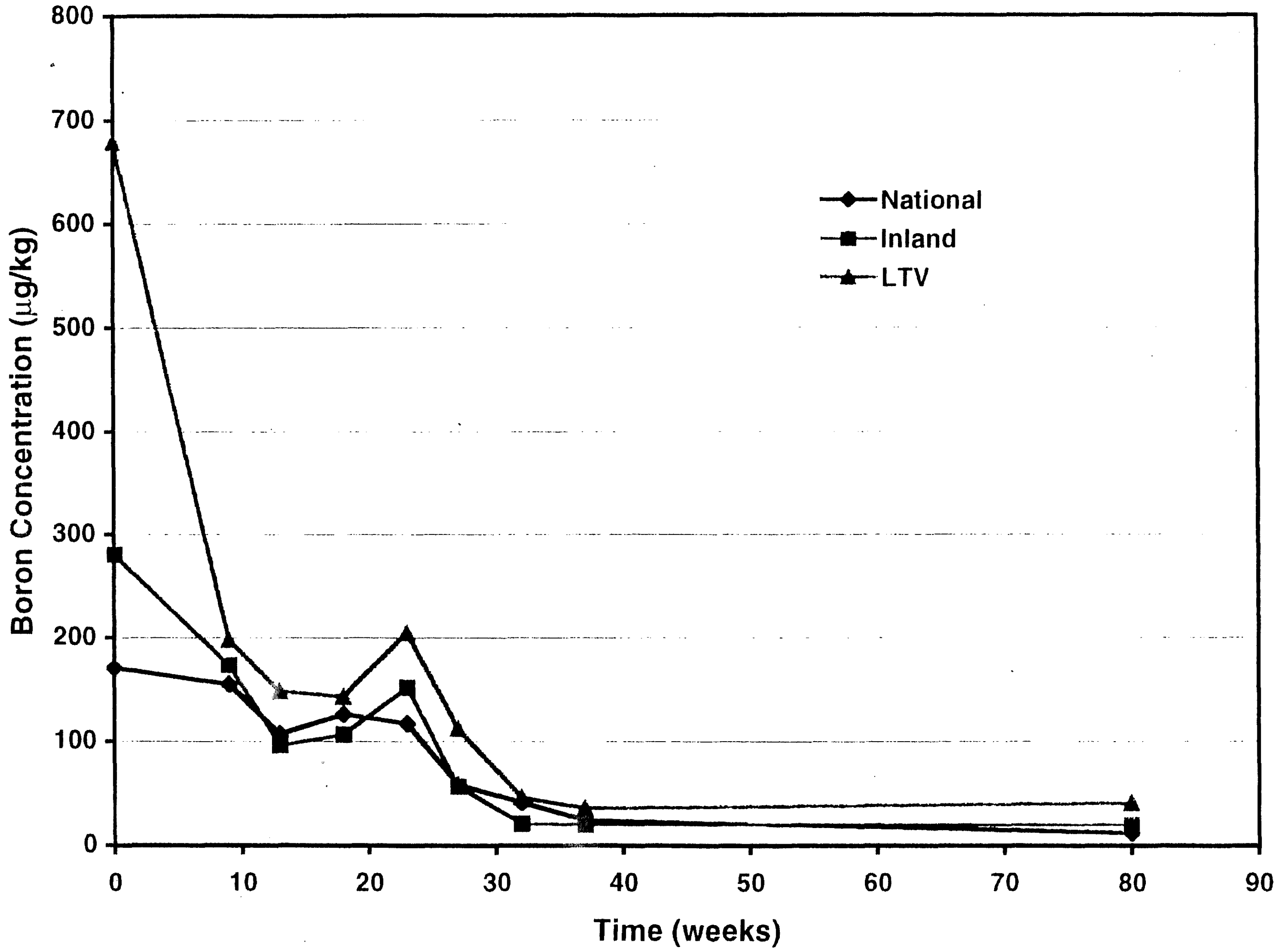

Boron Concentration (µg/kg)
800
700
600
500
400
300
200
100
0
Time (weeks)
0
10
20
30
40
50
60
70
80
90
National
Inland
LTV

Figure 32

Figure 32: Boron concentrations as a function of time in rainwater experiments (see Fig. 23). Boron appears to be gradually rinsed from tailings, although not as efficiently as either Cl or SO_4 (see Figs. 25-27). This suggests that concentrations of this element are partially controlled by adsorption/desorption reactions.

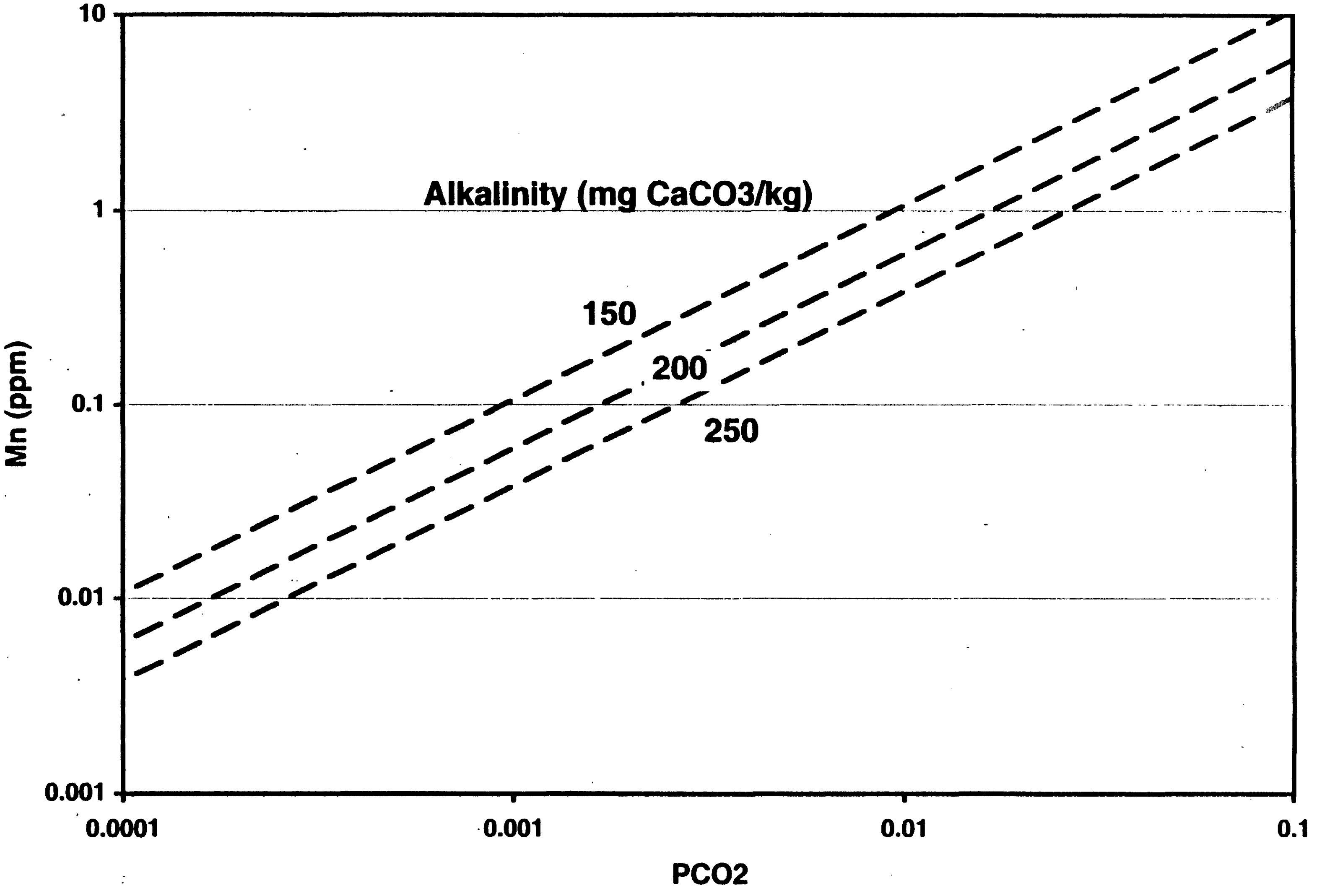
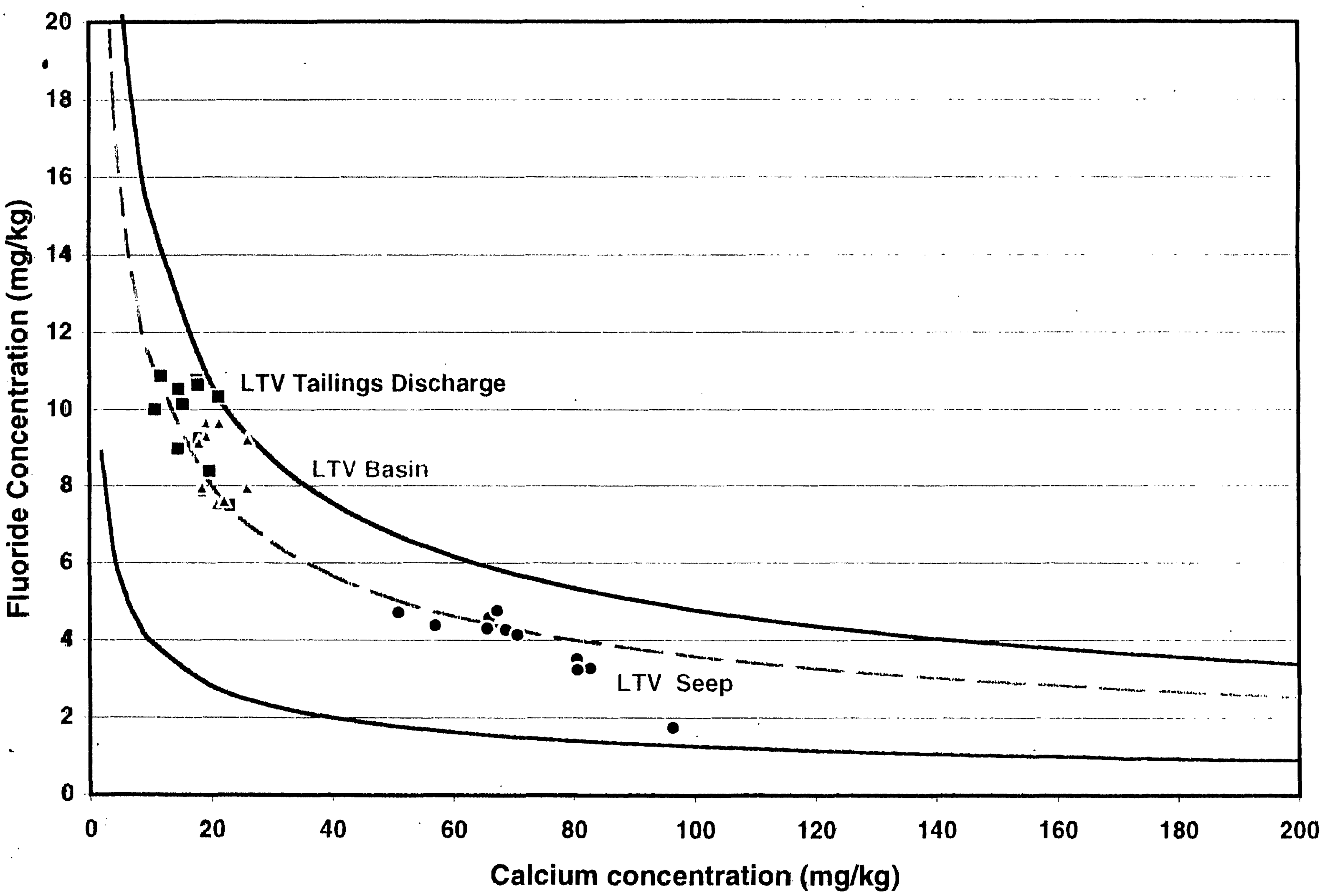

Alkalinity (mg CaCO3/kg)
150
200
250
Mn (ppm)
10
1
0.1
0.01
0.001
0.0001
0.001
0.01
0.1
PCO2

Figure 33

Figure 33: $MnCO_3$ saturation plot. Manganese concentration as a function of P_{CO2} and alkalinity. Manganese concentrations are highest in low alkalinity, high P_{CO2} waters. P_{CO2} for Inland's shallow wells and basin seeps are elevated to 0.1 atmospheres owing to degradation of buried plant matter in the subsurface (see carbon isotope section). Given P_{CO2} values in the more typical range between 0.001 and 0.01 atmospheres, Manganese concentrations should generally range between 0.05 to 1 ppm in tailings/pore fluid environments.



20
18
16
14
12
10
8
6
4
2
0
Fluoride Concentration (mg/kg)
0
20
40
60
80
100
120
140
160
180
200
Calcium concentration (mg/kg)
LTV Tailings Discharge
LTV Basin
LTV Seep

Figure 34

Figure 34: Fluorite solubility plot. Heavy lines represent range of literature values for solubility of CaF_2 in water at 25°C (log K= -9.8 to –10.96). Data for LTV's tailings basin discharges, reservoir waters, and seeps fall between these values. An intermediate value of –10.05 (dashed line) approximates the average range of values at LTV. Inland and National data are not plotted because they all fall well below this line. Fluoride and Ca concentrations in specific locations within the taconite processing lines at Inland and LTV's processing plants exceed fluorite saturation meaning that this mineral is probably initially present in the tailings.

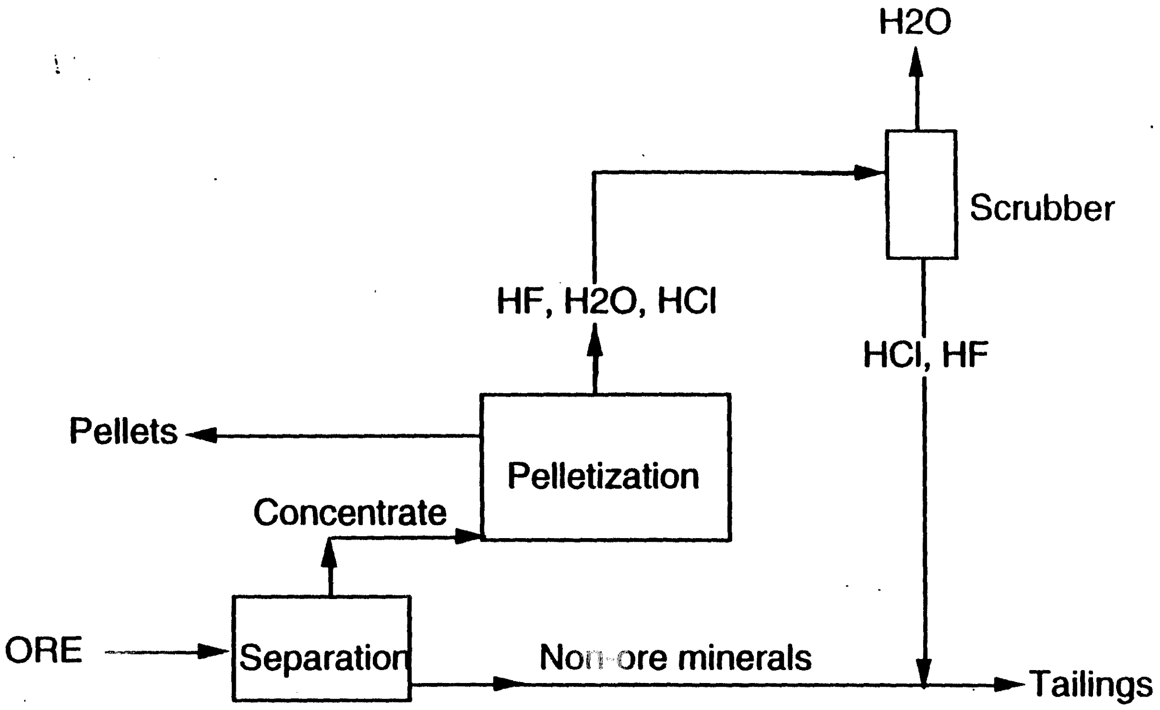

H2O
Scrubber
HF, H2O, HCl
HCl, HF
Pellets
Pelletization
Concentrate
ORE
Separation
Non-ore minerals
Tailings

Figure 35

Figure 35: Schematic diagram showing how F mobilization occurs in taconite processing plants that have wet scrubbing systems (Inland and LTV). F is initially bound in insoluble non-ore minerals (fluorapatite, amphiboles, clays) found in the primary ore. Because ore separation is not 100% efficient, a small fraction of non-ore minerals are incorporated into the concentrate. Intense heating during induration of pellets releases the F from the non-ore minerals into the air as HF. This HF is recaptured by the plant scrubber system and introduced back into the process stream as dissolved F^-. F will either remain in solution, adsorb to surfaces of minerals in the tailings, or precipitate as CaF_2 within the process stream and be diverted to the tailings basin. Because the majority of non-ore minerals are never subjected to pelletization, however, most of the F present in tailings remains locked in minerals and will not be released into waters that flow through the tailings.

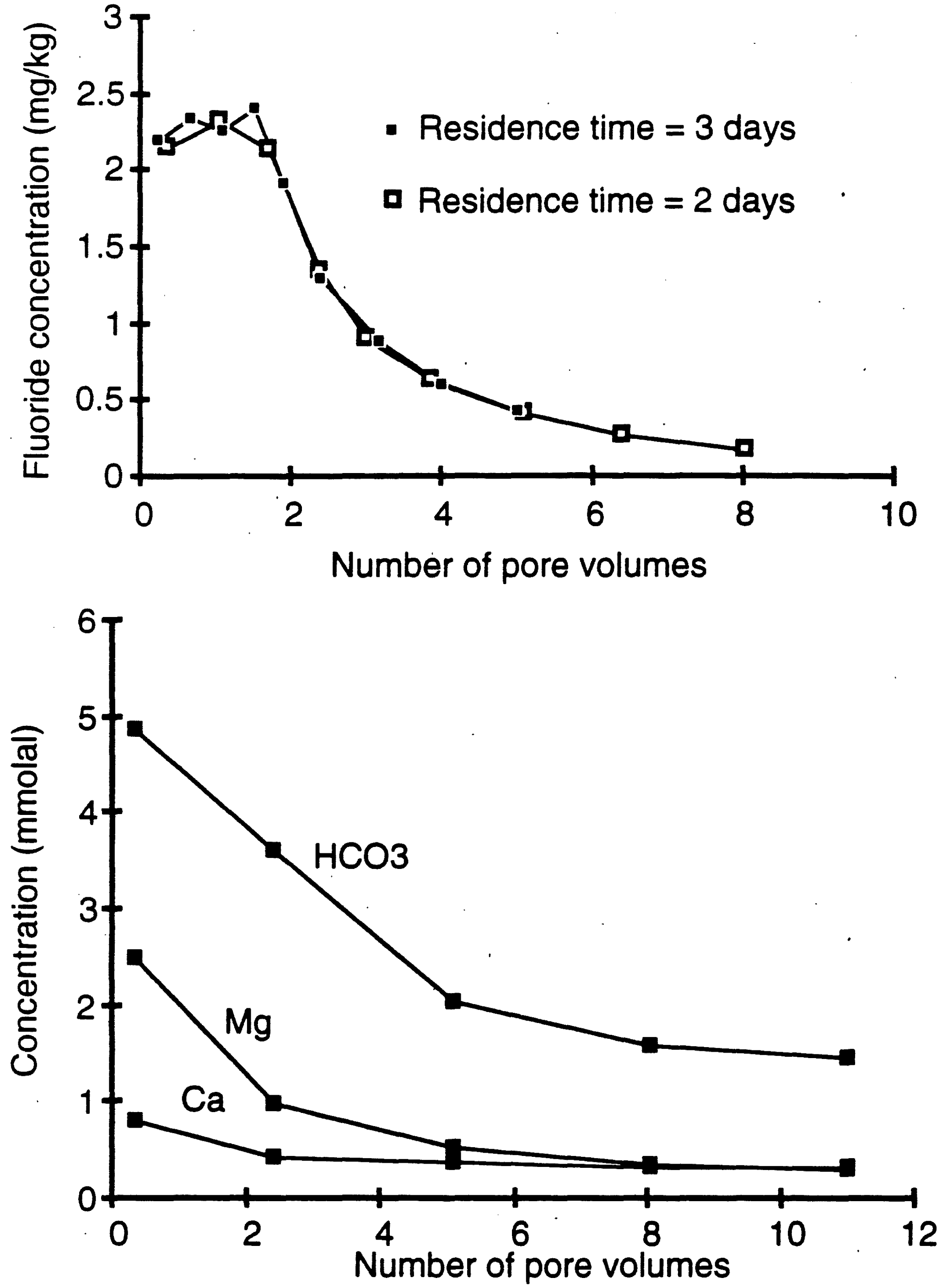

Fluoride concentration (mg/kg)
3
2.5
2
1.5
1
0.5
0
0
2
4
6
8
10
Number of pore volumes
■ Residence time = 3 days
□ Residence time = 2 days
Concentration (mmolal)
6
5
4
3
2
1
0
0
2
4
6
8
10
12
Number of pore volumes
HCO3
Mg
Ca

Figure 36

Figure 36: Fluoride concentrations as a function of the number of pore volumes and flow rate during fluoride leach experiments performed on tailings from Inland Steel. The fact that F is not readily rinsed from these tailings (as determined previously in the tailings/rainwater experiments) suggests an adsorption or dissolution process controls F mobility in taconite tailings. That there is no dependence on flow rate, and the fact that the waters in these experiments are below fluorite saturation values suggests that the element is adsorbed onto the tailings in this case.

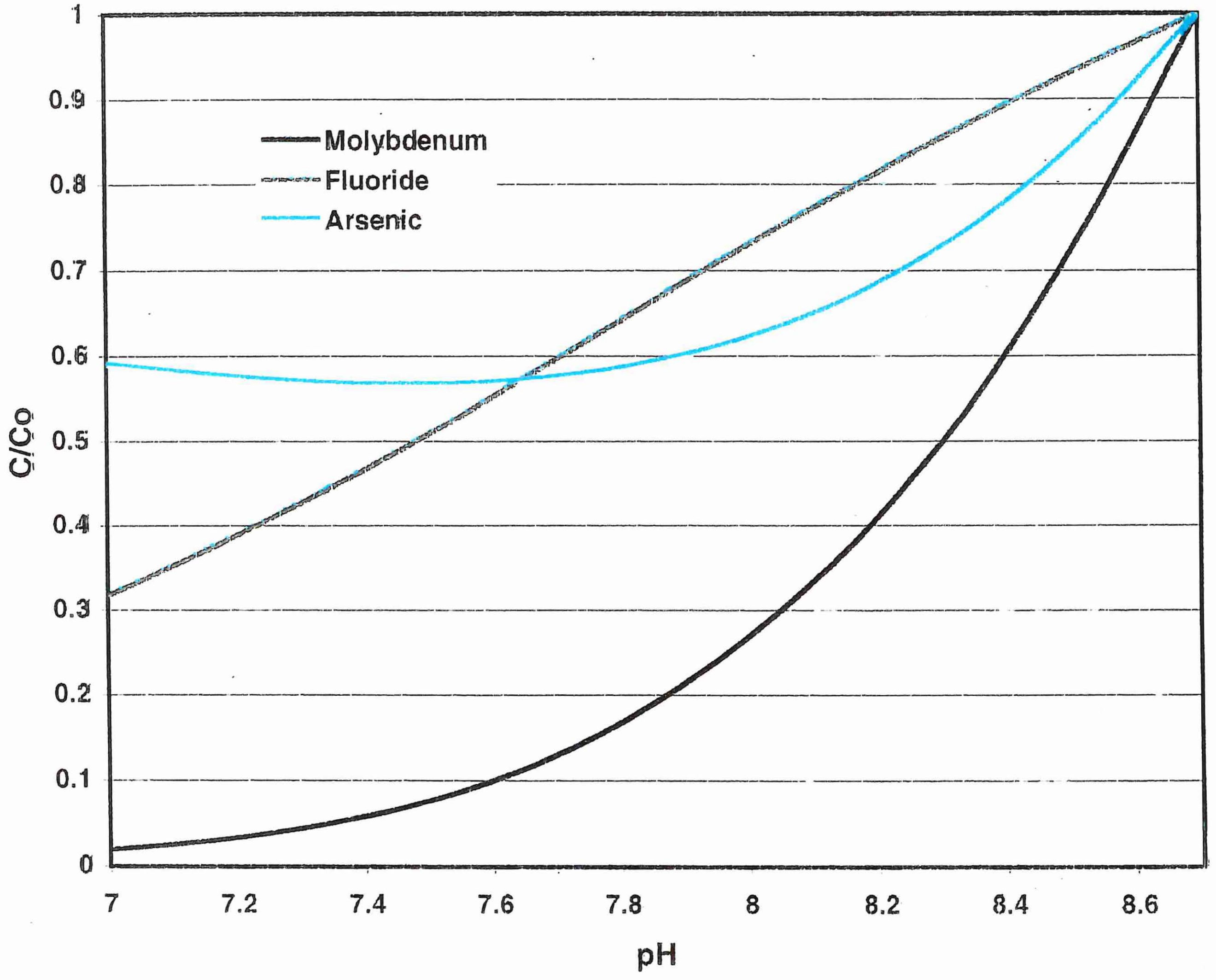
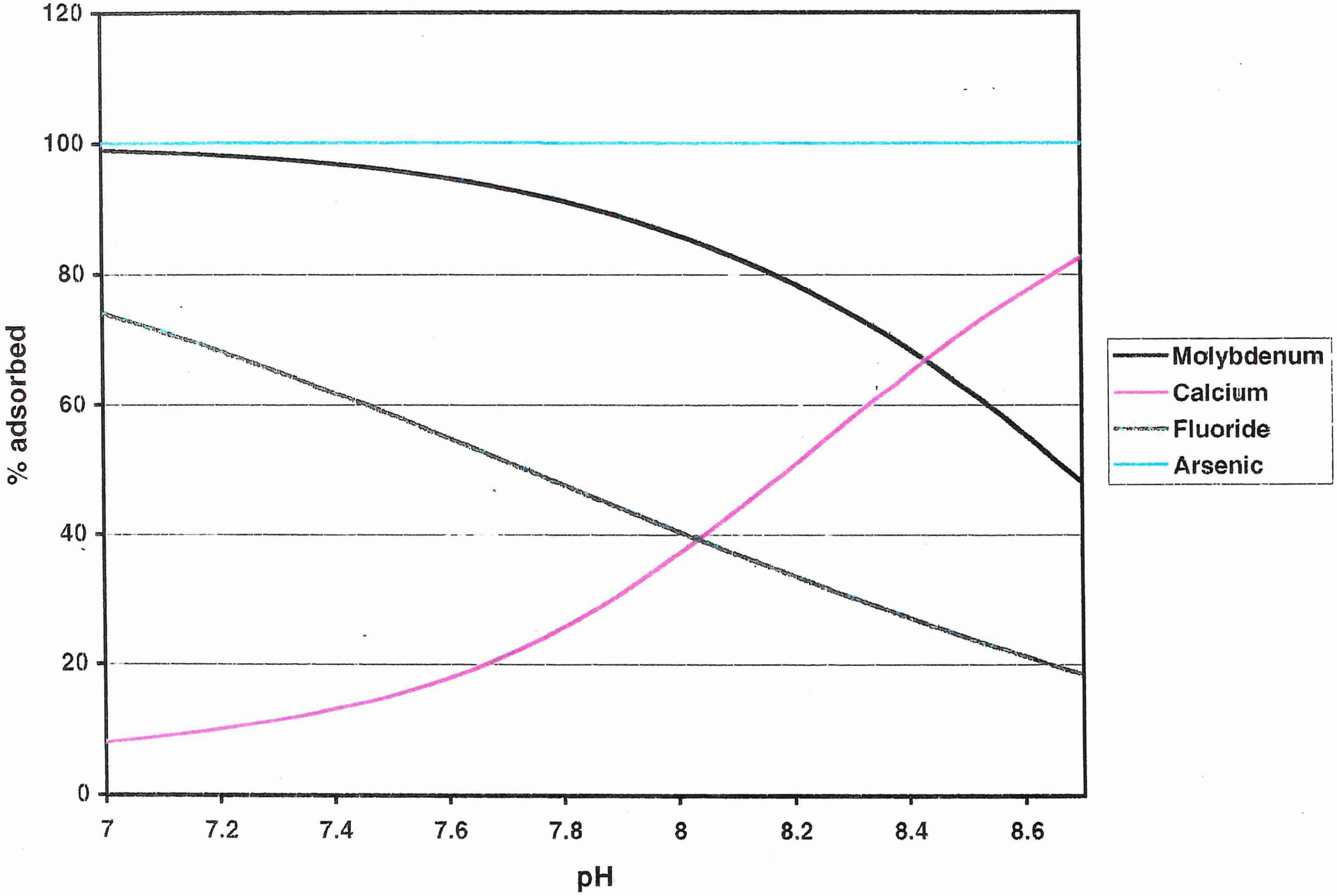

C/Co
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
7
7.2
7.4
7.6
7.8
8
8.2
8.4
8.6
pH
Molybdenum
Fluoride
Arsenic

Figure 37

Figure 37. Results of computer simulation where 1 kg water (similar to tailings basin water) was reacted with 6 grams of fine-grained hematite (=3.6e7 cm^2) and the pH of the solution was adjusted from 8.7 to 7.0. C/Co, in this case, is the concentration at indicated pH divided by the concentration at pH=8.7 (the initial pH for the simulation). As pH decreases during tailings/water interaction, the concentrations of all of these elements decrease. (Note: T=25°C, initial composition of fluid: F-=5 ppm, Cl- = 43.92 ppm, SO4--= 123.45 ppm, Ca++ = 26.15, Na+ = 21.3 ppm, K+ = 8.71 ppm, pH = 8.7 sliding to 7, Mo=48 ppb, As = 5 ppb, Mg++=36.6 ppb, HCO3- constrained by charge balance.)



120
100
80
60
40
20
0
% adsorbed
7
7.2
7.4
7.6
7.8
8
8.2
8.4
8.6
pH
Molybdenum
Calcium
Fluoride
Arsenic

Figure 38

Figure 38: % of element adsorbed as a function of pH. Water in tailings basins have high pH near 8.7 while pH in closed environments is generally less than this, generally approaching near neutral values. Mo, Ca, F, and As are all adsorbed to varying degrees at pH of 8.7. The degree of adsorption of Mo and F increases as pH is reduced, while adsorption of Ca decreases. Arsenic stays nearly fully adsorbed throughout the simulation. Computer simulation is described in caption for Figure 37.

Appendix I: Carbon isotope calculations

Most carbon present in aqueous fluids at pH of 9 or less is present as dissolved HCO_3^- and H_2CO_3. However, carbon enters the fluid initially as either CO_2 (anaerobic or aerobic decay of plants) or $CO_3^=$ (dissolution of carbonate minerals). The proportion of carbon added from either source can be easily calculated as follows:

Assemble a table containing solution pH and alkalinity of water before and after the carbon is added to the system, and also the $d^{13}C$ of both waters.

The H_2CO_3 concentration can be approximated through the reaction;

$$H_2CO_3 = HCO_3 + H^+$$

which for 25 °C, and inserting units of molality for HCO_3^-, results in the equilibrium expression:

$$\log [H_2CO_3] = \log [HCO_3^-] - pH - \log K$$

where log K = -6.35. If the temperature is different from this, use the appropriate log K value. (note: we are approximating concentrations as equal to activities, but for added accuracy, one could perform complete speciation to derive the relative amounts of carbonate species).

Calculate the total carbon in both the initial ($C_{T(initial)}$) and final ($C_{T(final)}$) solutions by adding the HCO_3^- and H_2CO_3 concentrations. $C_{T(added)}$, the difference between the initial and final total carbon values, is the amount of carbon that was added.

If no $SO_4^=$ increase is observed, the contribution from dissolution of carbonate minerals is calculated as half of the change in HCO_3^- and the remaining change in C_T is attributed to CO_2 addition.

If $SO_4^=$ increases accompany the change in total carbon and alkalinity, this suggests sulfide oxidation produced acid which, in turn, reacted with the carbonate minerals. In this case, one can assume an amount of HCO_3^- equal to twice the added $SO_4^=$ (molal scale) was derived from $CO_3^=$.

In either case, $\delta^{13}C$ of the added carbon ($\delta^{13}C_{added}$) can be calculated by solving the following mass balance relation:

$$\delta^{13}C_{(initial)} \times C_{T(initial)} + \delta^{13}C_{(added)} \times C_{(added)} = \delta^{13}C_{(final)} \times C_{(final)}$$

Appendix II: Mobile F calculation method

Tailings deposited in a slurry will eventually settle out into a densely packed column of tailings overlain by a column of water. The overlying water was decanted and the remaining tailings were rinsed thoroughly until F concentrations in the rinsing fluid were negligible. The following calculations were then made to calculate the concentration of mobile F in Inland's freshly deposited tailings.

(1) Measure the F/Cl ratio of the initial decanted fluid.
(2) Calculate $M_{F(total)}$, the total mass of F in waters rinsed from the column. This mass includes F from the original pore fluid.
(3) Calculate M_{cl}, the total mass of Cl in waters rinsed from the column. This mass includes Cl from the original pore fluid.
(4) Assuming Cl is not adsorbed to tailings, the mass of F that was in the pores of the tailings can be calculated by multiplying the total mass of Cl by the concentration ratio (F in mg/kg)/(Cl in mg/kg) of the decanted fluid.
(5) The remaining F mass (rinsed from the column) must have been adsorbed to the tailings. The concentration of mobile F in tailings can be calculated by dividing this remaining mass by the total mass of tailings used in the experiment (dried after completion of the experiment).

In the leach experiments we performed on tailings from Inland Steel Corporation, F concentration of the initial pore fluid was 2.2 milligrams per kilogram of water and it was found that the concentration of mobile F was 1.88 mg per kilogram of tailings. In this case, the adsorbed F represented approximately 1% of the total F in the tailings (200 ppm). The remaining 99% of the F in the tailings could not be rinsed from the column. The percentage of mobile F in tailings probably varies with grain size and mineralogy, as well as on solution chemistry.

Appendix III: Tailings basin maps from National, Inland, and LTV with sample locations marked

National

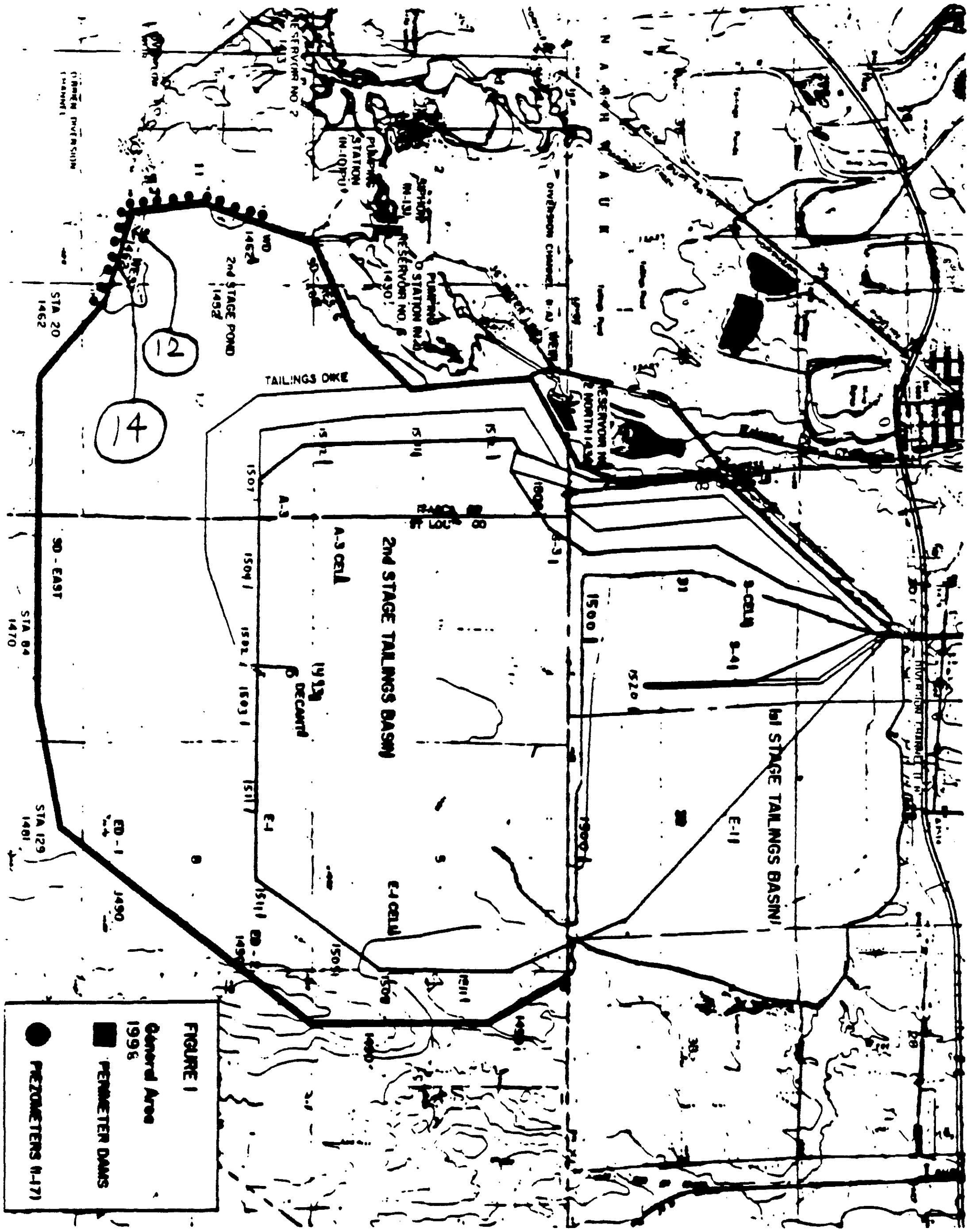
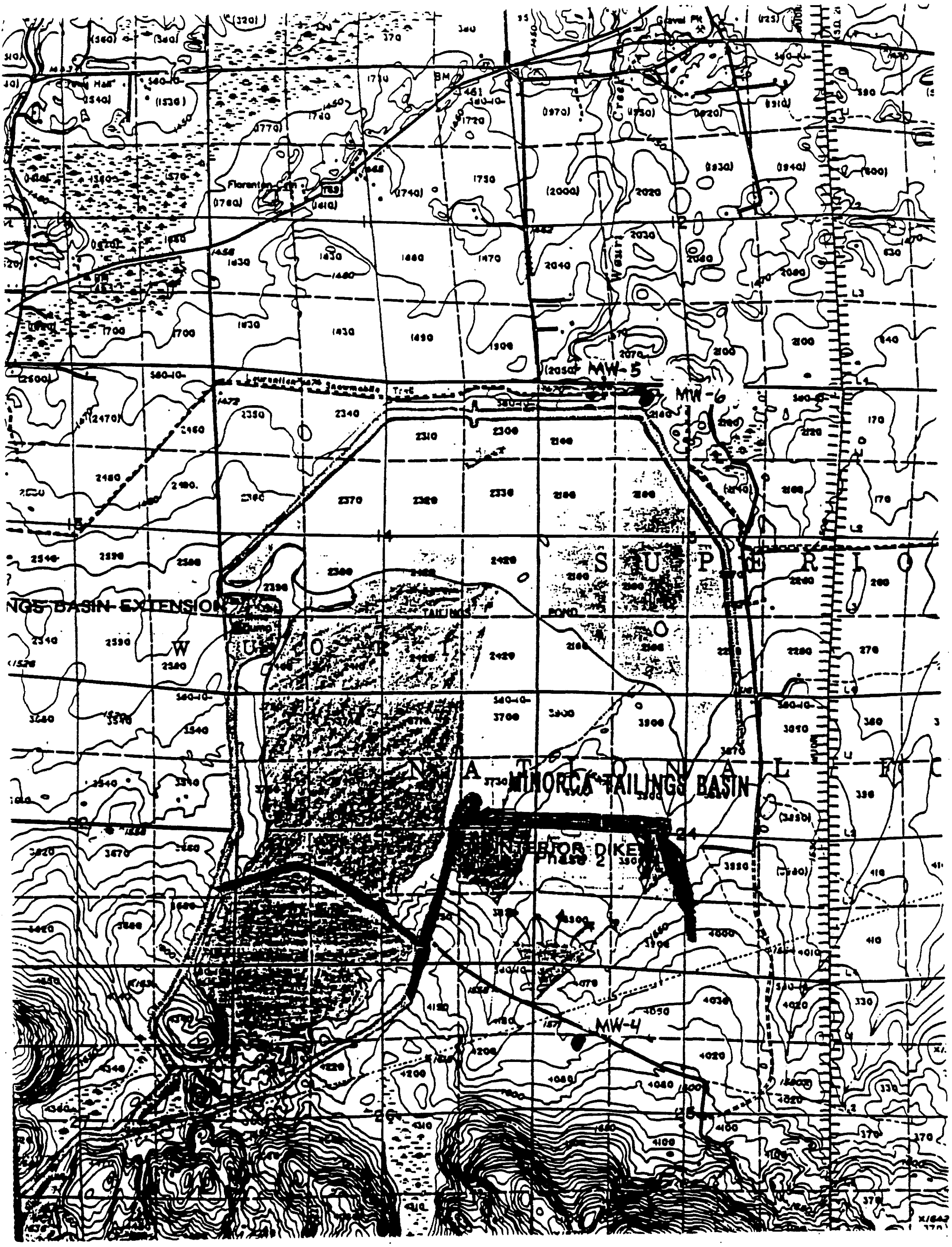
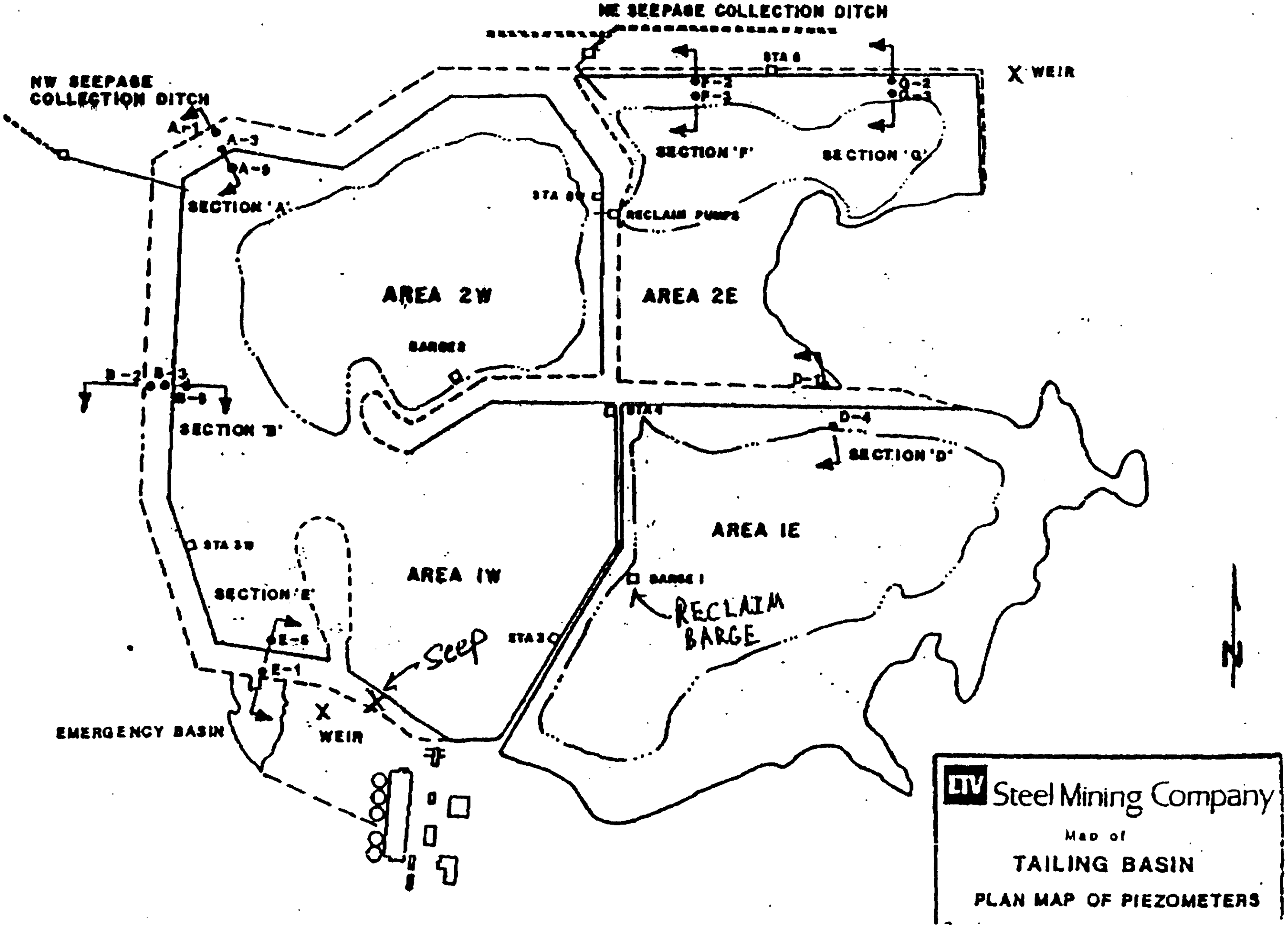


FIGURE 1
General Area
1996
■ PERIMETER DAMS
● PIEZOMETERS (1-17)



MW-5
MW-6
MW-4
MINORCA TAILINGS BASIN
INTERIOR DIKE
Phase 2
NGS BASIN EXTENSION
TAILINGS
POND
SUPERIO
NATIONAL F
W
Florenton
Gravel Pit
Creek
BM
Trail



LTV Steel Mining Company

Map of

TAILING BASIN

PLAN MAP OF PIEZOMETERS

Appendix IV: Well-logs for wells sampled at Inland and National tailings basins

AET JOB NO: 92-7109 #12

LOG OF BORING NO. 1 (p. 1 of 1)

PROJECT: Piezometer Replacement-National Steel Containment Dikes; Keewatin, MN

SURFACE ELEVATION:

DEPTH IN FEET	MATERIAL DESCRIPTION	GEOLOGY	N	MC	SAMPLE TYPE	REC. IN.	FIELD & LABORATORY TESTS WC	DEN	LL	PL	%-200
	TOPSOIL-GRAVELLY SAND, brown	TOPSOIL			AS						
1	SANDY SILT, waterbearing, loose, brown (ML)										
2											
3											
4			3	▼	SS						
5		GLACIAL OUTWASH									
6											
7	SAND WITH SILT, fine to medium grained, waterbearing, loose, brown (SP-SM)										
8											
9			4	W	SS						
10											
11											
12											
13	END OF BORING Piezometer #12 was installed in this boring Water level at 4.3' after well was installed										

DEPTH:	DRILLING METHOD
0-13'	4.25" HSA

BORING COMPLETED: 7/14/92

CC: LA CA: RW Rig: 3

WATER LEVEL MEASUREMENTS

DATE	TIME	SAMPLED DEPTH	CASING DEPTH	CAVE-IN DEPTH	DRILLING FLUID LEVEL	WATER LEVEL
07/14	12:00	105'	13'	13'	NONE	8'

NOTE: REFER TO THE ATTACHED SHEETS FOR AN EXPLANATION OF TERMINOLOGY ON THIS LOG

4/90

TESTING, INC.

AET JOB NO: 92-7109 #14

LOG OF BORING NO. 2 (p. 1 of 2)

PROJECT: Piezometer Replacement-National Steel Containment Dikes; Keewatin, MN

DEPTH IN FEET	SURFACE ELEVATION: ______ MATERIAL DESCRIPTION	GEOLOGY	N	MC	SAMPLE TYPE	REC. IN.	WC	DEN	LL	PL	%-200
	FILL-SAND AND GRAVEL, brown	FILL			AS						
1	SILTY SAND, fine grained, moist to waterbearing, loose, brown (SM)	GLACIAL OUTWASH									
2											
3											
4											
5			5	▼	SS						
6											
7											
8											
9			6	W	SS						
10											
11											
12											
13											
14											
15			7	W	SS						
16											
17											
18											
19			4	W	SS						
20											
21											

DEPTH	DRILLING METHOD
0-29.1':	4.25" HSA
BORING COMPLETED:	7/14/92
CREW CHIEF:	RW Rig: 3

WATER LEVEL MEASUREMENTS

DATE	TIME	SAMPLED DEPTH	CASING DEPTH	CAVE-IN DEPTH	DRILLING FLUID LEVEL	WATER LEVEL
7/14						4.8'

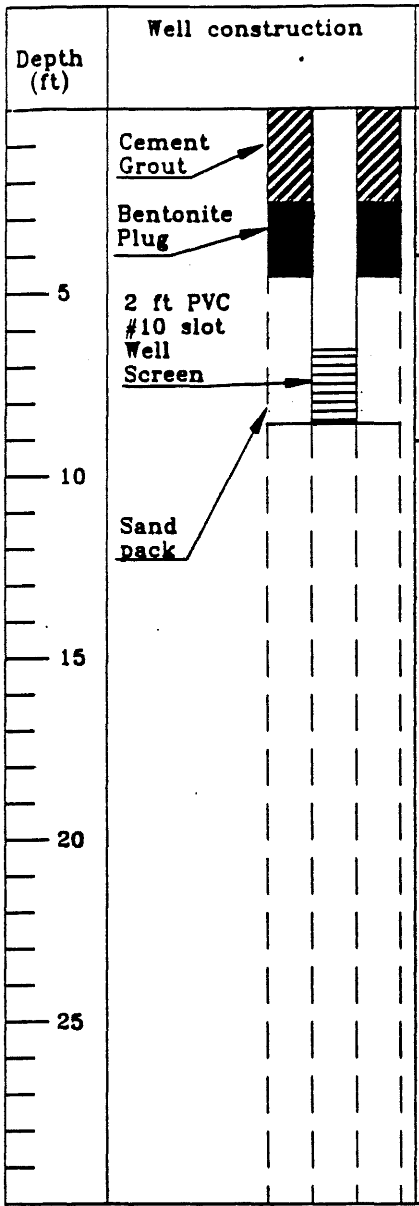
NOTE: REFER TO THE ATTACHED SHEETS FOR AN EXPLANATION OF TERMINOLOGY ON THIS LOG

4/90

#14

PROJECT Piezometer Replacement-National Steel Containment Dikes; Keewatin, MN

DEPTH IN FEET	MATERIAL DESCRIPTION	GEOLOGY	N	MC	SAMPLE TYPE	REC. IN.	FIELD & LABORATORY TESTS				
							WC	DEN	LL	PL	%-200
23	SILTY SAND, fine grained, wet, loose, brown (SM)	GLACIAL OUTWASH									
24	SILTY SAND WITH CLAY, wet, fine grained, loose, brown (SM)		8	W	■ SS						
25											
26											
27											
28	END OF BORING Piezometer #14 was installed in this boring Water level at 4.8' after piezometer was installed										



Soil Boring log	Instrument: h-Nu Units: ppm	Sample No. Type, and Interval	Blow Counts	Sample Recovery
Tailings; Black Strong sulphur odor; Wet at bottom	NA	S-1	1,1, 1,1	16"
Tan to Brn Silty Clay; Wet	NA	S-2	3,2, 2,3	16"
White to Black; weathered rock (Giants Ridge Granite); Hard	NA	S-3	40/6"	6"

End of boring at 9.60 ft below ground surface

No. MW-5	Sheet 1 of 1
Start 8/22/96 9:30	Completed 12:00
Elevation: Surface	Top of casing
Drilling method HSA	Contractor Boart Longyear
Driller Dan	Logged by GMV
Landowner Inland Steel	File Inland/MW-5

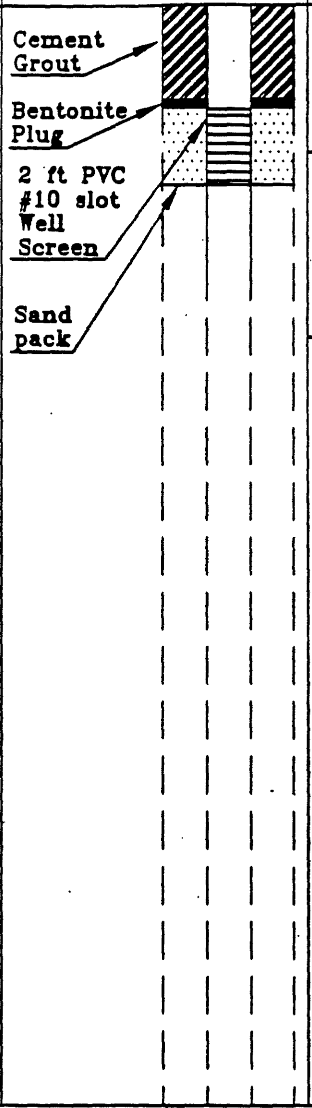
HDR Engineering, Inc.

Soil Boring Log Well Diagram

Site Name / Location

Inland Steel Mining Company
Tailings Basin Monitoring Wells

Well construction



Depth (ft)	Soil Boring log	Instrument: h-Nu Units: ppm	Sample No. type, and interval	Blow Counts	Sample Recovery
	Tailings; Black Strong sulphur odor; Wet at bottom	NA	S-1	1,1, 1,1	16"
5	Tan to Brn Silty Clay; Wet	NA	S-2	3,2, 2,3	16"
10	White to Black; weathered rock (Giants Ridge Granite); Hard	NA	S-3	40/6"	6"
15					
20					
25	End of boring at 4.80 ft below ground surface				

No. MW-6	Sheet 1 of 1
Start 8/22/96 3:00	Completed 4:30
Elevation: Surface	Top of casing
Drilling method HSA	Contractor Boart Longyear
Driller Dan	Logged by GMV
Landowner Inland Steel	File Inland/MW-6

HDR
HDR Engineering, Inc.

Soil Boring Log
Well Diagram

Site Name / Location
Inland Steel Mining Company
Tailings Basin Monitoring Wells

Appendix V: Compiled chemical data for water sampled from National, Inland, and LTV tailings basins

National Steel-Tailings Discharge Pipe

	06/13/96	09/11/96	01/22/97	04/09/97	07/16/97	10/08/97	02/05/98	04/09/98	07/22/98	10/08/98	02/11/99
Field Parameters											
Temperature	26	19	15	12	30	25	13	16	27	20	14
Conductivity	550	650	650	600	500	na	550	650	600	500	700
pH	8.18	8.00	8.54	8.45	8.31	8.06	8.31	8.19	8.32	8.27	8.37
Measured Eh	79	180	-172	255	188	na	137	129	53	72	147
Corrected Eh	279	386	37	466	384	na	348	337	252	276	357
majors (ppm)											
Al	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00
Si	18.3	17.1	14.2	14.3	21.4	16.7	12.6	13.8	17.6	15.4	14.7
P	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.01	0.00	0.00	0.00
Fe	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
Mn	0.02	0.05	0.06	0.09	0.01	0.03	0.06	0.14	0.04	0.03	0.10
Sr	0.11	0.08	0.08	0.08	0.06	0.08	0.08	0.09	0.08	0.09	0.10
Ba	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.01
Ca	30.0	29.0	27.8	32.7	27.7	38.0	39.1	37.1	33.9	36.3	37.5
Mg	34.0	37.2	42.8	38.8	30.4	34.6	35.7	41.5	31.5	33.7	48.1
Na	39.2	37.5	44.1	46.9	42.4	37.4	39.1	35.1	33.2	32.7	37.5
K	10.5	8.4	8.7	9.9	8.7	8.2	8.9	16.5	13.0	11.3	16.5
F	1.24	1.18	1.14	1.29	1.40	1.10	1.55	1.48	1.47	1.10	1.36
Cl	30.8	27.2	26.9	29.9	24.4	25.3	29.2	32.3	28.0	26.5	30.4
NO2-N	0.27	0.34	0.14	0.11	0.58	0.24	1.56	0.27	0.56	0.26	0.20
Br	0.05	0.05	0.06	0.07	0.07	0.06	0.08	0.07	0.07	0.07	0.08
NO3-N	3.76	5.66	4.04	5.36	4.22	3.89	4.13	5.66	4.60	4.44	4.88
SO4	54	55	61	59	52	61	72	72	62	59	74
HCO3-*	193	178	249	244	194	217	209	232	155	181	250
trace (ppb)											
Li	14	15	18	16	20	11	14	15	14	12	14
B	85	101	104	59	74	59	55	60	86	72	53
Sc	6.2	4.3	0.1	0.1	5.1	4.5	3.3	4.1			
Ti	16.0	0.9	0.1	1.5	4.1	3.7	5.0	4.2			
V	0.3	0.0	0.1	0.1	0.2	0.2	0.1	0.2			
Cr	0.4	6.4	5.7	6.5	4.3	3.9	5.0	2.6	6.0		4.0
Mn	17.0	45.4	65.5	91.9	11.0	30.9	61.3	129.7	46.3	30.8	100.4
Fe	0.0	15.8	6.3	0.0	0.0	5.0	18.8	23.7	0.0	0.0	0.0
Co	0.1	0.3	0.4	0.2	0.3	0.4	0.2	0.2	0.2	0.2	0.2
Ni	0.4	0.6	0.9	0.6	0.0	1.3	0.8	0.8	1.7	1.4	1.1
Cu	0.6	0.7	0.0	0.0	0.7	1.6	1.0	1.3	1.0	0.7	1.3
Zn	2.6	30.0	27.4	25.8	0.9	17.3	17.7	14.8	11.6	15.4	14.4
As	1.8	3.2	2.7	2.1	2.6	0.6	1.3	3.1	2.9	1.5	1.7
Se	2.1	3.6	3.6	6.1	5.8	0.0	3.6	5.1	4.2	4.5	4.4
Br					75	66	73	75	84	86	82
Rb	8.6	7.1	8.0	7.9	8.7	7.0	7.0	14.1	11.3	10.0	10.7
Sr	98	91	109	96	75	88	83	103	90	97	100
Mo	69	70	76	66	65	44	46	74	55	37	38
Cd	0.08	0.06	0.02	0.05	0.05	0.09	0.05	0.07	0.10	0.10	0.10
Sn	0.19	0.00	0.00	0.00	0.00	0.00	0.16	0.14			
Sb	0.20	0.08	0.01	0.00	0.09	0.03	0.01	0.02			
Cs	1.28	0.76	0.76	0.91	1.22	1.01	0.76	1.30	1.07	0.81	0.98
Ba	1.1	2.6	5.8	5.1	0.7	0.6	0.5	23.5	7.6	3.4	10.5
W	0.17	0.21	0.25	0.14	0.25	0.07	0.18	0.48	0.42	3.47	1.16
Pb	0.09	0.17	0.23	0.00	0.04	0.50	0.03	0.04	0.02	0.13	0.06
U	0.51	0.43	1.21	0.43	1.73	0.33	0.51	0.83	0.62	0.81	1.07
Nutrients (ppm)											
N			0.61	0.70	0.88	0.80	0.83	1.40			
NH3-N			0.56	0.61	0.74	0.82	0.75	1.25			
TP							0.11	0.21			
BOD (mg/L)	<1		<1	<1	<1		<2	3.6			
COD (mg/L)	<1		<2	3.5	2.0		3.5	<2			

Notes *Alkalinity reported as ppm $CaCO_3$

National Steel-Tailings Discharge Pipe

	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters					
pH	8.27	0.16	8.54	8.00	11
Measured Eh	107	115	255	-172	10
Corrected Eh	312	116	466	37	10
majors (ppm)					
Al	0.00	0.00	0.01	0.00	11
Si	16.0	2.5	21.4	12.6	11
P	0.00	0.01	0.02	0.00	11
Fe	0.01	0.01	0.02	0.00	11
Mn	0.06	0.04	0.14	0.01	11
Sr	0.09	0.01	0.11	0.06	11
Ba	0.01	0.01	0.02	0.00	11
Ca	33.6	4.3	39.1	27.7	11
Mg	37.1	5.3	48.1	30.4	11
Na	38.7	4.4	46.9	32.7	11
K	11.0	3.1	16.5	8.2	11
F	1.30	0.16	1.55	1.10	11
Cl	28.3	2.5	32.3	24.4	11
NO2-N	0.41	0.41	1.56	0.11	11
Br	0.07	0.01	0.08	0.05	11
NO3-N	4.60	0.69	5.66	3.76	11
SO4	61.8	7.6	74.2	51.9	11
HCO_3^{-*}	209	32	250	155	11
trace (ppb)					
Li	15	2	20	11	11
B	73	18	104	53	11
Sc	3.47	2.23	6.20	0.11	8
Ti	4.43	5.00	16.00	0.06	8
V	0.14	0.09	0.31	0.00	8
Cr	4.49	1.90	6.50	0.39	10
Mn	57.3	37.2	129.7	11.0	11
Fe	6.3	8.9	23.7	0.0	11
Co	0.23	0.08	0.37	0.13	11
Ni	0.87	0.48	1.70	0.00	11
Cu	0.81	0.50	1.60	0.00	11
Zn	16.2	9.3	30.0	0.9	11
As	2.13	0.83	3.20	0.60	11
Se	3.91	1.71	6.10	0.00	11
Br	77.3	7.0	86.0	66.3	7
Rb	9.13	2.22	14.11	7.04	11
Sr	93.50	9.64	109.20	74.57	11
Mo	58.1	14.7	76.2	36.8	11
Cd	0.07	0.03	0.10	0.02	11
Sn	0.06	0.09	0.19	0.00	8
Sb	0.06	0.07	0.20	0.00	8
Cs	0.99	0.21	1.30	0.76	11
Ba	5.59	6.77	23.52	0.54	11
W	0.62	0.99	3.47	0.07	11
Pb	0.12	0.14	0.50	0.00	11
U	0.77	0.42	1.73	0.33	11
Nutrients (ppm)					
N	0.87	0.28	1.40	0.61	6
NH3-N	0.79	0.25	1.25	0.56	6
TP	0.16	0.07	0.21	0.11	2
BOD (mg/L)	3.60		3.60	3.60	1
COD (mg/L)	3.00	0.87	3.50	2.00	3

Notes *Alkalinity reported as ppm $CaCO_3$

National Steel-Tailings Basin Reclaim

	06/13/96	09/11/96	01/22/97	04/09/97	07/16/97	10/08/97	02/05/98	04/09/98	07/22/98	10/08/98	02/11/99
Field Parameters											
Temperature	23	20	1	1	23	16	5	9	24	11	0
Conductivity	475	500	500	500	500	500	500	400	600	500	500
pH	8.74	8.67	8.20	8.66	8.78	8.48	8.15	8.38	8.75	8.56	7.98
Measured Eh	57	184	-159	259	211	201	132	100	20	37	128
Corrected Eh	259	389	62	479	413	409	348	314	222	249	349
majors (ppm)											
Al	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Si	7.6	5.6	7.1	9.3	8.8	6.7	8.7	9.0	5.8	7.9	8.2
P	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Fe	0.03	0.03	0.02	0.01	0.00	0.00	0.00	0.02	0.00	0.05	0.00
Mn	0.00	0.01	0.06	0.08	0.00	0.00	0.12	0.04	0.00	0.01	0.03
Sr	0.06	0.06	0.07	0.06	0.06	0.08	0.09	0.06	0.07	0.08	0.08
Ba	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01
Ca	23.1	20.1	22.6	21.4	20.7	25.7	33.1	25.7	25.0	27.0	28.0
Mg	35.6	32.5	35.8	35.4	32.5	33.5	38.0	31.6	34.2	35.2	31.1
Na	29.3	28.8	35.6	36.4	35.5	33.1	37.8	34.0	34.3	34.3	28.8
K	6.2	5.8	5.9	5.9	6.5	6.2	7.3	8.2	9.8	9.4	8.9
F	0.85	0.86	0.99	0.91	1.00	0.87	1.03	1.13	1.14	1.10	0.93
Cl	18.9	18.6	22.7	21.3	20.5	21.2	24.9	22.6	23.9	25.2	25.4
NO2-N	0.03	0.02	0.02	0.01	0.17	0.03	0.03	0.02	0.06	0.04	0.05
Br	0.04	0.04	0.04	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.05
NO3-N	2.65	0.71	1.97	2.69	2.68	1.14	2.23	3.18	2.08	1.71	2.40
SO4	48	42	50	48	46	52	65	55	57	59	53
HCO_3^-*	178	179	230	204	186	193	215	188	185	187	160
trace (ppb)											
Li	8.4	8.0	11.5	13.0	13.1	8.3	9.4	10.3	9.1	9.7	8.3
B	49	66	74	42	41	40	60	52	60	67	32
Sc	2.5	1.5	0.1	0.1	2.3	2.0	2.5	2.8			
Ti	1.2	0.6	0.1	1.0	2.9	1.4	4.2	3.6			
V	0.3	0.0	0.1	0.1	0.2	0.4	0.4	0.2			
Cr	0.5	5.5	4.5	5.8	3.2	0.8	7.0	1.8	6.0	2.0	2.0
Mn	2.5	6.4	68.2	77.3	3.9	1.8	120.6	37.5	1.9	5.5	26.9
Fe	1.0	20.5	14.9	0.0	0.0	7.9	25.1	23.1	0.0	6.5	3.0
Co	0.1	0.2	0.2	0.2	0.1	0.1	0.3	0.1	0.1	0.9	0.2
Ni	0.3	0.6	0.3	0.4	0.0	0.3	0.6	0.5	1.0	1.1	0.8
Cu	0.9	0.5	0.0	0.0	0.5	0.3	1.5	0.4	0.8	1.0	1.2
Zn	1.1	32.4	27.2	21.7	0.5	22.3	16.4	15.9	14.1	19.3	19.4
As	0.7	2.2	1.7	1.6	1.5	1.2	1.6	1.0	2.4	2.5	1.7
Se	0.0	1.5	1.3	3.7	0.8	0.0	1.7	2.7	1.9	2.4	2.0
Br					58	49	54	57	70	73	62
Rb	4.3	4.7	4.8	4.3	5.5	4.7	5.5	6.4	6.9	7.3	5.3
Sr	63	68	88	76	68	82	94	70	71	84	76
Mo	33	40	43	45	47	39	43	40	44	44	27
Cd	0.05	0.03	0.00	0.03	0.00	0.08	0.05	0.00	0.10	0.10	0.10
Sn	0.15	0.00	0.00	0.16	0.00	0.10	0.03	0.00			
Sb	0.07	0.04	0.01	0.00	0.05	0.02	0.01	0.00			
Cs	0.22	0.23	0.18	0.26	0.53	0.28	0.39	0.31	0.30	0.32	0.32
Ba	3.70	4.02	5.30	3.04	2.10	7.54	8.86	2.07	4.94	8.28	6.53
W	0.09	0.00	0.29	0.20	0.14	0.14	0.09	0.09	1.17	2.99	2.70
Pb	0.08	0.18	1.04	0.02	0.05	0.00	0.07	0.00	0.06	0.27	0.13
U	0.43	0.37	0.93	0.34	1.43	0.33	0.53	0.59	0.80	0.86	0.71
Nutrients (ppm)											
N		0.23	0.63	0.41	0.27	0.46	0.34	0.32			
NH3-N		0.04	0.13	0.16	0.11	0.07	0.15	0.21			
TP							<0.01	0.01			
BOD (mg/L)	1.5		<1	<1	<1		<2	4.2			
COD (mg/L)	7.5	<2	7.5	<2	<2		<2	7.5			

Notes *Alkalinity reported as ppm $CaCO_3$

National Steel-Tailings Basin Reclaim

	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters					
pH	8.49	0.27	8.78	7.98	11
Measured Eh	106	116	259	-159	11
Corrected Eh	318	116	479	62	11
majors (ppm)					
Al	0.00	0.00	0.01	0.00	11
Si	7.7	1.3	9.3	5.6	11
P	0.00	0.00	0.01	0.00	11
Fe	0.01	0.02	0.05	0.00	11
Mn	0.03	0.04	0.12	0.00	11
Sr	0.07	0.01	0.09	0.06	11
Ba	0.01	0.00	0.01	0.00	11
Ca	24.8	3.8	33.1	20.1	11
Mg	34.1	2.1	38.0	31.1	11
Na	33.5	3.1	37.8	28.8	11
K	7.3	1.5	9.8	5.8	11
F	0.98	0.11	1.14	0.85	11
Cl	22.3	2.4	25.4	18.6	11
NO2-N	0.04	0.04	0.17	0.01	11
Br	0.05	0.01	0.06	0.04	11
NO3-N	2.13	0.73	3.18	0.71	11
SO4	52	6	65	42	11
HCO_3^{-*}	191	19	230	160	11
trace (ppb)					
Li	9.9	1.9	13.1	8.0	11
B	53	13	74	32	11
Sc	1.7	1.1	2.8	0.1	8
Ti	1.9	1.5	4.2	0.1	8
V	0.2	0.1	0.4	0.0	8
Cr	3.6	2.3	7.0	0.5	11
Mn	32.0	40.1	120.6	1.8	11
Fe	9.3	9.9	25.1	0.0	11
Co	0.2	0.2	0.9	0.1	11
Ni	0.5	0.3	1.1	0.0	11
Cu	0.6	0.5	1.5	0.0	11
Zn	17.3	9.7	32.4	0.5	11
As	1.6	0.6	2.5	0.7	11
Se	1.6	1.1	3.7	0.0	11
Br	60	9	73	49	7
Rb	5.4	1.0	7.3	4.3	11
Sr	76	10	94	63	11
Mo	41	6.0	47	27	11
Cd	0.05	0.04	0.10	0.00	11
Sn	0.06	0.07	0.16	0.00	8
Sb	0.03	0.03	0.07	0.00	8
Cs	0.30	0.09	0.53	0.18	11
Ba	5.13	2.41	8.86	2.07	11
W	0.72	1.10	2.99	0.00	11
Pb	0.17	0.30	1.04	0.00	11
U	0.67	0.33	1.43	0.33	11
Nutrients (ppm)					
N	0.38	0.14	0.63	0.23	7
NH3-N	0.12	0.06	0.21	0.04	7
TP	0.01		0.01	0.01	1
BOD (mg/L)	2.85	1.91	4.20	1.50	2
COD (mg/L)	7.50	0.00	7.50	7.50	3

Notes *Alkalinity reported as ppm $CaCO_3$

National Steel-Tailings Basin Well #12

Date	10/08/97	02/05/98	04/09/98	07/22/98	10/08/98	02/11/99	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters											
Temperature	12	8	6	15	11	5					
Conductivity	700	550	550	650	500	600					
pH	7.16	7.12	7.26	6.99	7.26	7.18	7.16	0.10	7.26	6.99	6
Measured Eh	68	192	133	69	99	218	130	64	218	68	6
Corrected Eh	279	407	349	278	311	435	343	66	435	278	6
majors (ppm)											
Al	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	6
Si	11.3	10.1	10.4	10.4	10.5	9.9	10.4	0.5	11.3	9.9	6
P	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	6
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6
Mn	0.07	0.01	0.01	0.01	0.01	0.00	0.02	0.03	0.07	0.00	6
Sr	0.13	0.11	0.12	0.11	0.10	0.11	0.11	0.01	0.13	0.10	6
Ba	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.00	0.07	0.06	6
Ca	82.3	69.1	76.5	72.4	69.2	75.0	74.1	5.0	82.3	69.1	6
Mg	29.9	26.9	29.6	28.0	26.1	28.7	28.2	1.5	29.9	26.1	6
Na	25.0	30.0	28.2	29.2	33.1	32.9	29.7	3.0	33.1	25.0	6
K	2.6	2.2	2.2	2.4	2.3	1.8	2.3	0.3	2.6	1.8	6
F	0.51	0.62	0.54	0.62	0.65	0.56	0.58	0.05	0.65	0.51	6
Cl	21.3	21.1	20.0	22.3	24.7	24.0	22.2	1.8	24.7	20.0	6
NO2-N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6
Br	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.00	0.07	0.07	6
NO3-N	0.49	0.21	0.21	0.15	0.26	0.28	0.27	0.12	0.49	0.15	6
SO4	39	43	38	48	59	51	46.4	8.1	59.5	38.2	6
HCO_3^-*	310	281	326	285	249	285	289	27	326	249	6
trace (ppb)											
Li	8.4	7.1	8.3	7.1	7.8	6.8	7.6	0.7	8.4	6.8	6
B	28	43	40	50	55	29	41	11	55	28	6
Sc	2.98	2.70	2.92				2.87	0.15	2.98	2.70	3
Ti	5.05	8.20	7.44				6.90	1.64	8.20	5.05	3
V	0.41	0.24	0.34				0.33	0.09	0.41	0.24	3
Cr	2.01	9.28	7.03	10.00	3.00	4.00	5.89	3.37	10.00	2.01	6
Mn	67.5	12.8	7.1	8.7	7.6	4.5	18.0	24.4	67.5	4.5	6
Fe	13.9	15.2	16.1	0.0	0.0	0.0	7.5	8.3	16.1	0.0	6
Co	0.34	0.21	0.71	0.20	0.90	0.20	0.43	0.30	0.90	0.20	6
Ni	1.18	0.75	1.79	2.80	2.60	1.90	1.84	0.79	2.80	0.75	6
Cu	0.68	4.95	1.20	1.70	1.10	1.40	1.84	1.56	4.95	0.68	6
Zn	23.6	20.8	14.4	13.8	16.4	17.0	17.7	3.8	23.6	13.8	6
As	0.48	0.51	0.14	0.50	0.50	0.50	0.44	0.15	0.51	0.14	6
Se	0.00	0.70	0.00	0.70	0.60	0.40	0.40	0.33	0.70	0.00	6
Br	69	61	72	74	84	82	74	9	84	61	6
Rb	1.34	1.37	1.49	1.70	2.10	1.60	1.60	0.28	2.10	1.34	6
Sr	138	111	127	115	123	114	121	10	138	111	6
Mo	8.1	10.0	8.7	10.9	13.6	10.8	10.3	2.0	13.6	8.1	6
Cd	0.09	0.04	0.13	0.00	0.00	0.00	0.04	0.06	0.13	0.00	6
Sn	0.00	0.11	0.06				0.06	0.06	0.11	0.00	3
Sb	0.01	0.00	0.00				0.00	0.01	0.01	0.00	3
Cs	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	6
Ba	63	58	62	63	74	61	63	5.6	74	58	6
W	0.05	0.12	0.15	0.31	0.85	0.71	0.37	0.34	0.85	0.05	6
Pb	0.05	0.04	0.04	0.09	0.04	0.03	0.05	0.02	0.09	0.03	6
U	0.68	0.98	1.33	1.77	2.07	1.86	1.45	0.54	2.07	0.68	6
Nutrients (ppm)											
N	0.55	-0.20	0.11				0.15	0.38	0.55	-0.20	3
NH3-N	0.05	0.02	0.03				0.03	0.02	0.05	0.02	3
TP		0.35	0.14				0.25	0.15	0.35	0.14	2
BOD (mg/L)							0.00				0
COD (mg/L)							0.00				0

Notes *Alkalinity reported as ppm $CaCO_3$

National Steel-Tailings Basin Well #14

Date	10/08/97	02/05/98	04/09/98	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters								
Temperature	12	8	10					
Conductivity	450	500	500					
pH	7.24	7.08	7.45	7.26	0.19	7.45	7.08	3
Measured Eh	242	254	138	211	64	254	138	3
Corrected Eh	453	468	351	424	64	468	351	3
majors (ppm)								
Al	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3
Si	12.8	13.2	11.3	12.4	1.0	13.2	11.3	3
P	0.02	0.00	0.01	0.01	0.01	0.02	0.00	3
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3
Mn	0.01	0.01	0.11	0.04	0.05	0.11	0.01	3
Sr	0.09	0.09	0.07	0.08	0.01	0.09	0.07	3
Ba	0.05	0.05	0.04	0.05	0.01	0.05	0.04	3
Ca	89.3	89.6	72.2	83.7	9.9	89.6	72.2	3
Mg	30.4	30.3	24.2	28.3	3.6	30.4	24.2	3
Na	5.8	6.0	4.7	5.5	0.7	6.0	4.7	3
K	1.2	1.0	1.0	1.0	0.1	1.2	1.0	3
F	0.13	0.12	0.11	0.12	0.01	0.13	0.11	3
Cl	6.7	7.2	5.3	6.4	1.0	7.2	5.3	3
NO2-N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3
Br	0.06	0.06	0.04	0.05	0.01	0.06	0.04	3
NO3-N	0.82	0.66	0.13	0.53	0.36	0.82	0.13	3
SO4	16	18	15	16	1.2	18	15	3
HCO_3^{-}*	337	337	303	326	20	337	303	3
trace (ppb)								
Li	7.7	7.7	6.4	7.3	0.8	7.7	6.4	3
B	7.3	12.8	0.0	6.7	6.4	12.8	0.0	3
Sc	3.3	3.3	3.2	3.3	0.1	3.3	3.2	3
Ti	4.9	8.4	6.8	6.7	1.7	8.4	4.9	3
V	0.7	0.8	0.6	0.7	0.1	0.8	0.6	3
Cr	3.3	11.2	5.1	6.5	4.2	11.2	3.3	3
Mn	12.1	13.3	100.5	42.0	50.7	100.5	12.1	3
Fe	15.3	24.7	14.5	18.2	5.7	24.7	14.5	3
Co	0.3	0.2	0.3	0.3	0.1	0.3	0.2	3
Ni	1.3	0.9	1.4	1.2	0.3	1.4	0.9	3
Cu	0.7	10.1	3.2	4.7	4.9	10.1	0.7	3
Zn	36	48	16	33	17	48	16	3
As	0.2	0.2	0.3	0.2	0.0	0.3	0.2	3
Se	0.0	0.3	0.0	0.1	0.2	0.3	0.0	3
Br	52	49	38	46	8	52	38	3
Rb	1.03	0.63	0.57	0.74	0.25	1.03	0.57	3
Sr	101	96	76	91	13	101	76	3
Mo	0.4	0.4	0.3	0.4	0.1	0.4	0.3	3
Cd	0.10	0.07	0.03	0.07	0.04	0.10	0.03	3
Sn	0.00	0.05	0.06	0.04	0.03	0.06	0.00	3
Sb	0.01	0.01	0.01	0.01	0.00	0.01	0.01	3
Cs	0.00	0.01	0.00	0.00	0.01	0.01	0.00	3
Ba	51.16	52.58	39.14	47.63	7.38	52.58	39.14	3
W	0.00	0.04	0.00	0.01	0.02	0.04	0.00	3
Pb	0.08	0.03	0.07	0.06	0.03	0.08	0.03	3
U	0.12	0.24	0.26	0.21	0.08	0.26	0.12	3
Nutrients (ppm)								
N	1.50	<0.2	1.90	1.13	1.00	1.90	0.00	2
NH3-N	0.03	0.03	0.04	0.03	0.01	0.04	0.03	3
TP		1.80	7.30	4.55	3.89	7.30	1.80	2
BOD (mg/L)								0
COD (mg/L)								0

Notes *Alkalinity reported as ppm $CaCO_3$

Inland Steel-Tailings Discharge Pipe

Date	06/14/96	09/12/96	01/22/97	07/17/97	10/09/97	02/04/98	04/08/98	07/23/98	10/07/98	02/10/99
Field Parameters										
Temperature	33	21	11	31	27	17	20	24	24	17
Conductivity	520	650	600	650	750	650	750	800	750	800
pH	8.46	8.61	8.40	8.32	8.23	8.52	8.08	8.11	8.53	8.51**
Measured Eh		102	-138	137	113		71	19	100	236
Corrected Eh		306	74	333	312		276	221	301	443
majors (ppm)										
Al	0.01	0.00	0.00	0.00	0.01	3.00	0.00	0.01	0.01	0.00
Si	11.3	9.8	9.4	12.5	10.2	10.5	10.1	14.2	10.8	11.0
P	0.00	0.07	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00
Fe	0.01	0.10	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.00
Mn	0.05	0.07	0.05	0.06	0.11	0.05	0.06	0.07	0.05	0.06
Sr	0.16	0.15	0.10	0.17	0.19	0.13	0.13	0.19	0.21	0.16
Ba	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.01	0.01
Ca	25.1	27.8	27.0	34.6	32.0	32.9	32.7	32.9	27.7	30.3
Mg	37.9	42.6	47.4	45.6	42.0	50.4	50.8	49.8	43.6	55.0
Na	34.5	33.5	37.8	33.9	47.7	44.1	46.3	40.8	57.5	55.7
K	9.1	10.2	8.3	14.4	12.8	8.7	10.2	13.5	8.2	7.8
F	2.88	2.30	2.76	5.60	7.62	5.24	4.17	4.50	5.33	5.26
Cl	51.9	60.5	58.9	84.5	76.3	71.8	81.9	95.5	83.9	86.5
NO2-N	0.06	0.08	0.09	0.12	0.11	0.08	0.14	0.15	0.13	0.15
Br	0.33	0.40	0.39	0.63	0.58	0.53	0.62	0.73	0.61	0.65
NO3-N	1.06	1.84	1.22	1.09	4.63	2.06	2.23	1.17	3.58	1.89
SO4	51	52	59	57	60	74	71	67	70	79
HCO_3^-*	162	182	213	170	217	196	200	165	195	215
trace (ppb)										
Li	16	24	20	194	20	22	28	26	23	31
B	92	141	66	212	97	87	96	192	126	102
Sc	3.8	2.5	0.1	3.0	2.8	2.8	2.5			
Ti	1.0	0.5	0.0	5.0	1.9	4.1	3.5			
V	0.5	0.1	0.3	0.5	0.5	0.3	0.6			
Cr	0.4	4.3	4.3	3.3	0.6	5.4	3.4	6.0	2.0	3.0
Mn	48.9	65.6	54.5	59.6	93.8	48.7	57.3	75.9	52.0	59.3
Fe	0.4	3.8	0.0	3.7	556.2	11.0	26.8	0.0	0.0	1.0
Co	0.2	0.1	0.2	0.3	0.2	0.2	0.3	0.3	0.3	0.2
Ni	0.8	0.6	1.0	0.7	1.6	1.1	1.2	1.7	1.2	1.3
Cu	2.0	0.2	0.0	1.4	1.3	1.2	1.3	1.1	1.1	1.3
Zn	45.9	28.8	27.9	2.9	20.9	12.7	18.4	11.9	17.5	17.0
As	3.8	2.5	2.8	3.8	1.9	2.7	2.7	5.5	5.4	4.5
Se	0.4	0.7	2.6	1.0	0.0	2.1	2.7	0.7	2.5	2.9
Br				665	524	464	507	745	657	672
Rb	8.3	9.1	7.2	13.8	11.5	7.6	8.4	12.3	6.7	7.5
Sr	167	152	118	206	180	145	133	203	216	165
Mo	86	85	77	68	73	96	143	155	156	157
Cd	0.13	0.08	0.14	0.00	0.10	0.07	0.19	0.20	0.20	0.20
Sn	0.54	0.09	0.00	0.17	0.08	0.13	0.17			
Sb	0.32	0.13	0.03	0.16	0.05	0.04	0.06			
Cs	1.46	1.60	1.06	2.54	1.65	0.90	1.50	1.93	0.80	1.02
Ba	7.29	6.10	4.32	7.03	6.30	3.32	4.71	4.33	5.63	7.62
W	0.84	0.87	1.95	1.57	0.53	1.10	1.08	1.35	4.59	2.27
Pb	0.01	0.09	0.00	0.14	0.00	0.01	0.20	0.00	0.11	0.05
U	0.30	0.15	0.60	0.47	0.12	0.41	0.49	0.43	0.55	0.80
Nutrients (ppm)										
N		0.23	0.22	0.43	0.63	0.45	0.74			
NH3-N		0.23	0.35	0.64	0.81	0.43	0.32			
TP						1.70	0.04			
BOD (mg/L)	<1		<1	<1		<2	2.8			
COD (mg/L)	2.0		2.0	<2		11.5	7.5			

Notes *Alkalinity reported as ppm $CaCO_3$

**pH reading approx. 1 unit high (9.57-1.06)

Inland Steel-Tailings Discharge Pipe

	Average	Standard Deviation	Maximum	Minimum	N
pH	8.38	0.18	8.61	8.08	10
Measured Eh	80	107	236	-138	8
Corrected Eh	283	105	443	74	8
majors (ppm)					
Al	0.30	0.95	3.00	0.00	10
Si	11.0	1.4	14.2	9.4	10
P	0.01	0.02	0.07	0.00	10
Fe	0.03	0.06	0.17	0.00	10
Mn	0.06	0.02	0.11	0.05	10
Sr	0.16	0.03	0.21	0.10	10
Ba	0.01	0.00	0.01	0.00	10
Ca	30.3	3.2	34.6	25.1	10
Mg	46.5	5.1	55.0	37.9	10
Na	43.2	8.7	57.5	33.5	10
K	10.3	2.4	14.4	7.8	10
F	4.57	1.61	7.62	2.30	10
Cl	75.2	14.1	95.5	51.9	10
NO2-N	0.11	0.03	0.15	0.06	10
Br	0.55	0.13	0.73	0.33	10
NO3-N	2.08	1.18	4.63	1.06	10
SO4	63.9	9.6	79.3	50.9	10
HCO_3^-*	191	21	217	162	10
trace (ppb)					
Li	40	54	194	16	10
B	121	48	212	66	10
Sc	2.5	1.2	3.8	0.1	7
Ti	2.3	1.9	5.0	0.0	7
V	0.4	0.2	0.6	0.1	7
Cr	3.3	1.9	6.0	0.4	10
Mn	61.6	14.0	93.8	48.7	10
Fe	60.3	174.4	556.2	0.0	10
Co	0.2	0.1	0.3	0.1	10
Ni	1.1	0.4	1.7	0.6	10
Cu	1.1	0.6	2.0	0.0	10
Zn	20.4	11.7	45.9	2.9	10
As	3.6	1.3	5.5	1.9	10
Se	1.6	1.1	2.9	0.0	10
Br	605	105	745	464	7
Rb	9.2	2.4	13.8	6.7	10
Sr	168	33	216	118	10
Mo	110	38	157	68	10
Cd	0.13	0.07	0.20	0.00	10
Sn	0.17	0.17	0.54	0.00	7
Sb	0.11	0.10	0.32	0.03	7
Cs	1.45	0.53	2.54	0.80	10
Ba	5.67	1.45	7.62	3.32	10
W	1.62	1.17	4.59	0.53	10
Pb	0.06	0.07	0.20	0.00	10
U	0.43	0.20	0.80	0.12	10
Nutrients (ppm)					
N	0.45	0.21	0.74	0.22	6
NH3-N	0.46	0.22	0.81	0.23	6
TP	0.87	1.17	1.70	0.04	2
BOD (mg/L)	2.80		2.80	2.80	1
COD (mg/L)	5.75	4.63	11.50	2.00	4

Notes *Alkalinity reported as ppm $CaCO_3$

Inland Steel-Tailings Basin Reclaim

Date	06/14/96	09/12/96	01/22 97	04/10/97	07/17 97	10/09/97	02/04/98	04/08/98	07/23/98	10/07/98	02/10/99
Field Parameters											
Temperature	21	17	1	1	24	11	4	6	20	11	2
Conductivity	500	550	500	320	500	500	550	550	675	625	650
pH	8.76	8.70	8.73	8.20	8.79	8.58	8.14	8.61	8.96	8.50	8.00**
Measured Eh	93	191	-140	163	88	136	na	103	35	147	249
Corrected Eh	297	398	81	384	290	348	na	319	240	359	468
majors (ppm)											
Al	0.01	0.15	0.01	0.00	0.01	0.00	3.00	0.00	0.01	0.00	0.00
Si	2.7	4.2	5.0	3.3	1.7	3.5	3.9	3.4	3.1	4.0	4.3
P	0.00	0.00	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.01	0.01	0.00	0.07	0.00	0.00	0.00	0.01	0.00	0.01	0.00
Sr	0.10	0.10	0.10	0.06	0.10	0.11	0.12	0.11	0.12	0.12	0.14
Ba	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ca	27.8	26.0	27.9	17.3	28.7	29.2	32.2	28.9	29.7	31.5	35.3
Mg	38.5	38.2	39.8	22.0	40.0	41.4	45.5	41.7	46.1	48.8	53.5
Na	20.3	21.7	22.7	11.5	25.1	26.3	30.1	25.9	32.2	34.1	38.6
K	9.5	9.5	9.9	5.3	8.8	9.3	10.2	9.0	10.0	10.1	11.0
F	2.44	2.59	2.55	1.31	2.49	2.89	3.26	2.70	3.23	3.24	3.46
Cl	44.4	47.2	49.7	23.1	47.3	51.8	56.1	47.9	59.8	64.6	69.3
NO2-N	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Br	0.29	0.31	0.33	0.17	0.34	0.38	0.41	0.36	0.46	0.48	0.52
NO3-N	0.41	0.07	1.07	0.70	0.45	1.24	0.27	0.91	0.19	0.44	0.65
SO4	43	40	43	29	47	45	50	54	58	57	64
HCO_3^-*	162	172	188	104	181	193	197	203	188	210	220
trace (ppb)											
Li	10.4	11.0	11.0	0.0	8.1	10.8	13.1	11.4	12.7	13.3	14.4
B	60	76	62	27	61	60	81	72	91	100	83
Sc	0.9	1.1	0.0	0.0	0.4	1.0	1.2	0.9			
Ti	0.9	0.6	0.0	1.0	4.0	0.1	3.6	3.2			
V	0.3	0.0	0.2	0.2	0.3	0.2	0.3	0.3			
Cr	0.1	4.5	0.8	0.4	3.3	1.0	5.0	3.4	6.0	2.0	4.0
Mn	4.4	5.6	1.9	76.0	2.3	1.2	2.5	5.3	3.9	4.7	1.5
Fe	2.7	13.8	8.3	8.6	22.3	19.5	27.5	18.0	0.0	3.4	6.0
Co	0.2	0.3	0.4	0.5	0.3	0.2	0.4	0.2	0.3	0.2	0.3
Ni	0.7	0.6	0.6	0.5	1.1	0.5	0.8	0.6	1.2	1.2	1.1
Cu	1.2	0.9	0.0	0.0	1.4	0.5	0.6	0.7	0.5	0.5	1.3
Zn	4.2	33.0	28.7	31.2	0.8	22.3	19.0	14.9	12.6	15.3	14.3
As	3.1	7.4	5.4	3.8	4.5	4.6	4.6	3.4	7.1	6.4	5.6
Se	0.6	0.4	2.7	1.5	0.7	0.8	0.9	1.5	1.7	1.6	1.6
Br					374	343	370	291	457	488	531
Rb	9.8	10.5	11.1	6.4	10.0	10.5	11.4	9.2	10.6	10.9	11.6
Sr	104	112	121	67	120	112	132	117	121	124	143
Mo	49	48	42	16	29	28	33	28	35	34	38
Cd	0.07	0.04	0.00	0.03	0.01	0.01	0.13	0.03	0.10	0.10	0.10
Sn	0.20	0.03	0.00	0.00	0.00	0.00	0.00	0.00			
Sb	0.06	0.03	0.00	0.00	0.03	0.01	0.01	0.01			
Cs	0.93	1.08	0.97	0.39	0.93	0.87	0.83	0.77	0.84	0.92	0.83
Ba	9.3	8.9	11.0	4.6	9.7	9.4	10.5	9.0	12.0	14.1	13.9
W	0.14	0.21	0.67	0.03	0.13	0.16	0.14	0.11	2.62	3.34	4.73
Pb	0.01	0.17	0.27	0.00	0.04	0.07	0.06	0.01	0.03	0.06	0.06
U	0.25	0.18	0.46	0.15	0.73	0.10	0.24	0.36	0.42	0.42	0.42
Nutrients (ppm)											
N		0.28	0.27	0.39	0.43	0.43	0.34	0.48			
NH3-N		0.04	0.21	0.24	0.03	0.04	0.07	0.03			
TP							0.01	0.02			
BOD (mg/L)	1.4		<1	<1			<2	4.0			
COD (mg/L)	15.0	17.0	15.0	3.5			<2	18.7			

Notes *Alkalinity reported as ppm $CaCO_3$

**pH reading approx. 1 unit high (9.11-1.11)

Inland Steel-Tailings Basin Reclaim

	Average	Standard Deviation	Maximum	Minimum	N
pH	8.54	0.30	8.96	8.00	11
Measured Eh	106	105	249	-140	10
Corrected Eh	318	105	468	81	10
majors (ppm)					
Al	0.29	0.90	3.00	0.00	11
Si	3.6	0.9	5.0	1.7	11
P	0.03	0.09	0.30	0.00	11
Fe	0.00	0.00	0.02	0.00	11
Mn	0.01	0.02	0.07	0.00	11
Sr	0.11	0.02	0.14	0.06	11
Ba	0.01	0.00	0.01	0.00	11
Ca	28.6	4.5	35.3	17.3	11
Mg	41.4	8.0	53.5	22.0	11
Na	26.2	7.4	38.6	11.5	11
K	9.3	1.5	11.0	5.3	11
F	2.74	0.60	3.46	1.31	11
Cl	51.0	12.2	69.3	23.1	11
NO2-N	0.00	0.00	0.01	0.00	11
Br	0.37	0.10	0.52	0.17	11
NO3-N	0.58	0.37	1.24	0.07	11
SO4	48.1	9.8	64.1	28.6	11
HCO_3^-*	183	31	220	104	11
trace (ppb)					
Li	10.6	3.9	14.4	0.0	11
B	70	20	100	27	11
Sc	0.7	0.5	1.2	0.0	8
Ti	1.7	1.6	4.0	0.0	8
V	0.2	0.1	0.3	0.0	8
Cr	2.8	2.0	6.0	0.1	11
Mn	9.9	22.0	76.0	1.2	11
Fe	11.8	9.0	27.5	0.0	11
Co	0.3	0.1	0.5	0.2	11
Ni	0.8	0.3	1.2	0.5	11
Cu	0.7	0.5	1.4	0.0	11
Zn	17.8	10.4	33.0	0.8	11
As	5.1	1.4	7.4	3.1	11
Se	1.3	0.7	2.7	0.4	11
Br	408	86	531	291	7
Rb	10.2	1.4	11.6	6.4	11
Sr	116	19	143	67	11
Mo	35	10	49	16	11
Cd	0.06	0.05	0.13	0.00	11
Sn	0.03	0.07	0.20	0.00	8
Sb	0.02	0.02	0.06	0.00	8
Cs	0.85	0.17	1.08	0.39	11
Ba	10.22	2.62	14.12	4.63	11
W	1.12	1.65	4.73	0.03	11
Pb	0.07	0.08	0.27	0.00	11
U	0.34	0.18	0.73	0.10	11
Nutrients (ppm)					
N	0.37	0.08	0.48	0.27	7
NH3-N	0.09	0.09	0.24	0.03	7
TP	0.02	0.01	0.02	0.01	2
BOD (mg/L)	2.70	1.84	4.00	1.40	2
COD (mg/L)	13.84	5.98	18.70	3.50	5

Notes *Alkalinity reported as ppm $CaCO_3$

Inland Steel-North Seep

Date	06/14/96	04/10/97	07/17/97	10/09/97	04/08/98	07/23/98	10/07/98	02/10/99	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters													
Temperature	18	1	19	10	11	18	9	5					
Conductivity		450	600	750	600	875	700	650					
pH	7.46	7.72	7.83	7.43	7.17	6.75	6.85	6.85**	7.26	0.42	7.83	6.75	8
Measured Eh	122	134	214	102	77	96	141	147	129	42	214	77	8
Corrected Eh	328	355	419	315	289	302	355	364	341	42	419	289	8
majors (ppm)													
Al	0.02	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.02	0.00	8
Si	3.3	3.9	5.3	4.4	4.9	6.2	6.0	2.8	4.6	1.2	6.2	2.8	8
P	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8
Fe	0.02	0.02	0.00	0.00	0.00	0.00	0.30	0.00	0.04	0.11	0.30	0.00	8
Mn	0.00	3.58	1.71	3.83	3.06	3.14	3.05	4.08	2.81	1.34	4.08	0.00	8
Sr	0.09	0.12	0.14	0.17	0.14	0.28	0.19	0.18	0.16	0.06	0.28	0.09	8
Ba	0.00	0.02	0.04	0.03	0.07	0.09	0.09	0.09	0.05	0.04	0.09	0.00	8
Ca	30.0	27.1	41.3	41.1	39.8	56.9	48.5	39.3	40.5	9.4	56.9	27.1	8
Mg	33.3	32.9	54.9	58.2	45.3	74.3	62.3	46.5	51.0	14.3	74.3	32.9	8
Na	9.1	15.8	19.6	19.0	22.8	21.5	25.4	30.1	20.4	6.3	30.1	9.1	8
K	6.7	6.8	9.9	8.2	10.1	11.6	9.5	7.2	8.8	1.8	11.6	6.7	8
F	1.18	1.78	3.02	2.27	2.69	2.62	1.98	2.54	2.26	0.59	3.02	1.18	8
Cl	17.0	20.4	44.0	45.5	48.2	48.3	56.1	61.9	42.7	15.9	61.9	17.0	8
NO2-N	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	8
Br	0.12	0.16	0.33	0.34	0.37	0.37	0.43	0.48	0.32	0.12	0.48	0.12	8
NO3-N	0.22	0.30	0.22	0.37	0.70	0.25	0.43	1.22	0.46	0.35	1.22	0.22	8
SO4	22	20	42	33	41	54	45	46	38	12	54	20	8
HCO_3^-*	179	199	291	303		380	316	235	272	71	380	179	7
trace (ppb)													
Li	3.9	0.0	25.8	2.0	1.9	0.6	1.1	1.0	4.5	8.7	25.8	0.0	8
B	40	34	52	37	41	69	71	76	52	17	76	34	8
Sc	1.1	0.0	1.3	1.3	1.4				1.0	0.6	1.4	0.0	5
Ti	0.3	0.0	6.0	0.1	0.1				1.3	2.6	6.0	0.0	5
V	0.1	0.0	0.1	0.0	0.2				0.1	0.1	0.2	0.0	5
Cr	0.1	4.0	5.4	2.1	4.5	15.0	4.0	2.0	4.6	4.5	15.0	0.1	8
Mn	0.5		over	over	over	over	over	over					
Fe	0.0	0.3	7.2	11.6	19.3	18.6	330.7	131.0	64.8	115.8	330.7	0.0	8
Co	0.1	4.4	1.0	4.0	2.7	3.0	3.5	4.5	2.9	1.6	4.5	0.1	8
Ni	0.7	2.2	1.0	2.2	1.7	3.9	2.6	2.5	2.1	1.0	3.9	0.7	8
Cu	0.9	4.3	1.7	3.8	1.9	2.1	0.7	0.9	2.0	1.4	4.3	0.7	8
Zn	3.1	23.0	2.8	21.4	16.2	12.7	14.5	24.0	14.7	8.3	24.0	2.8	8
As	0.5	0.7	0.8	0.5	0.5	2.1	1.9	1.8	1.1	0.7	2.1	0.5	8
Se	0.0	0.0	1.0	0.0	0.2	2.0	0.3	0.5	0.5	0.7	2.0	0.0	8
Br			360	298	300	376	455	503	382	83	503	298	6
Rb	8.6	8.0	12.0	10.5	10.1	13.2	10.0	8.8	10.1	1.7	13.2	8.0	8
Sr	97	127	167	156	148	289	200	180	170	57	289	97	8
Mo	5.1	1.5	13.7	3.8	11.1	11.7	3.8	5.8	7.1	4.5	13.7	1.5	8
Cd	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.01	0.03	0.00	8
Sn	0.14	0.01	0.31	0.00	0.09				0.11	0.13	0.31	0.00	5
Sb	0.01	0.00	0.00	0.00	0.00				0.00	0.00	0.01	0.00	5
Cs	0.23	0.40	1.00	0.63	0.86	1.08	0.94	0.74	0.73	0.30	1.08	0.23	8
Ba	0.51	17	45	30	65	89	91	87	53	35	91	0.51	8
W	0.00	0.04	0.12	0.00	0.16	0.68	0.64	0.60	0.28	0.30	0.68	0.00	8
Pb	0.03	0.00	0.07	0.00	0.05	0.07	0.03	0.07	0.04	0.03	0.07	0.00	8
U	0.09	0.17	0.62	0.13	0.30	2.17	0.50	0.69	0.58	0.68	2.17	0.09	8
Nutrients (ppm)													
N		<0.3	0.35	<0.2	0.45				0.40	0.07	0.45	0.35	2
NH3-N		0.02	0.25	0.03	0.16				0.12	0.11	0.25	0.02	4
TP					0.02				0.02		0.02	0.02	1
BOD (mg/L)													0
COD (mg/L)													0

Notes *Alkalinity reported as ppm $CaCO_3$

**pH reading approx. 1 unit high (7.96-1.11)

Inland Steel-Shallow Well (MW-6)

Date	09/12/96	04/10/97	07/17/97	10/09/97	02/04/98	04/08/98	07/23/98	10/07/98	02/10/99	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters														
Temperature	17	4	16	10	4	10	16	10	3					
Conductivity	600	500	550	600	500	500	700	600	650					
pH	6.91	7.31	7.18	7.11	7.50	7.02	7.02	6.77	6.77	7.07	0.24	7.50	6.77	9
Measured Eh	-18	-11	-54	-53		43	-63	134	29	1.0	66	134	-63	8
Corrected Eh	189	207	154	160		256	146	347	248	213	68	347	146	8
majors (ppm)														
Al	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.00	9
Si	6.4	6.5	7.2	5.9	6.0	8.9	6.4	11.3	5.4	7.1	1.9	11.3	5.4	9
P	0.01	0.00	0.02	0.08	0.00	0.02	0.00	0.02	0.00	0.02	0.03	0.08	0.00	9
Fe	10.80	8.62	11.30	11.85	11.49	2.34	3.70	2.84	9.00	7.99	3.94	11.85	2.34	9
Mn	4.12	4.26	4.00	4.20	3.76	6.08	1.18	7.24	3.53	4.26	1.68	7.24	1.18	9
Sr	0.19	0.17	0.19	0.17	0.16	0.24	0.14	0.29	0.17	0.19	0.05	0.29	0.14	9
Ba	0.12	0.11	0.14	0.12	0.13	0.10	0.08	0.11	0.11	0.11	0.02	0.14	0.08	9
Ca	34.8	34.5	38.4	33.9	32.1	48.0	40.2	58.1	35.5	39.5	8.4	58.1	32.1	9
Mg	36.2	36.2	40.4	37.1	35.3	26.8	43.8	30.9	43.2	36.6	5.5	43.8	26.8	9
Na	17.8	19.1	20.6	22.0	24.6	19.7	24.2	22.8	31.4	22.5	4.1	31.4	17.8	9
K	9.8	9.1	11.0	8.8	9.3	3.0	9.1	3.5	9.9	8.1	2.9	11.0	3.0	9
F	3.11	3.38	3.27	3.39	3.58	1.64	2.88	1.77	3.64	2.96	0.75	3.64	1.64	9
Cl	46.9	46.8	52.4	47.1	51.6	49.1	52.0	56.0	62.9	51.6	5.2	62.9	46.8	9
NO2-N	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.01	0.02	0.06	0.00	9
Br	0.32	0.35	0.40	0.37	0.40	0.38	0.41	0.42	0.48	0.39	0.05	0.48	0.32	9
NO3-N	0.08	0.05	0.12	0.50	0.22	0.40	0.45	0.69	0.72	0.36	0.26	0.72	0.05	9
SO4	13	20	23	12	18	28	21	36	23	22	7.2	36	12	9
HCO_3^-*	217	230	245	220	196	186	220	240	230	220	19	245	186	9
trace (ppb)														
Li	0.1	0.0	0.0	1.6	0.0	3.4	0.8	3.3	0.5	1.1	1.4	3.4	0.0	9
B	42	34	47	45	66	30	60	54	77	51	15	77	30	9
Sc	2.0	0.1	1.8	1.8	2.1	2.7				1.7	0.9	2.7	0.1	6
Ti	0.5	2.1	5.0	0.0	3.5	4.4				2.6	2.0	5.0	0.0	6
V	1.0	0.9	1.5	1.0	1.0	1.5				1.2	0.3	1.5	0.9	6
Cr	7.4	4.1	6.1	1.1	6.5	3.5	9.0	3.0	3.0	4.9	2.5	9.0	1.1	9
Mn	over	over	over	over	over	over	over	over	over					
Fe	over	over	over	over	over	over	over	over	over					
Co	2.6	3.5	2.2	1.9	2.7	2.5	0.4	3.0	1.8	2.3	0.9	3.5	0.4	9
Ni	2.0	1.9	2.7	0.9	15.6	2.3	1.6	3.4	1.4	3.5	4.6	15.6	0.9	9
Cu	0.0	0.0	0.6	0.1	1.3	0.6	0.9	2.4	1.2	0.8	0.8	2.4	0.0	9
Zn	33	25	2.9	26	21	16	12	43	25	22	12	43	2.9	9
As	7.3	4.5	8.1	5.6	4.8	1.5	4.5	2.7	3.3	4.7	2.1	8.1	1.5	9
Se	1.1	0.2	1.8	0.0	0.0	0.0	1.1	1.7	0.7	0.7	0.7	1.8	0.0	9
Br			433	337	329	294	407	465	504	395	78	504	294	7
Rb	11.4	7.3	10.6	6.3	6.7	1.0	8.4	1.7	8.5	6.9	3.6	11.4	1.0	9
Sr	215	185	227	161	155	236	140	323	176	202	56	323	140	9
Mo	6.9	8.4	5.8	8.0	6.8	6.5	3.0	6.8	4.6	6.3	1.7	8.4	3.0	9
Cd	0.01	0.00	0.00	0.01	0.04	0.15	0.00	0.30	0.10	0.07	0.10	0.30	0.00	9
Sn	0.01	0.00	0.39	0.07	0.22	0.03				0.12	0.15	0.39	0.00	6
Sb	0.01	0.00	0.00	0.00	0.00	0.01				0.00	0.01	0.01	0.00	6
Cs	0.52	0.76	1.20	0.62	0.57	0.02	0.72	0.03	0.66	0.57	0.36	1.20	0.02	9
Ba	124	114	135	111	127	91	78	122	115	113	18	135	78	9
W	0.04	0.00	0.07	0.03	0.10	0.06	0.39	1.21	1.49	0.38	0.57	1.49	0.00	9
Pb	0.11	0.00	0.05	0.02	0.11	0.03	0.02	0.16	0.07	0.06	0.05	0.16	0.00	9
U	0.03	0.03	0.08	0.00	0.01	0.72	0.30	0.85	0.04	0.23	0.33	0.85	0.00	9
Nutrients (ppm)														
N	0.98	0.82	1.70	0.78	0.91	0.65				0.97	0.37	1.70	0.65	6
NH3-N	0.88	0.82	1.20	1.10	0.93	0.09				0.84	0.39	1.20	0.09	6
TP					0.19	0.17				0.18	0.01	0.19	0.17	2
BOD (mg/L)										0.00				0
COD (mg/L)	13.0									13.00		13.00	13.00	1

Notes *Alkalinity reported as ppm $CaCO_3$

**pH reading approx. 1 unit high (7.89-1.12)

Inland Steel-Deep Well (MW-5)

Date	09/12/96	04/10/97	07/17/97	10/09/97	04/08/98	07/23/98	10/07/98	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters												
Temperature	12	5	13	9	10	13	9					
Conductivity		500	500	550	500	600	650					
pH	6.72	7.23	6.99	7.07	7.30	7.20	6.94	7.06	0.20	7.30	6.72	7
Measured Eh	72	165	126	65	-39	23	116	76	68	165	-39	7
Corrected Eh	283	382	337	279	174	233	330	288	70	382	174	7
majors (ppm)												
Al	0.05	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.05	0.01	7
Si	9.9	9.4	9.7	10.3	6.1	10.4	6.8	8.9	1.7	10.4	6.1	7
P	0.00	0.00	0.00	0.01	0.09	0.00	0.04	0.02	0.03	0.09	0.00	7
Fe	1.19	0.01	0.17	0.70	11.18	0.90	6.01	2.88	4.20	11.18	0.01	7
Mn	4.36	5.43	5.98	6.58	3.90	6.27	3.45	5.14	1.24	6.58	3.45	7
Sr	0.21	0.24	0.25	0.26	0.17	0.27	0.17	0.22	0.04	0.27	0.17	7
Ba	0.13	0.12	0.01	0.12	0.13	0.12	0.11	0.11	0.04	0.13	0.01	7
Ca	53.4	51.0	50.9	52.0	35.5	52.0	38.7	47.6	7.3	53.4	35.5	7
Mg	25.9	28.9	27.8	28.6	38.0	28.1	43.3	31.5	6.5	43.3	25.9	7
Na	31.1	18.8	18.8	18.8	23.7	21.2	29.1	23.1	5.1	31.1	18.8	7
K	3.1	3.5	3.5	3.3	9.5	3.6	9.5	5.2	3.0	9.5	3.1	7
F	0.56	1.36	1.54	1.59	3.53	1.76	3.35	1.96	1.09	3.53	0.56	7
Cl	50.1	49.1	52.3	50.6	53.5	54.0	56.9	52.4	2.7	56.9	49.1	7
NO2-N	0.00	0.00	0.00	0.00	0.00	<0.005	0.00	0.00	0.00	0.00	0.00	6
Br	0.36	0.38	0.41	0.39	0.41	0.42	0.42	0.40	0.02	0.42	0.36	7
NO3-N	1.81	0.22	0.19	1.12	0.15	0.60	0.29	0.63	0.63	1.81	0.15	7
SO4	72.8	35.0	31.1	31.2	25.8	35.0	12.8	34.8	18.4	72.8	12.8	7
HCO_3^{-*}	181	197	181	199	213	180	252	200	26	252	180	7
trace (ppb)												
Li	3.7	4.3	74	4.1	1.4	3.1		15	29	74	1.4	6
B	44	27	41	34	48	55		41	10	55	27	6
Sc	2.9	0.1	2.6	3.0	1.8			2.1	1.2	3.0	0.1	5
Ti	15.5	0.1	0.1	2.6	4.1			4.5	6.4	15.5	0.1	5
V	1.6	1.8	3.5	2.5	1.3			2.1	0.9	3.5	1.3	5
Cr	1.2	3.8	3.5	0.8	3.2	8.0		3.4	2.6	8.0	0.8	6
Mn			over	over	over	over						3
Fe	over	66.0	137.7	over	over	over						6
Co	4.1	2.3	3.4	2.4	1.9	2.6		2.8	0.8	4.1	1.9	6
Ni	3.9	2.1	2.8	2.4	9.0	13.4		5.6	4.6	13.4	2.1	6
Cu	0.8	0.0	0.8	0.6	0.5	1.5		0.7	0.5	1.5	0.0	6
Zn	53.7	21.6	4.3	30.0	14.3	16.7		23.4	17.1	53.7	4.3	6
As	2.6	3.3	3.3	2.2	4.3	3.5		3.2	0.7	4.3	2.2	6
Se	1.0	0.0	0.9	0.0	0.9	1.7		0.8	0.7	1.7	0.0	6
Br			424	373	351	429		394	38	429	351	4
Rb	1.6	1.7	1.4	1.1	7.1	1.5		2.4	2.3	7.1	1.1	6
Sr	225	266	293	251	177	287		250	43	293	177	6
Mo	3.4	8.1	6.5	6.8	6.7	7.8		6.5	1.7	8.1	3.4	6
Cd	0.03	0.00	0.00	0.01	0.10	0.20		0.06	0.08	0.20	0.00	6
Sn	0.10	0.00	0.00	0.00	0.13			0.05	0.06	0.13	0.00	5
Sb	0.04	0.00	0.02	0.01	0.01			0.02	0.02	0.04	0.00	5
Cs	0.04	0.05	0.02	0.01	0.54	0.03		0.11	0.21	0.54	0.01	6
Ba	128	126	133	109	120	128		124	8	133	109	6
W	0.14	0.25	0.21	0.12	0.16	2.14		0.50	0.80	2.14	0.12	6
Pb	0.21	0.00	0.11	1.35	0.03	0.01		0.29	0.53	1.35	0.00	6
U	0.58	2.09	2.32	0.39	0.05	1.11		1.09	0.93	2.32	0.05	6
Nutrients (ppm)												
N	1.20	1.30	0.37	0.74	1.20			0.96	0.40	1.30	0.37	5
NH3-N	0.14	0.36	0.18	0.24	0.85			0.35	0.29	0.85	0.14	5
TP					0.12			0.12		0.12	0.12	1
BOD (mg/L)								0.00				0
COD (mg/L)								0.00				0

Notes *Alkalinity reported as ppm $CaCO_3$

Inland Steel-Interior Dike

Date	02/10/99
Field Paramters	
Temperature	8
Conductivity	1050
pH	8.41
Measured Eh	212
Corrected Eh	426
majors (ppm)	
Al	0.00
Si	7.1
P	0.00
Fe	0.00
Mn	0.08
Sr	0.25
Ba	0.00
Ca	61.5
Mg	74.6
Na	62.2
K	14.6
F	4.60
Cl	85.9
NO2-N	0.00
Br	0.64
NO3-N	9.38
SO4	122.2
HCO_3^{-*}	338
trace (ppb)	
Li	19
B	113
Sc	
Ti	
V	
Cr	6.0
Mn	77.8
Fe	0.0
Co	0.4
Ni	1.4
Cu	0.9
Zn	16.3
As	2.8
Se	3.0
Br	655
Rb	15.4
Sr	252
Mo	42
Cd	0.10
Sn	
Sb	
Cs	1.14
Ba	3.4
W	2.1
Pb	0.02
U	1.41

LTV-Tailings Discharge Pipe

Date	06/13/96	09/11 96	01.22.97	04.09/97	07 16/97	10/09/97	02.04/98	04/08/98	07/23/98	10/07/98	02/10/99
Field Parameters											
Temperature	29	21	11	14	31	23	14	18	29	22	16
Conductivity	850	850	850	850	900	800	950	900	900	750	1000
pH	8.66	8.51	8.37	8.68	8.56	8.64	8.99	8.67	8.47	8.43	8.50**
Measured Eh	64	145	-181	182	130	69	111	117	58	89	42
Corrected Eh	259	347	30	391	323	270	319	322	253	290	249
majors (ppm)											
Al	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Si	10.5	7.7	7.7	7.7	10.8	9.0	7.2	7.8	10.3	6.5	8.1
P		0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Fe	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.02	0.03	0.03	0.03	0.02	0.02	0.02	0.03	0.03	0.04	0.03
Sr	0.08	0.12	0.13	0.09	0.13	0.11	0.08	0.14	0.10	0.13	0.10
Ba	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Ca	10.7	18.0	21.2	14.5	15.3	14.6	11.7	17.6	17.8	22.9	19.7
Mg	22.4	29.3	34.9	33.1	30.8	30.5	28.9	31.5	32.0	31.5	39.0
Na	156	108	138	135	130	120	183	114	111	103	132
K	18.5	16.5	16.4	17.1	22.0	12.9	15.5	18.0	19.2	15.1	16.6
F	10.0	9.3	10.3	9.0	10.1	10.5	10.9	10.8	10.7	7.5	8.4
Cl	39.9	36.0	39.7	36.3	39.3	34.5	34.0	30.2	38.2	36.4	34.6
NO2-N	0.10	0.06	0.09	0.09	0.13	0.07	0.08	0.05	0.17	0.06	0.10
Br	0.16	0.16	0.18	0.19	0.22	0.19	0.19	0.17	0.22	0.23	0.21
NO3-N	1.36	1.15	2.74	2.11	1.30	1.24	1.71	2.47	1.73	1.33	3.05
SO4	112	108	124	112	112	113	127	111	120	113	127
HCO_3^{-}*	260	233	289	301	277	264	370	273	230	195	320
trace (ppb)											
Li	83	85	91	64	265	44	71	48	71	69	46
B	392	447	334	270	434	294	362	204	501	379	223
Sc	3.5	2.0	0.1	0.1	2.8	2.3	2.0	1.8			
Ti	2.4	1.5	0.0	1.1	2.5	1.2	1.9	2.1			
V	0.9	0.1	0.3	0.4	0.8	0.5	0.7	0.4			
Cr	0.6	7.1	5.9	0.8	4.5	1.9	8.8	0.7	8.0	3.0	3.0
Mn	23.0	31.6	36.8	27.7	16.4	15.8	17.7	25.7	31.1	51.6	32.2
Fe	6.6	13.8	17.4	0.0	0.0	0.0	16.8	11.9	0.0	0.0	0.0
Co	0.1	0.3	0.2	0.3	0.2	0.2	0.5	0.2	0.2	0.3	0.2
Ni	0.7	0.9	1.1	0.7	0.5	0.8	1.0	0.6	3.3	1.7	1.4
Cu	2.5	1.1	0.0	0.6	0.8	0.5	1.2	0.8	1.8	1.5	1.8
Zn	1.4	27.7	24.5	22.1	0.1	15.3	14.9	14.1	12.6	16.0	17.5
As	5.4	5.4	2.8	2.1	6.4	4.7	4.6	1.5	5.6	2.8	3.1
Se	0.0	1.1	0.8	0.9	0.0	0.0	1.1	0.0	1.8	2.0	1.3
Br					251	171	161	141	223	253	210
Rb	23	21	18	16	23	13	16	16	21	18	16
Sr	86	129	167	105	137	107	85	144	107	146	103
Mo	368	342	434	315	355	307	326	282	370	332	313
Cd	0.33	0.27	0.39	0.22	0.23	0.41	0.30	0.26	0.50	0.50	0.30
Sn	0.54	0.50	0.00	0.23	0.26	0.13	0.06	0.03			
Sb	1.00	0.26	0.06	0.03	0.42	0.16	0.12	0.11			
Cs	4.40	3.68	2.99	2.44	4.48	2.49	1.80	2.43	2.59	2.26	2.34
Ba	7.5	7.7	8.9	4.9	2.8	2.3	4.7	6.3	5.3	6.2	5.3
W	4.7	2.8	4.0	3.9	7.6	5.1	8.1	3.8	5.0	3.6	5.3
Pb	0.11	0.03	0.00	0.04	0.05	0.00	0.01	0.02	0.00	0.06	0.11
U	0.41	0.38	0.76	0.26	0.78	0.33	0.47	0.58	0.56	0.56	0.72
Nutrients (ppm)											
N		0.23	0.49	0.68	0.55	0.44	0.70	1.00			
NH3-N		0.23	0.43	0.56	0.51	0.28	0.34	0.44			
TP							0.32	0.33			
BOD (mg/L)	1.0		1.5	<1	<1		<2	3.4			
COD (mg/L)	3.5		9.5	<2	3.5		3.5	18.7			

Notes *reported as ppm $CaCO_3$

**pH reading approx. 1 unit high (9.61-1.11)

LTV-Tailings Discharge Pipe

	Average	Standard Deviation	Maximum	Minimum	N
pH	8.59	0.17	8.99	8.37	11
Measured Eh	75	95	182	-181	11
Corrected Eh	278	93	391	30	11
majors (ppm)					
Al	0.01	0.01	0.02	0.00	11
Si	8.5	1.5	10.8	6.5	11
P	0.00	0.00	0.01	0.00	10
Fe	0.00	0.00	0.01	0.00	11
Mn	0.03	0.01	0.04	0.02	11
Sr	0.11	0.02	0.14	0.08	11
Ba	0.01	0.00	0.01	0.00	11
Ca	16.7	3.8	22.9	10.7	11
Mg	31.3	4.1	39.0	22.4	11
Na	130	23	183	103	11
K	17.1	2.4	22.0	12.9	11
F	9.8	1.1	10.9	7.5	11
Cl	36.3	2.9	39.9	30.2	11
NO2-N	0.09	0.03	0.17	0.05	11
Br	0.19	0.02	0.23	0.16	11
NO3-N	1.84	0.66	3.05	1.15	11
SO4	116	6.9	127	108	11
HCO_3^-*	274	47	370	195	11
trace (ppb)					
Li	85	62	265	44	11
B	349	95	501	204	11
Sc	1.8	1.2	3.5	0.1	8
Ti	1.6	0.8	2.5	0.0	8
V	0.5	0.3	0.9	0.1	8
Cr	4.0	3.0	8.8	0.6	11
Mn	28.1	10.5	51.6	15.8	11
Fe	6.0	7.5	17.4	0.0	11
Co	0.2	0.1	0.5	0.1	11
Ni	1.1	0.8	3.3	0.5	11
Cu	1.1	0.7	2.5	0.0	11
Zn	15.1	8.5	27.7	0.1	11
As	4.0	1.6	6.4	1.5	11
Se	0.8	0.7	2.0	0.0	11
Br	201	45	253	141	7
Rb	18.1	3.1	22.7	13.2	11
Sr	120	26	167	85	11
Mo	340	41	434	282	11
Cd	0.34	0.10	0.50	0.22	11
Sn	0.22	0.21	0.54	0.00	8
Sb	0.27	0.32	1.00	0.03	8
Cs	2.90	0.89	4.48	1.80	11
Ba	5.6	2.0	8.9	2.3	11
W	4.9	1.6	8.1	2.8	11
Pb	0.04	0.04	0.11	0.00	11
U	0.53	0.18	0.78	0.26	11
Nutrients (ppm)					
N	0.58	0.24	1.00	0.23	7
NH3-N	0.40	0.12	0.56	0.23	7
TP	0.33	0.01	0.33	0.32	2
BOD (mg/L)	1.97	1.27	3.40	1.00	3
COD (mg/L)	7.74	6.65	18.70	3.50	5

Notes *reported as ppm $CaCO_3$

LTV-Tailings Basin Reclaim

Date	06/13/96	09/11/96	01/22/97	04/09/97	07/16/97	10/09/97	02/04/98	04/08/98	07/23/98	10/07/98	02/10/99
Field Parameters											
Temperature	22	19	1	1	24	13	3	6	19	9	1
Conductivity	800	850	750	720	800	750	1000	750	850	600	850
pH	9.06	8.66	8.68	8.56	8.91	8.81	8.75	8.55	9.03	8.77	8.45
Measured Eh	65	184	-148	216	97	138	160	200	79	86	133
Corrected Eh	266	388	72	436	296	348	379	415	283	299	353
majors (ppm)											
Al	0.01	0.03	0.00	0.01	0.01	0.01	4.00	0.01	0.01	0.01	0.01
Si	3.5	5.3	7.3	7.4	4.3	6.5	8.2	6.5	5.8	6.4	7.1
P		0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.02	0.02	0.18	0.00	0.02	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.07	0.08	0.00	0.00	0.04	0.01	0.00	0.00	0.08
Sr	0.10	0.13	0.15	0.12	0.12	0.12	0.14	0.11	0.13	0.14	0.14
Ba	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Ca	18.2	19.2	26.1	20.9	18.5	18.0	21.4	18.5	19.2	22.2	25.9
Mg	34.2	33.5	39.6	35.1	33.2	33.5	38.2	32.4	36.3	34.4	42.2
Na	119	120	125	105	113	121	128	105	116	102	129
K	12.4	15.7	13.9	12.0	14.2	14.6	12.1	11.1	15.2	13.9	13.0
F	7.9	9.3	9.2	7.5	7.9	9.1	9.7	8.0	9.7	7.6	8.0
Cl	35.5	37.1	36.3	32.5	32.2	31.0	31.9	26.0	33.5	32.9	35.5
NO2-N	0.04	0.04	0.06	0.06	0.03	0.03	0.05	0.03	0,03	0.02	0.05
Br	0.14	0.16	0.16	0.16	0.17	0.18	0.17	0.14	0.18	0.18	0.21
NO3-N	0.79	0.46	1.36	1.40	0.79	1.78	1.40	0.17	1.05	1.11	1.81
SO4	109	118	132	114	109	116	128	108	123	122	135
HCO_3^{-}*	256	262	280	259	276	283	309	266	268	243	325
trace (ppb)											
Li	46	64	78	55	307	43	58	37	53	53	48
B	319	453	326	280	330	226	336	263	411	446	279
Sc	1.3	1.5	0.1	0.1	1.1	1.6	2.0	1.6			
Ti	0.7	1.6	0.1	1.5	3.3	1.7	2.8	2.1			
V	1.3	1.6	0.3	0.3	0.8	0.7	0.4	0.4			
Cr	1.5	7.4	7.2	1.5	1.3	1.6	9.1	2.1	8.0	4.0	3.0
Mn	1.0	3.4	79.9	78.5	2.2	1.0	39.7	10.4	4.1	2.7	74.2
Fe	11.3	0.0	19.3	182.0	2.6	9.8	19.8	2.6	1.3	2.3	10.0
Co	0.1	0.1	0.3	0.6	0.4	0.2	0.2	0.2	0.5	0.2	0.6
Ni	0.4	0.6	1.1	1.2	0.5	1.0	1.1	0.9	1.2	1.3	1.8
Cu	1.4	0.9	0.0	0.5	11.0	0.7	1.3	0.9	2.3	1.2	2.2
Zn	2.3	26.3	28.4	12.2	1.5	21.3	14.0	12.3	14.2	14.1	18.7
As	9.3	21.9	6.2	5.9	11.3	10.3	7.4	5.9	20.2	15.5	8.2
Se	0.0	0.9	0.9	0.0	0.9	0.0	1.0	1.3	2.6	0.9	3.1
Br					184	184	149	115	191	222	211
Rb	12	17	14	12	15	15	11	10	16	17	12
Sr	100	133	189	136	142	122	150	113	132	159	138
Mo	263	316	323	259	257	264	273	215	303	321	271
Cd	0.29	0.28	0.27	0.16	0.08	0.37	0.19	0.23	0.40	0.40	0.30
Sn	0.11	0.00	0.00	0.06	0.61	0.00	0.16	0.08			
Sb	0.63	0.24	0.04	0.02	0.25	0.18	0.09	0.08			
Cs	1.90	2.60	1.87	1.54	2.26	2.10	1.45	1.45	2.01	2.13	1.38
Ba	4.0	7.0	7.4	6.0	4.6	3.3	4.2	4.0	5.8	6.2	5.6
W	2.7	3.2	3.5	2.0	4.7	4.6	5.1	3.5	6.3	3.9	8.5
Pb	0.06	0.03	0.00	0.09	0.79	0.00	0.18	0.03	0.17	0.05	0.11
U	0.33	0.32	0.68	0.21	1.02	0.24	0.50	0.53	0.72	0.63	0.74
Nutrients (ppm)											
N		0.22	0.39	0.46	0.26	0.27	0.38	0.34			
NH3-N		0.09	0.28	0.20	0.04	0.06	0.17	0.07			
TP							0.02	0.03			
BOD (mg/L)	<1		1.4	<1	<1		<2	3.8			
COD (mg/L)	5.5	2.0	9.5	3.5	<2		<2	18.7			

Notes *reported as ppm $CaCO_3$

**pH reading approx. 1 unit high (9.58-1.13)

LTV-Tailings Basin Reclaim

	Average	Standard Deviation	Maximum	Minimum	N
pH	8.75	0.20	9.06	8.45	11
Measured Eh	110	99	216	-148	11
Corrected Eh	321	100	436	72	11
majors (ppm)					
Al	0.37	1.20	4.00	0.00	11
Si	6.2	1.4	8.2	3.5	11
P	0.00	0.00	0.01	0.00	10
Fe	0.02	0.05	0.18	0.00	11
Mn	0.03	0.03	0.08	0.00	11
Sr	0.13	0.01	0.15	0.10	11
Ba	0.01	0.00	0.01	0.00	11
Ca	20.7	2.9	26.1	18.0	11
Mg	35.7	3.1	42.2	32.4	11
Na	117	9.3	129	102	11
K	13.5	1.5	15.7	11.1	11
F	8.5	0.9	9.7	7.5	11
Cl	33.1	3.1	37.1	26.0	11
NO2-N	0.04	0.01	0.06	0.02	11
Br	0.17	0.02	0.21	0.14	11
NO3-N	1.10	0.52	1.81	0.17	11
SO4	119.5	9.5	135.2	108.0	11
HCO_3^{-}*	275	24	325	243	11
trace (ppb)					
Li	77	77	307	37	11
B	334	75	453	226	11
Sc	1.1	0.7	2.0	0.1	8
Ti	1.7	1.0	3.3	0.1	8
V	0.7	0.5	1.6	0.3	8
Cr	4.2	3.1	9.1	1.3	11
Mn	27.0	34.3	79.9	1.0	11
Fe	23.7	53.0	182.0	0.0	11
Co	0.3	0.2	0.6	0.1	11
Ni	1.0	0.4	1.8	0.4	11
Cu	2.0	3.1	11.0	0.0	11
Zn	15.0	8.5	28.4	1.5	11
As	11.1	5.7	21.9	5.9	11
Se	1.0	1.0	3.1	0.0	11
Br	179	37	222	115	7
Rb	14	2.6	17	10	11
Sr	137	24	189	100	11
Mo	279	33	323	215	11
Cd	0.27	0.10	0.40	0.08	11
Sn	0.13	0.20	0.61	0.00	8
Sb	0.19	0.20	0.63	0.02	8
Cs	1.88	0.39	2.60	1.38	11
Ba	5.3	1.3	7.4	3.3	11
W	4.4	1.8	8.5	2.0	11
Pb	0.14	0.22	0.79	0.00	11
U	0.54	0.25	1.02	0.21	11
Nutrients (ppm)					
N	0.33	0.09	0.46	0.22	7
NH3-N	0.13	0.09	0.28	0.04	7
TP	0.03	0.01	0.03	0.02	2
BOD (mg/L)	2.60	1.70	3.80	1.40	2
COD (mg/L)	7.84	6.69	18.70	2.00	5

Notes *reported as ppm $CaCO_3$

LTV-Seep

Date	06/13/96	09/11/96	01/22/97	04/09/97	07/16/97	10/09/97	02/04/98	04/08/98	07/23/98	10/07/98	02/10/99
Field Parameters											
Temperature	13	14	11	10	11	14	10	10	10	9	9
Conductivity	1430	1200	1300	1050	1100	1200	1150	900	1350	1100	1250
pH	7.23	7.70	7.30	7.41	7.31	7.45	7.38	7.28	7.22	7.16	7.12
Measured Eh	-48	171	-178	25	2.4	-23	32	117	-38	103	25
Corrected Eh	161	380	33	237	213	186	244	329	174	316	237
majors (ppm)											
Al	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00
Si	11.2	9.3	10.0	10.5	9.3	10.2	10.6	11.1	11.1	12.3	11.4
P			0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
Fe	2.18	0.09	0.73	1.73	1.20	1.50	2.42	2.49	2.50	2.66	2.70
Mn	1.43	1.23	0.82	0.69	1.00	0.94	0.88	0.91	1.00	0.98	0.99
Sr	0.50	0.24	0.28	0.27	0.33	0.35	0.35	0.38	0.43	0.43	0.40
Ba	0.05	0.02	0.04	0.04	0.04	0.05	0.05	0.05	0.06	0.06	0.05
Ca	96.3	57.0	65.9	50.9	67.3	68.7	65.6	70.6	80.5	82.7	80.6
Mg	109.0	65.4	68.7	49.0	70.9	72.3	69.8	74.1	84.8	87.8	86.8
Na	91	107	140	110	114	107	107	107	102	103	100
K	15.4	16.2	20.9	16.4	17.3	16.3	16.3	16.2	16.2	15.6	15.4
F	1.8	4.4	4.6	4.8	4.8	4.3	4.3	4.2	3.5	3.3	3.3
Cl	31.7	31.9	36.2	35.5	35.7	34.6	32.4	31.4	29.1	28.9	29.1
NO2-N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Br	0.12	0.16	0.16	0.18	0.17	0.16	0.18	0.17	0.15	0.14	0.14
NO3-N	0.18	0.19	0.43	0.47	0.09	1.47	0.11	0.16	0.27	0.35	0.86
SO4	284	207	263	169	237	217	206	220	251	243	234
HCO_3^-*	530	415	427	342	439	462	450	500	490	524	515
trace (ppb)											
Li	29	27	30	19	109	22	29	23	25	27	25
B	383	468	515	457	455	338	453	483	526	527	422
Sc	3.8	2.5	0.1	0.1	2.6	2.8	2.9	2.8			
Ti	3.4	2.4	0.2	3.1	9.5	3.7	7.7	7.4			
V	0.2	0.0	0.2	0.1	0.2	0.0	0.1	0.2			
Cr	0.4	1.5	1.6	2.1	1.8	0.8	2.0	1.2	18.0	8.0	5.0
Mn				over	over	over	over	over	over	over	over
Fe	over	over	over	over	over	over	over	over	over	over	over
Co	5.1	1.9	3.7	1.6	4.0	2.4	2.0	1.6	2.3	2.0	2.2
Ni	1.9	1.5	0.9	1.7	1.3	1.2	1.7	1.5	3.3	2.7	2.0
Cu	1.2	1.1	0.0	0.0	0.8	0.8	0.9	0.6	1.5	0.5	0.6
Zn	7.8	28.9	30.2	23.7	5.0	17.7	18.1	12.5	15.0	13.9	17.7
As	3.7	2.2	4.8	5.8	4.9	3.7	5.9	4.7	6.1	5.8	5.5
Se	0.0	0.2	2.2	0.7	0.0	0.0	0.3	0.4	1.4	2.2	1.6
Br					191	146	142	133	155	161	154
Rb	11	16	17	13	14	11	12	12	13	13	12
Sr	450	257	369	303	354	322	338	336	456	455	397
Mo	15	129	123	106	102	86	95	84	67	71	74
Cd	0.04	0.12	0.07	0.09	0.03	0.09	0.06	0.05	0.10	0.10	0.10
Sn	0.17	0.13	0.40	0.00	0.00	0.09	0.07	0.00			
Sb	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00			
Cs	1.00	1.72	1.25	1.06	1.03	0.91	1.06	1.17	1.05	1.06	0.95
Ba	47	21	39	45	43	43	49	52	59	62	52
W	0.11	0.18	0.75	0.15	0.13	0.12	0.22	0.23	0.81	3.81	1.65
Pb	0.03	0.08	0.48	0.08	0.10	0.00	0.07	0.00	0.09	0.07	0.06
U	0.16	0.21	0.44	0.19	0.66	0.11	0.27	0.19	0.33	0.35	0.37
Nutrients (ppm)											
N		<.20	0.22	<0.3	0.28	0.29	0.33	0.46			
NH3-N		0.12	0.32	0.24	0.34	0.27	0.31	0.23			
TP							0.01	0.03			
BOD (mg/L)	<1			<1							
COD (mg/L)	7.5	<2		<2							

Notes *reported as ppm $CaCO_3$
**pH reading approx. 1 unit high (8.23-1.11)

LTV-Seep

	Average	Standard Deviation	Maximum	Minimum	N
pH	7.32	0.16	7.70	7.12	11
Measured Eh	17	94	171	-178	11
Corrected Eh	228	94	380	33	11
majors (ppm)					
Al	0.00	0.00	0.01	0.00	11
Si	10.6	0.9	12.3	9.3	11
P	0.00	0.01	0.01	0.00	9
Fe	1.84	0.87	2.70	0.09	11
Mn	0.99	0.20	1.43	0.69	11
Sr	0.36	0.08	0.50	0.24	11
Ba	0.05	0.01	0.06	0.02	11
Ca	71.5	12.8	96.3	50.9	11
Mg	76.2	15.5	109.0	49.0	11
Na	108	12	140	91	11
K	16.6	1.5	20.9	15.4	11
F	3.9	0.9	4.8	1.8	11
Cl	32.4	2.7	36.2	28.9	11
NO2-N	0.00	0.00	0.00	0.00	11
Br	0.16	0.02	0.18	0.12	11
NO3-N	0.42	0.41	1.47	0.09	11
SO4	230	31	284	169	11
HCO_3^-*	463	57	530	342	11
trace (ppb)					
Li	33	25	109	19	11
B	457	59	527	338	11
Sc	2.2	1.3	3.8	0.1	8
Ti	4.7	3.2	9.5	0.2	8
V	0.1	0.1	0.2	0.0	8
Cr	3.8	5.2	18.0	0.4	11
Mn					
Fe					
Co	2.6	1.1	5.1	1.6	11
Ni	1.8	0.7	3.3	0.9	11
Cu	0.7	0.5	1.5	0.0	11
Zn	17.3	7.9	30.2	5.0	11
As	4.8	1.2	6.1	2.2	11
Se	0.8	0.9	2.2	0.0	11
Br	155	18	191	133	7
Rb	13	2	17	11	11
Sr	367	66	456	257	11
Mo	86	31	129	15	11
Cd	0.08	0.03	0.12	0.03	11
Sn	0.11	0.13	0.40	0.00	8
Sb	0.01	0.01	0.04	0.00	8
Cs	1.11	0.22	1.72	0.91	11
Ba	47	11	62	21	11
W	0.74	1.12	3.81	0.11	11
Pb	0.10	0.13	0.48	0.00	11
U	0.30	0.16	0.66	0.11	11
Nutrients (ppm)					
N	0.32	0.09	0.46	0.22	5
NH3-N	0.26	0.07	0.34	0.12	7
TP	0.02	0.01	0.03	0.01	2
BOD (mg/L)	0.00				0
COD (mg/L)	7.50		7.50	7.50	1

Notes *reported as ppm $CaCO_3$

Appendix VI: Compiled data from experiments between tailings (from National, Inland, and LTV) and process waters

Chemical composition of fluids produced during National tailings/process water interaction in laboratory column Nat-A.

Days	0	14	28	42	70	95	146	175	216
*pH	8.32	8.32	8.28	8.04	8.06	7.91	7.97	8.07	7.96
ANIONS (ppm)									
F	1.18	1.21	1.21	1.23	1.18	1.13	1.10	1.09	1.24
Cl	27.3	27.4	28.1	35.8	28.8	28.1	29.1	28.9	29.5
NO2-N	0.331	0.016	0	0.065	0	0.016	0	0	0
Br	0.053	0.058	0.055	0.062	0.059	0.06	0.058	0.056	0.047
NO3-N	3.37	0.088	0.011	0.023	0	4.94	0.007	0.007	0.007
SO4	56	57.4	58.7	58.9	60	59.1	57.1	58.6	59.03
**HCO3	n.a.	245	240	256	255	290	286	291	301
CATIONS (ppm)									
Al	0.005	0.001	0.015	0.002	0.005		0.001	0.009	0.003
Si	22.0	22.3	21.4	22.2	19.2	19.3	20.4	22.1	21.2
Ca	27.2	25.0	20.9	19.8	20.4	22.2	25.1	25.5	26.1
Mg	43.1	47.7	44.6	47.2	53.8	56.7	58.3	58.3	59.8
Na	42.2	37.0	36.4	37.7	36.3	37.6	35.2	37.5	39.5
K	9.3	7.2	6.2	6.5	3.9	3.0	2.5	2.6	2.5
TRACE (ppb)									
Li	14	10	9	11	8	7.4	5	4.7	3.46
B	125	159	134	143	137	134	141	169	137
Mn	44.3	605.1	784	702.3	864	637	491	430	410
Fe	18	4	30	9	0	0	19	9	0
Co	0.2	0.2	0.2	0.2	0.1	0.1	0.3	0.2	0.1
Ni	0.4	0.3	0.3	0.3	0.1	0.1	0.3	0.2	0.2
Cu	1.6	0.1	1.2	0.3	0.1	0.0	0.4	0.0	0.0
Zn	16	27	31	31	134	17	138	144	213
As	3.4	4.9	4.2	3.9	3.9	4.1	3.7	4.1	4.1
Se	2.8	2.5	0.0	1.3	0.9	3.2	0.4	1.0	0.0
Rb	8.3	6.7	5.6	5.9	3.4	2.6	2.1	2.1	2.2
Sr	103	143	156	193	278	295	306	355	374
Mo	80.4	94.6	91.5	81.3	59.0	69.0	48.3	48.7	45.9
Cd	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0
Cs	1.09	0.76	0.54	0.61	0.37	0.33	0.24	0.26	0.19
Ba	20.0	22.3	23.4	37.8	41.2	25.5	22.3	20.7	37.7
W	0.58	0.42	0.37	0.47	0.28	.27	0.12	0.16	0.24
Pb	0.21	0.03	0.14	0.01	0.06	n.d.	0.1	6	n.d.
U	0.51	0.39	0.41	0.24	0.11	0.11	n.d.	0.01	0.22

* pH is uncorrected for CO_2 degassing effects ** HCO3 as alkalinity in mg/kg CaCO3

Chemical composition of fluids produced during National tailings/process water interaction in laboratory column NAT-B.

Days	0	14	28	42	71	95	146	175	216
*pH	8.32	8.27	8.18	7.95	7.84	7.83	7.75	7.82	7.57
ANIONS (ppm)									
F	1.24	1.23	1.19	1.09	1.13	1.13	1.12	1.07	1.09
Cl	27.5	27.95	28	28.4	28.9	28.25	29	28.9	28.7
NO2-N	0.303	0	0	0	0	0	0	0	0
Br	0.056	0.055	0.057	0.056	0.057	0.06	0.054	0.054	0.06
NO3-N	3.33	0.053	0.008	0.013	0.002	0.088	0.006	0	0
SO4	56.7	58.09	58.4	56.2	54.4	55.5	54.6	54.4	56.7
**HCO3	n.a.	216	246	261	233	285	300	319	331
CATIONS (ppm)									
Al	0.004	0.004	0.003	0.003	0.007	0.000	0.002	0.001	0.017
Si	20.7	19.7	19.2	18.5	18.6	18.2	20.4	21.2	20.1
Ca	27.7	26.0	23.9	28.2	26.0	29.2	31.5	34.3	34.9
Mg	42.0	45.6	45.6	55.3	59.2	60.7	60..7	62.7	62.5
Na	43.2	33.0	31.9	20.6	20.3	21.6	24.8	31.6	32.2
K	8.6	4.9	3.5	2.1	0.9	1.0	1.1	1.3	1.3
TRACE (ppb)									
Li	14.7	10.8	8.9	7.5	4.9	5.9	4.6	5.2	6.7
B	107	132	143	150	139	140	145	119	120
Mn	42	1022	1255	1390	1330	645	561	497	438
Fe	8	274	377	46	4	18	110	14	22
Co	0.1	0.2	0.2	0.2	0.5	0.3	0.4	0.2	0.2
Ni	0.3	0.5	0.3	0.3	0.2	0.3	0.3	0.1	0.3
Cu	1.2	0.1	0.2	0.4	0.1	n.d.	0.4	0.4	n.d.
Zn	11	40	23	65	94	24	114	87	192
As	3.0	5.3	3.9	3.6	4.5	3.1	3.2	2.3	1.5
Se	2.1	2.2	0.0	0.4	1.2	1.7	0.6	1.2	0.0
Rb	7.9	4.6	3.1	2.0	1.0	0.9	1.0	1.2	1.3
Sr	109	198	227	249	329	192	233	317	355
Mo	70.8	80.9	56.1	20.2	20.4	21.8	20.0	22.7	20.0
Cd	0.1	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1
Cs	1	0.58	0.36	0.22	0.17	0.14	0.12	0.17	0.1
Ba	17.5	22.0	18.9	26.9	28.0	17.2	5.9	17.3	20.8
W	0.27	0.43	0.18	0.27	0.05	0.15	0.16	0.24	0.38
Pb	0.04	0.1	0.16	0.82	0.13	0.05	0.37	0.08	0.2
U	0.53	0.31	0.26	0.12	0.04	0.03	0.02	0.03	0.12

* pH is uncorrected for CO_2 degassing effects ** HCO3 as alkalinity in mg/kg CaCO3

Chemical composition of fluids produced during Inland tailings/process water interaction in laboratory column INL-A.

Days	1	14	28	41	71	95	146	175	216
*pH	8.25	8.09	8.06	8.03	7.86	8.06	7.9	7.88	7.95
ANIONS (ppm)									
F	3.7	3	3.1	3.15	3.05	3.1	2.87	2.79	2.98
Cl	55.1	53.3	55.2	56	57.5	57.4	58	57.8	59.5
NO2-N	0.503	0	0	0	0	0.027	0	0	0
Br	0.368	0.355	0.362	0.371	0.376	0.415	0.384	0.378	0.352
NO3-N	0.575	0.721	0.007	0.048	0.004	0.102	0.066	0	0.008
SO4	53.8	49.9	51.3	50.9	52	54.3	56	56.4	58.7
**HCO3	n.a.	226	231	n.a.	289	283	307	333	353
CATIONS (ppm)									
Al	.001	0.003	0.011	0.006	0.008	0.008	0.002	0.012	0.002
Si	18.9	21.5	19.4	20.5	20.3	19	19.7	19.9	19.8
Ca	27.1	30.9	31.6	33.8	36.1	38.2	43.8	45.2	47.9
Mg	42.6	51.6	52.4	55.5	64.3	66.6	73.1	73.8	78.9
Na	34.0	27.7	26.1	25.6	24.9	24	23.4	22.3	22.2
K	8.9	6.0	5.2	4.7	4.3	3.91	4.0	3.9	3.8
TRACE (ppb)									
Li	15.2	14.75	9.8	8.7	9.3	9.37	9.3	7.8	5.24
B	151	206	189	206	223	209	167	220	290
Mn	177.4	336.4	390.4	589.9	341.9	315	474	698	453
Fe	24	31	89	16	1	238	36	25	5
Co	0.3	0.5	0.7	0.3	0.2	0.3	0.7	0.3	0.2
Ni	0.8	0.8	0.9	1.0	0.3	0.4	0.5	0.5	0.2
Cu	0.5	0.1	2.0	1.0	0.1	0.4	0.6	0.5	0.0
Zn	27	47	50	80	147	111	115	164	142
As	8.3	11.5	7.6	6.3	5.4	3.8	5.0	3.0	3.8
Se	1.9	0.9	1.3	0.0	0.8	0.0	3.1	0.0	1.7
Rb	9.0	5.7	4.6	3.9	3.6	3.1	3.1	3.0	3.0
Sr	189	237	247	272	328	283	328	355	405
Mo	100.4	60.1	45.5	40.0	36.0	40.2	33.5	28.8	25.2
Cd	0.2	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.0
Cs	1.5	0.85	0.6	0.54	0.46	0.35	0.39	0.36	0.32
Ba	26.1	24.0	22.0	41.6	38.5	19.8	22.1	20.2	27.2
W	1.06	0.69	0.71	0.56	0.52	0.44	0.29	0.34	0.23
Pb	0.08	0.07	7.1	0.8	0.06	0.04	6.3	0.38	0
U	0.46	0.11	0.09	0.09	0.09	0.07	0.03	0.04	0.24

* pH is uncorrected for CO_2 degassing effects ** HCO3 as alkalinity in mg/kg CaCO3

Chemical composition of fluids produced during Inland tailings/process water interaction in laboratory column INL-B.

Days	1	14	28	41	71	95	146	175	216
*pH	8.32	8.05	8.02	8.05	8.3	7.85	7.73	7.8	7.55
ANIONS (ppm)									
F	3.50	3.16	3.23	3.16	3.02	2.91	2.89	2.81	2.75
Cl	54.9	55.7	56	56.6	58	56.9	59.3	59.6	61.5
NO2-N	0.55	0.022	0	0	0	0			
Br	0.372	0.37	0.371	0.372	0.38	0.374	0.367	0.382	0.372
NO3-N	0.56	0.084	0.037	0.011	0.005	0.027	0.02	0.005	0.01
SO4	53.6	53.1	51.3	51.1	49.9	51.94	54.36	54.8	55.12
**HCO3	n.a.	222	231	220	282	294	318	331	336
CATIONS (ppm)									
Al	0.006	0.002	0.005	0.006	0.013	0.001	0.015	0.004	0.002
Si	18.7	20.1	20.0	20.7	20.8	19.0	21.6	20.6	19.6
Ca	26.1	31.0	33.1	33.8	38.4	41.5	46.8	47.3	49.3
Mg	42.6	51.2	55.0	56.0	68.9	72.1	78.0	76.2	82.3
Na	34.2	27.8	26.7	26.7	22.0	18.0	16.2	15.7	15.2
K	8.9	6.0	5.2	5.1	3.9	3.0	2.6	2.2	1.7
TRACE (ppb)									
Li	13.3	12.6	9.6	9.8	8.8	8.4	6.9	5.8	2.0
B	135	204	190	226	255	204	250	235	267
Mn	112	333	409	404.8	424	446	567	587	597
Fe	24	33	383	33	9	23	108	33	23
Co	0.4	0.5	0.8	0.4	0.5	1.0	1.1	0.4	0.5
Ni	1.0	1.0	0.6	0.5	0.4	0.4	1.1	0.4	0.3
Cu	1.0	0.1	0.0	0.3	0.1	0.1	0.4	0.3	0.0
Zn	27	46	51	108	84	47	140	103	218
As	6.1	11.3	7.8	7.6	4.1	2.3	5.0	2.8	2.1
Se	1.2	2.9	0.0	1.1	1.2	0.0	1.4	0.2	1.8
Rb	8.7	5.8	4.9	4.9	3.2	2.3	2.2	1.8	1.6
Sr	184	235	260	280	325	267	293	304	306
Mo	94.3	61.0	46.0	46.0	32.2	26.7	21.2	18.7	14.9
Cd	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0
Cs	1.42	0.83	0.69	0.71	0.44	0.3	0.27	0.25	0.11
Ba	30.0	24.0	15.1	44.4	33.5	14.1	11.3	16.2	13.0
W	1.45	0.98	0.95	0.93	0.58	0.62	0.4	0.4	0.27
Pb	0.39	0.21	0.15	0.29	0.14	0	0.22	0.25	0
U	0.38	0.1	0.09	0.08	0.08	0.05	0.03	0.02	0.15

* pH is uncorrected for CO_2 degassing effects ** HCO3 as alkalinity in mg/kg CaCO3

Chemical composition of fluids produced during LTV tailings/process water interaction in laboratory column LTV-A.

Days	0	14	28	43	71	95	146	175	216
***pH**	8.37	8.15	8.05	7.84	7.85	7.77	7.82	7.82	7.84
ANIONS (ppm)									
F	9.20	7.62	7.37	7.31	7.09	6.70	6.36	6.21	6.29
Cl	36.6	37.07	38.2	38.2	39.47	39.8	51.5	50.8	62.2
NO2-N		0	0	0	0	0	0	0	0
Br	0.154	0.153	0.162	0.16	0.16	0.16	0.17	0.166	0.157
NO3-N	0.044	0.118	0	0.012	0	0.843	0.009	0.006	0.02
SO4	105.4	104.8	105.4	103.2	106.1	100.7	91.2	88	69.4
**HCO3	306	305	326	334	332	338	381	385	397
CATIONS (ppm)									
Al	0.010	0.002	0.004	0.006	0.007	0.023	0.003	0.005	0.002
Si	13.2	15.0	16.7	18.2	18.1	17.4	18.8	20.3	19.0
Ca	18.8	29.6	40.1	43.8	43.1	44.4	47.7	47.8	47.6
Mg	29.7	41.3	49.7	48.1	52.2	55.5	60.0	60.4	64.2
Na	121.0	101.5	87.4	83.4	89.2	80.5	80.1	79.8	81.5
K	17.8	12.0	8.5	7.3	6.2	4.3	4.5	4.3	4.4
TRACE (ppb)									
Li	60	54.03	50.8	45	41	39.9	33.6	34	39.6
B	347	424	514	541	730	542	566	555	634
Mn	67.5	321.2	388	362	379	266	173	169	128
Fe	25	14	41	31	23	99	44	31	46
Co	0.2	0.5	0.5	0.6	0.2	0.4	0.4	0.5	0.5
Ni	1.3	0.6	0.6	0.5	0.4	0.7	0.5	0.4	0.3
Cu	3.7	0.3	0.8	0.7	0.3	1.1	0.5	0.0	0.0
Zn	20	33	26	38	96	86	142	140	126
As	3.1	5.0	3.5	3.4	3.4	2.0	1.6	1.4	0.9
Se	0.0	0.5	0.5	0.0	0.7	1.5	1.0	0.3	0.0
Rb	20.0	13.8	10.2	8.7	7.4	4.9	4.7	4.5	4.5
Sr	148	559	440	486	571	493	514	652	689
Mo	337.8	75.3	46.2	42.4	32.7	25.7	18.0	13.7	12.3
Cd	0.4	0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.0
Cs	3.7	2.28	1.57	1.4	1.43	0.97	0.79	0.7	0.65
Ba	16.7	24.4	25.0	29.8	20.8	16.3	15.2	16.2	30.4
W	2.75	1.29	0.78	0.73	0.59	0.37	0.66	0.93	0.72
Pb	0.1	0.05	0.14	0.17	0.13	0.1	0.02	0.23	0.1
U	0.38	0.06	0.06	0.06	0.05	0.03	0	0.01	0.04

* pH is uncorrected for CO_2 degassing effects ** HCO3 as alkalinity in mg/kg CaCO3

Chemical composition of fluids produced during LTV tailings/process water interaction in laboratory column LTV-B.

Days	0	14	28	43	71	95	146	175	216
*pH	8.28	8.13	8.09	7.99	8.43	7.82	7.67	7.82	7.99
ANIONS (ppm)									
F	9.30	7.96	7.50	7.11	7.00	6.87	6.67	6.38	6.10
Cl	35.9	36.8	37.7	38	39	38.3	39.5	39.2	39.2
NO2-N	0.381	0	0	0	0	0	0	0	
Br	0.152	0.155	0.158	0.157	0.163	0.161	0.169	0.162	0.165
NO3-N	1.013	0.624	0.009	0.018	0	0.023	0.011	0.011	0.005
SO4	104.8	106.5	106.7	103.6	104.7	105.2	104.7	102.6	98.05
**HCO3	n.a.	318	313	n.a.	339	336	358	376	393
CATIONS (ppm)									
Al	0.009	0.006	0.009	0.006	0.006	0.000	0.001	0.006	0.034
Si	13.5	15.7	16.4	19.3	19.8	19.0	20.7	20.1	19.3
Ca	17.4	24.6	31.2	37.5	43.7	47.3	46.9	44.1	44.1
Mg	28.9	40.0	49.8	56.1	58.5	60.1	60.7	60.3	63.9
Na	121.5	99.6	87.9	79.8	78.1	71.0	74.6	78.8	77.6
K	17.9	12.0	9.6	9.3	6.5	5.1	5.1	4.9	4.5
TRACE (ppb)									
Li	59.4	51.8	43.4	48.67	44.5	40.8	32.2	29.6	25.12
B	343	442	686	590	616	543	589	480	767
Mn	72.4	290	297	288.1	357	355	250	163	147.4
Fe	13	20	54	19	28	283	43	28	28
Co	0.2	0.3	0.4	0.3	0.5	0.5	1.7	0.6	0.2
Ni	0.6	0.8	0.6	0.4	0.4	0.4	0.5	0.2	0.2
Cu	1.0	0.4	0.7	0.5	0.2	0.7	0.5	0.2	0.0
Zn	13	30	15	68	103	80	116	113	374
As	4.0	5.9	4.2	5.7	4.6	3.7	5.3	2.7	2.2
Se	0.7	1.0	0.0	0.3	0.0	1.4	0.9	0.2	1.0
Rb	20.8	13.9	10.6	11.3	7.5	5.6	5.3	5.0	5.0
Sr	133	243	339	439	570	443	499	612	656
Mo	335.0	72.6	41.4	37.7	30.9	23.7	20.1	16.6	14.6
Cd	0.3	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0
Cs	3.9	2.2	1.6	1.8	1.21	0.83	0.82	0.79	0.67
Ba	16.0	24.4	24.8	31.4	24.1	13.1	8.7	18.0	13.7
W	2.7	1.64	0.99	0.7	0.46	0.36	0.4	0.46	0.37
Pb	0.19	0.04	0.08	0.5	0.06	0.06	0	3.7	0.14
U	0.41	0.08	0.07	0.05	0.04	0.02	0.01	0	0.04

* pH is uncorrected for CO_2 degassing effects ** HCO3 as alkalinity in mg/kg CaCO3

Appendix VII: Compiled Data from experiments between tailings (from National, Inland, and LTV) and rainwater

NATIONAL RAINWATER EXPERIMENT

Days		68	90	124	158	188	222	259	560
	Nat	Nat	Nat	Nat	Nat	Nat	Nat	Nat	Nat
Date		1/5/04							
Weeks	0	9	13	18	23	27	32	37	80
pH	7.89	7.7	7.8	8.19	8.17	8.28	8.36	7.65	
Alk	323	212	207	218	217	211	163	137	
Volume	0	3702	4219	4284	4375	6247	8021	10840	
majors (ppm)									
Al	0.001	0.000	0.006	0.025		0.001	0.001	0.004	0.001
Si	19.9	15.7	17.1	18.4	18.8	16.4	17.3	15.95	15
P	0			0.03					0
Fe	0.02	0.04	0.02	0.16	0.08	0.00	0.00	0	0
Mn	0.28	0.17	0.29	0.29	0.28	0.18	0.15	0.166	0.2
Sr	0.41	0.18	0.17	0.19	0.19		0.10	0.0822	0.1
Ba	0.02	0.11	0.06	0.04	0.01		0.00	0.008	0
Ca	31.4	19.0	19.5	21.2	21.3	16.4	14.7	14.1	17.9
Mg	62.6	28.4	30.3	33.4	34.4	31.9	27.6	24.6	28.4
Na	39.9	21.7	19.4	19.4	19.4	11.7	7.4	5.339	5.5
K	1.7	3.8	3.2	3.8	3.6	2.4	1.9	1.5	1.0
F	1.08	0.79	0.88	0.85	0.85	0.75	0.41	0.03	0.16
Cl	28.7	2.3	3.7	5.7	3.7	9.2	1.6	1.4	3.4
NO2-N	0.0			0.0	0.0	0.0		0.0	0.6
Br	0.070	0.000			1.830	0.000	0.000	0.000	0.000
NO3-N	0.01	0.01	0.01	0.62	0.00	0.04	0.81	1.10	0.00
SO4	51.8	2.4	0.8	0.6	1.0	0.1	0.8	0.5	0.4
trace (ppb)									
Li	6	5	4	6	8	4	3	2	3
B	171	155	107	126	117	59	41	24	12
Al									0
Sc	6.34	5.99	3.49	6.01	4.2				
Ti	2.96	0	0	1.99	0				
V	0.91	0.06	0.01	0.24	0.21				
Cr	1.6	0.2	0.3	0.0	1.2	0.3	0.2	0.2	8.0
Mn	258	162	264	256	263	194	168	180	147
Fe	20	46	22	171	89	0	1	7	0
Co	1.1	0.0	0.3	2.0	0.9	1.6	0.5	0.3	0.8
Ni	0.3	0.3	0.2	2.0	0.4	0.9	1.1	1.2	0.6
Cu	0.9	0.1	0.3	6.0	53.6	23.3	0.4	1.8	0.6
Zn	74	48	50	114	116	40	41	62	11
Ge	0.34	0.13	0.12	0.14	0.16				
As	0.9	2.6	3.5	2.8	2.2	2.9	2.5	2.6	2.3
Se	0.7	0.0	0.0	0.0	0.0	0.0	0.5	0.3	1.4
Br	65	8.5	8.95	3.56	7.3		7.7	3.3	16
Rb	1.6	2.3	1.8	2.2	2.2	1.5	1.2	1.0	0.9
Sr	447	180	178	203	199	144	106	87	85
Y	0.01	0	0	0.02	0				
Mo	19.8	33.8	35.6	31.3	31.0	25.9	17.3	8.5	18.3
Ag	0	0	0	0.05	0				
Cd	0.0	0.0	0.0	1.4	0.2	0.1	0.0	0.1	0.0
Sn	1.8	0.2	0.1	0.3	0.9				
Sb	0	0	0	0	0				
Te	0	0	0	0	0				
Cs	0.17	0.22	0.16	0.20	0.16	0.12	0.09	0.08	0.02
Ba	16.5	105.0	52.5	41.3	16.0	5.6	2.8	2.9	0.3
W	0.05	0.16	0.16	0.10	0.17	0.39	0.31	0.66	101.63
Pb	0.01	0.00	0.03	2.47	0.00	0.06	0.03	0.10	0.00
U	0.03	0.17	0.08	0.19	0.14	0.30	0.39	0.36	0.19

INLAND RAINWATER EXPERIMENT

Days	0	68	90	124	158	188	222	259	560
	lnl	lnl	lnl	lnl	lnl	lnl	lnl	lnl	lnl
Date									
Weeks	0	9	13	18	23	27	32	37	80
pH	7.69	7.46	7.59	8.57	8.04	8.45	8.17	8.05	
Alk	375	435	330	344	335	283	218	160	
Volume	0	3401	4354	4446	4572	6442	8419	11327	
majors (ppm)									
Al	0.000	0.000	0.001	0.009	0.006	0.001	0.009	0.001	0.002
Si	22.1	17.0	15.9	16.9	17.1	15.0	14.5	14.5	15.4
P	0								0
Fe	0.02	0.55	0.16	0.74	0.02	0.01	0.01	0.00	0.00
Mn	0.31	0.36	0.32	0.39	0.35	0.24	0.20	0.20	0.30
Sr	0.34	0.20	0.15	0.16	0.16		0.11	0.09	0.11
Ba	0.03	0.03	0.02	0.00	9.81		0.00	0.00	0.00
Ca	53.7	38.9	33.9	35.9	37.1	33.4	31.3	31.6	45.4
Mg	86.4	80.8	59.3	61.6	63.3	37.2	25.2	17.5	18.4
Na	18.2	11.3	8.5	8.7	9.0	7.8	5.9	5.1	4.9
K	1.6	1.0	0.8	0.9	0.9	0.8	0.7	0.7	0.8
F	2.70	3.20	4.05	3.85	3.50	1.70	1.12	0.79	0.42
Cl	71.5	5.5	4.3	4.8	5.1	7.0	2.4	1.9	3.3
NO2-N	0.0			0.0	0.0	0.0	0.0	0.0	0.1
Br	0.433	0.057	0.028	0.030	0.270	0.019	0.000	0.000	0.000
NO3-N	0.00			0.39	3.00	0.03	0.86	1.98	0.00
SO4	54.1	0.8	1.7	1.7	1.9	0.5	0.4	0.4	0.4
trace (ppb)									
Li	7	5	4	5	5	4	3	3	3
B	281	174	97	107	152	57	21	20	20
Al									3
Sc	7.05	6.17	3.49	5.18	4				
Ti	3.26	0	4.36	2.92	4.4				
V	0.52	0.08	0	0.04	0				
Cr	1.6	2.0	0.0	0.6	0.6	0.2	0.6	0.4	1.0
Mn	281	316	282	342	313	258	223	216	311
Fe	36	477	167	1260	12	0	4	2	20
Co	0.3	0.3	0.2	1.0	0.8	1.2	0.4	0.3	0.4
Ni	0.7	0.7	0.6	1.1	1.1	1.3	1.1	1.7	0.9
Cu	0.4	0.2	0.2	1.8	0.5	0.5	0.5	0.8	0.3
Zn	98	54	52	68	66	37	32	52	52
Ge	0.27	0.25	0.22	0.19	0.17				
As	2.6	7.2	3.7	6.1	5.1	4.9	4.3	4.5	1.8
Se	1.5	0.0	0.0	0.0	0.0	0.5	0.0	0.5	0.0
Br	438	58.5	28.11	24.55	20		17.8	13.8	6
Rb	1.4	0.8	0.7	0.8	0.7	0.7	0.7	0.8	0.8
Sr	328	203	154	167	172	144	111	92	111
Y	0.01	0	0.01	0.01	0.01				
Mo	13.5	7.1	8.0	9.3	9.3	19.3	17.9	16.0	10.2
Ag	0	0	0	0	0				
Cd	0.0	0.0	0.0	0.1	0.1	0.0	0.1	0.0	0.0
Sn	3.0	0.1	0.1	0.1	0.1				
Sb	0	0	0	0	0				
Te	0	0	0	0	0				
Cs	0.22	0.12	0.13	0.13	0.13	0.10	0.09	0.11	0.10
Ba	33.7	27.8	19.8	1.5	0.9	0.5	0.4	0.8	0.5
W	0.22	0.05	0.20	0.17	0.12	0.16	0.26	1.32	0.31
Pb	0.01	0.01	0.02	0.40	0.12	0.04	0.01	0.09	0.04
U	0.04	0.04	0.05	0.07	0.08	0.13	0.09	0.07	0.03

LTV RAINWATER EXPERIMENT

Days	0	68	75	124	158	188	222	259	560
	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV
Date									
Weeks	0	10	11	18	23	27	32	37	80
pH	7.5	7.55	7.62	8.09	8	8.33	8.03	7.84	
Alk	432	359	331	348	350	256	231	176	
Volume	0	3760	4470	4553	4678	6568	8479	11812	
majors (ppm)									
Al	0.000	0.000	0.001	0.010	0.005	0.001	0.002	0	0.001
Si	20.4	13.4	13.1	14.3	14.5	13.1	12.5	11.9	12
P									0
Fe	0.01	0.37	0.30	1.65	0.02	0.00	0.01	0	0
Mn	0.14	0.25	0.24	0.33	0.17	0.22	0.19	0.169	0.2
Sr	0.74	0.35	0.32	0.34	0.35		0.19	0.137	0.17
Ba	0.02	0.05	0.02	0.01	0.00		0.00		0
Ca	49.5	36.3	37.9	40.5	40.6	37.9	34.5	32.2	44.5
Mg	73.2	47.4	42.5	47.1	46.7	30.3	22.6	16.03	19.4
Na	79.0	42.0	38.4	39.3	39.8	30.5	23.1	18.6	19.5
K	5.0	3.7	3.5	3.6	3.5	3.0	2.4	2.04	1.9
F	5.49	8.60	7.40	7.32	6.70	3.31	2.03	1.19	0.751
Cl	50.7	2.0	4.3	7.9	5.1	3.2	1.8	1.4	1.931
NO2-N	0.0			0.0	0.0	0.0	0.0	0	0.0895
Br	0.190	0.018	0.015	0.015	0.00	0.000	0.015	0	0
NO3-N	0.01	0.01	0.01	0.04	0.01	0.04	0.34	0.27	0
SO4	76.6	2.5	1.6	0.2	0.7	0.8	0.7	0.79	1.013
trace (ppb)									
Li	37	56	49	52	49	40	33	24.4	23.3
B	679	198	148	143	205	112	46	35.8	41
Al									1.4
Sc	6.55	5.2	2.94	4.31	3.3				
Ti	4.13	3.1	4.62	3.17	4.5				
V	0.47	0.03	0	0	0				
Cr	0.2	0.0	0.0	0.1	0.0	0.2	0.6	0.35	0
Mn	132	221	211	296	170	225	197	185	200.9
Fe	26	356	285	1450	21	0	5	2.5	0
Co	0.6	0.1	0.3	1.0	0.4	5.5	1.1	0.24	0.3
Ni	0.2	0.5	0.6	1.9	1.5	2.0	1.6	1.15	0.8
Cu	0.4	0.1	0.2	7.3	0.5	2.0	1.1	1.36	0.2
Zn	38	48	53	121	55	41	40	47.8	47.4
Ge	0.02	0.3	0.24	0.5	0.52				
As	1.0	0.6	0.6	0.3	0.1	0.3	0.5	0.69	0.7
Se	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.28	0
Br	179	20.3	14.5	17.3	13.4		11.5	5.4	4
Rb	5.3	3.2	3.1	3.1	3.0	2.7	2.2	1.95	2
Sr	704	343	306	334	328	249	195	143	169.4
Y	0.01	0	0.01	0.01	0				
Mo	6.9	60.4	59.7	28.2	21.2	34.6	29.2	15.4	11.2
Ag	0	0	0	0.01	0				
Cd	0.0	0.0	0.1	0.8	0.0	0.1	0.1	0.023	0
Sn	1.2	0.2	0.1	0.3	0.1				
Sb	0	0	0	0	0				
Te	0	0	0	0	0				
Cs	0.74	0.42	0.45	0.42	0.43	0.32	0.26	0.25	0.25
Ba	19.2	44.7	21.2	11.0	2.8	2.1	1.6	1.31	1.15
W	0.54	0.52	0.63	0.67	0.72	0.72	1.09	0.595	0.77
Pb	0.00	0.00	0.04	1.20	1.40	0.20	0.08	0.084	0.03
U	0.04	0.01	0.01	0.02	0.01	0.02	0.01	0.009	0

Appendix VIII: Compiled Data from experiments between tailings (from National, Inland, and LTV) and groundwater

GROUNDWATER EXPERIMENT (NATIONAL)

	Nat	Nat	Nat	Nat	Nat	Nat	Nat	Nat	Nat	Nat
Date	preinj		9/26/97	10/13/97	11/12/97	12/18/97	1/14/98	2/11/98	3/17/98	4/22/98
Weeks	0	0	1	3	7	12	16	20	25	30
pH	7.98	7	7.42	7.33	7.25	7.95	7.8	8.01	8	8.2
Alk	350	196	232	227	241	251	276	273	282	266
majors (ppm)										
Al	0.001	0.001	0.009	0.000	0.007	0.004	0.004	0.015	0.001	0.003
Si	19.9	5.1	12.8	12.7	14.8	14.5	14.5	15.7	15.3	15.6
P	0	0	0	0	0	0				
Fe	0.02	0.23	0.03	0.00	0.01	2.60	2.05	3.24	0.04	0.00
Mn	0.28	0.46	0.63	0.61	0.90	0.63	0.72	0.57	0.52	0.46
Sr	0.41	0.19	0.19	0.19	0.21	0.21	0.23	0.26	0.28	
Ba	0.02	0.07	0.01	0.02	0.03	0.01	0.01	0.01	0.00	
Ca	31.4	71.2	68.0	67.9	67.6	63.9	62.9	68.1	65.6	62.8
Mg	62.6	28.6	29.5	31.0	32.8	35.4	38.0	42.4	45.1	47.6
Na	39.9	8.7	15.3	15.4	17.0	18.1	19.8	22.0	23.7	26.1
K	1.7	1.6	2.2	1.5	1.4	1.3	1.5	1.6	1.7	1.8
F	1.08	0.86	1.04	1.02	0.99	0.98	0.94	0.93	0.96	0.99
Cl	28.7	7.7	6.6	7.3	15.7	15.0	10.0	29.4	37.0	44.3
NO2-N	0.0	0.0				0.0			0.0	0.0
Br	0.070	0.027	0.024	0.024	0.027	0.029	0.034	0.049	0.630	0.074
NO3-N	0.01	0.08	0.01	0.01	0.01	0.11	0.75	0.05	1.86	0.63
SO4	51.8	104.3	85.6	85.6	85.3	84.7	83.8	76.3	67.8	58.9
trace (ppb)										
Li	6	8	14	9	8	8	8	10	12	10
B	171	71	46	67	64	93	88	75	97	128
Sc	6.34	1.8	3.3	3	4.2	5.8	2.98	5.35	3.63	
Ti	2.96	5.7	4.6	7.1	6.36	5.5	8.51	6.47	7.71	
V	0.91	0.06	0.04	0	0.13	0.08	0.03	0.21	0.23	
Cr	1.6	0.3	0.0	0.2	0.0	0.4	0.2	0.0	0.7	1.4
Mn	258	418	721	540	797	558	874	485	443	522
Fe	20	282	35	14	12				20	0
Co	1.1	0.5	0.4	1.2	0.9	0.5	0.5	0.3	4.6	0.6
Ni	0.3	0.8	0.5	1.7	0.8	2.3	2.5	1.1	2.3	2.3
Cu	0.9	6.4	2.4	0.2	0.4	21.6	2.9	1.6	2.0	1.1
Zn	74	75	3	51	57	60	61	71	48	40
Ge	0.34	0.06	0.14	0.13	0.16	0.15	0.13	0.31	0.17	
As	0.9	0.5	1.6	0.7	1.1	1.2	1.1	1.6	0.5	1.2
Se	0.7	0.0	0.0	0.0	0.0	0.0	0.3	0.1	0.0	0.0
Br	65	27.7	25.4	19	26	28	28.3	39.09	51	
Rb	1.6	1.2	1.5	1.3	1.3	0.9	1.0	1.1	1.1	1.4
Sr	447	236	200	197	219	221	227	253	280	312
Y	0.01	0	0.01	0.01	0.02	0.02	0.02	0.06	0	
Mo	19.8	0.0	3.8	4.3	4.9	5.4	6.2	6.4	6.2	7.2
Ag	0	0	0	0	0	0	0	0	0	
Cd	0.0	0.0	0.0	0.0	0.0	0.6	0.2	0.0	0.1	0.0
Sn	1.8	1.7	0.2	0.1	0.1	0.4	0.2	2.3	0.2	
Sb	0	0	0.01	0.01	0	0	0	0	0	
Te	0	0	0	0	0	0	0	0	0	
Cs	0.17	0.06	0.20	0.11	0.20	0.10	0.11	0.12	0.12	0.12
Ba	16.5	73.6	13.8	17.5	30.8	5.0	6.5	4.9	4.6	5.5
W	0.05	0.00	0.03	0.08	0.08	0.15	0.14	0.09	0.13	0.13
Pb	0.01	0.86	0.17	0.00	0.01	0.66	0.63	0.42	0.04	0.04
U	0.03	0.15	0.09	0.08	0.04	0.04	0.04	0.05	0.10	0.11

INLAND GROUNDWATER EXPERIMENT

	Inl	Inl	Inl	Inl	Inl	Inl	Inl	Inl	Inl	Inl
Date	pre-inj		9/26/97	10/13/97	11/12/97	12/18/97	1/14/98	2/11/98	3/17/98	4/22/98
Weeks	0	0	1	3	7	12	16	20	25	30
pH	7.67	7	7.35	7.32	7.26	8.05	8	8.31	7.96	8.35
Alk	399	196	255	303	321.2	332	400	406	444	400
majors (ppm)										
Al	0.000	0.001	0.001	0.003	0.001	0.024	0.016	0.003	0.012	0.003
Si	22.1	5.1	14.1	14.3	17.3	16.9	18.0	18.2	19.1	19.0
P	0	0	0	0	0	0	0	0		
Fe	0.02	0.23	0.36	0.01	0.00	1.41	1.15	0.96	0.047	0.00
Mn	0.31	0.46	0.63	0.52	0.30	0.21	0.23	0.18	0.17	0.18
Sr	0.34	0.19	0.24	0.26	0.29	0.29	0.31	0.38	0.39	
Ba	0.03	0.07	0.01	0.02	0.03	0.00	0.01	0.00	0.003	
Ca	53.7	71.2	75.4	78.6	77.4	72.7	70.3	70.0	68.1	63.5
Mg	86.4	28.6	35.2	41.4	49.5	55.3	61.1	78.7	83.8	84.3
Na	18.2	8.7	11.9	12.7	14.2	14.6	15.3	18.0	19.08	20.0
K	1.6	1.6	1.8	1.6	1.6	1.5	1.4	1.5	1.61	1.6
F	2.70	0.86	1.16	1.26	1.52	1.62	1.78	2.07	2.25	2.23
Cl	71.5	7.7	13.8	17.1	24.2	25.7	31.6	44.6	49.6	54.5
NO2-N	0.0	0.0				0.0	0.0	0.0	0.0	0.0
Br	0.433	0.027	0.023	0.060	0.108	0.126	0.188	0.280	0.310	0.335
NO3-N	0.00	0.08	0.01	0.00	0.01	0.19	0.93	0.28	0.15	0.53
SO4	54.1	104.3	100.0	96.0	87.7	82.3	77.6	69.4	65.4	50.8
trace (ppb)										
Li	7	8	8	7	9	7	7	9	11	10
B	281	71	72	75	128	117	144	163	196	256
Sc	7.05	1.8	3.5	3.4	4.45	6.5	3.65	5.41	4.4	
Ti	3.26	5.7	3.8	6.4	7.6	5.4	7.61	4.5	7.8	
V	0.52	0.06	0.11	0	0.04	0.2	0.19	0.29	0.18	
Cr	1.6	0.3	0.3	0.0	0.0	0.5	0.5	0.5	1.5	0.2
Mn	281	418	758	439	282	192	214	167	161	189
Fe	36	282	531	16	8				45	9
Co	0.3	0.5	2.1	2.0	1.2	1.2	4.1	1.1	1.5	2.0
Ni	0.7	0.8	0.8	1.0	0.8	3.0	4.0	1.1	2.1	2.4
Cu	0.4	6.4	0.2	0.2	0.4	29.8	4.7	2.3	0.9	1.1
Zn	98	75	4	63	57	85	104	55	78	57
Ge	0.27	0.06	0.12	0.14	0.14	0.24	0.19	0.17	0.19	
As	2.6	0.5	3.4	1.2	1.7	3.1	2.7	3.0	2.5	2.1
Se	1.5	0.0	0.0	0.0	0.0	0.0	0.6	0.0	1.1	0.0
Br	438	27.7	28	52.8	97.45	125.4	139.5	230.6	238	
Rb	1.4	1.2	1.8	1.4	1.7	1.2	1.3	1.4	1.4	1.4
Sr	328	236	243	253	301	291	298	367	395	414
Y	0.01	0	0.01	0.01	0.02	0.03	0.02	0.02	0.01	
Mo	13.5	0.0	3.6	3.7	5.6	6.5	8.1	8.7	9.6	9.9
Ag	0	0	0	0	0	0	0	0	0	
Cd	0.0	0.0	0.0	0.0	0.0	18.9	0.2	0.0	0.1	0.1
Sn	3.0	1.7	0.0	0.1	0.3	0.5	0.2	0.2	0.2	
Sb	0	0	0	0.02	0	0.01	0.02	0	0	
Te	0	0	0	0	0	0	0	0	0.01	
Cs	0.22	0.06	0.35	0.25	0.29	0.16	0.16	0.18	0.20	0.17
Ba	33.7	73.6	9.3	15.2	29.5	4.2	12.0	2.4	2.6	2.4
W	0.22	0.00	0.06	0.01	0.14	0.27	0.15	0.18	0.23	0.49
Pb	0.01	0.86	0.00	0.07	0.01	3.79	1.48	0.45	0.10	0.24
U	0.04	0.15	0.04	0.02	0.04	0.05	0.05	0.08	0.11	0.17

LTV GROUNDWATER EXPERIMENT

	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV
Date	pre-inj		9/26/97	10/13/97	11/12/97	12/18/97	1/14/98	2/11/98	3/17/98	4/22/98
Weeks		0	1	3	7	12	16	20	25	30
pH	7.9	7	7.5	7.44	7.42	7.89	7.89	8.03	8.12	8.38
Alk	452	196	284	292.3	333.7	339.5	395	386	415	368
majors (ppm)										
Al	0.000	0.001	0.002	0.002	0.002	0.005	0.006	0.027	0.003	0.002
Si	20.4	5.1	14.6	14.3	16.6	16.3	15.9	17.0	16.8	17.0
P		0	0	0	0			0.0193		
Fe	0.01	0.23	0.22	0.00	0.00	1.48	1.02	1.31	0.03	0.01
Mn	0.14	0.46	0.28	0.28	0.22	0.15	0.24	0.27	0.22	0.17
Sr	0.74	0.19	0.26	0.29	0.32	0.34	0.41	0.47	0.51	
Ba	0.02	0.07	0.01	0.02	0.03	0.01	0.01	0.01	0.01	
Ca	49.5	71.2	65.6	67.3	65.9	64.4	68.9	71.8	73.4	65.2
Mg	73.2	28.6	37.5	43.8	45.7	50.0	53.2	58.3	62.4	64.4
Na	79.0	8.7	26.3	28.5	31.7	33.8	37.7	42.0	46.0	47.7
K	5.0	1.6	2.8	2.5	2.8	2.8	3.0	3.5	3.9	4.1
F	5.49	0.86	1.90	2.20	2.31	2.43	2.67	2.70	2.98	3.03
Cl	50.7	7.7	13.6	12.0	14.2	15.4	20.6	27.7	35.0	42.2
NO2-N	0.0	0.0				0.0	0.0		0.0	0.0
Br	0.190	0.027	0.026	0.034	0.036	0.038	0.070	0.085	0.100	0.140
NO3-N	0.01	0.08	0.01	0.00	0.01	0.10	0.51	0.13	0.85	0.49
SO4	76.6	104.3	86.6	87.0	82.5	85.2	90.2	78.1	73.3	58.4
trace (ppb)										
Li	37	8	26	28	28	35	40	53	54	53
B	679	71	138	144	185	211	252	215	339	470
Sc	6.55	1.8	4.1	3.2	4.5	6.47	3.75	5.7	4.25	
Ti	4.13	5.7	4.1	6	6.07	5.12	8.71	6.13	9.21	
V	0.47	0.06	0.02	0	0.18	0.08	0.01	0.07	0.12	
Cr	0.2	0.3	0.2	0.8	0.5	0.4	0.3	0.8	1.0	0.6
Mn	132	418	235	255	211	133	228	268	196	195
Fe	26	282	276	20	7				13	2
Co	0.6	0.5	0.3	0.7	0.9	0.9	0.6	0.4	0.2	1.3
Ni	0.2	0.8	0.2	0.7	0.9	2.4	1.1	2.0	0.5	2.3
Cu	0.4	6.4	1.5	0.1	0.4	14.2	2.6	7.1	0.6	1.3
Zn	38	75	3	59	39	78	63	78	43	43
Ge	0.02	0.06	0.3	0.31	0.42	0.38	0.41	0.38	0.4	
As	1.0	0.5	1.1	0.6	1.7	1.1	1.1	0.9	0.5	1.0
Se	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Br	179	27.7	26.3	22.6	39.8	46.5	59.15	80	92	
Rb	5.3	1.2	3.0	2.8	3.8	2.7	3.1	3.5	3.6	4.2
Sr	704	236	260	280	334	330	394	469	464	518
Y	0.01	0	0.01	0.01	0.02	0.02	0.02	0.04	0.11	
Mo	6.9	0.0	3.7	4.0	4.7	3.9	4.0	3.5	3.4	4.0
Ag	0	0	0	0	0	0.01	0	0	0.01	
Cd	0.0	0.0	0.0	0.0	0.0	0.5	0.2	2.4	0.0	0.0
Sn	1.2	1.7	0.2	0.3	0.2	0.5	0.1	0.3	0.1	
Sb	0	0	0	0.02	0	0	0	0	0	
Te	0	0	0	0	0	0	0	0	0	
Cs	0.74	0.06	0.59	0.47	0.74	0.39	0.42	0.53	0.49	0.47
Ba	19.2	73.6	9.8	20.0	32.4	5.1	6.9	6.8	6.0	6.6
W	0.54	0.00	0.35	0.18	0.39	0.40	0.38	0.37	0.42	0.31
Pb	0.00	0.86	0.35	0.06	0.00	1.08	0.37	0.55	0.04	0.03
U	0.04	0.15	0.00	0.03	0.03	0.00	0.00	0.04	0.03	0.04

Appendix IX: Compiled Data from USX Minntac's Snively in-pit disposal site

US Steel-Snively Pit MW-1

Date	11/21/96	09/09/97	10/10/97	02/05/98	04/09/98	02/11/99	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters											
Temperature	6	9.5 **		7	9	2					
Conductivity	1200	1700	1200	1000	1000	900					
pH	8.16	7.40	7.32	7.52	7.32	8.11***	7.64	0.39	8.16	7.32	6
Measured Eh	80	45	82	73	108		77.58	22.64	108.20	44.90	5
Corrected Eh	296	258	295	288	322		291.87	22.78	321.85	258.15	5
majors (ppm)											
Al	0.20	0.00	0.01	0.00	0.00	0.02	0.04	0.08	0.20	0.00	6
Si	9.2	9.2	9.5	10.4	10.3	9.5	9.7	0.5	10.4	9.2	6
P	0.08	0.00	0.00	0.00	0.01	0.00	0.01	0.03	0.08	0.00	6
Fe	12.50	0.69	0.71	0.73	0.17	0.10	2.48	4.92	12.50	0.10	6
Mn	1.87	1.02	1.07	1.22	1.61	1.00	1.30	0.36	1.87	1.00	6
Sr	0.31	0.25	0.24	0.24	0.21	0.19	0.24	0.04	0.31	0.19	6
Ba	0.04	0.03	0.03	0.05	0.02	0.02	0.03	0.01	0.04	0.02	6
Ca	125	112	109	108	102	96	109	9.9	125	96	6
Mg	94.6	91.4	90.0	91.9	86.0	68.4	87.0	9.6	94.6	68.4	6
Na	22.2	20.9	19.7	20.5	19.0	20.9	20.5	1.1	22.2	19.0	6
K	9.0	8.7	8.7	9.2	9.6	7.9	8.9	0.6	9.6	7.9	6
F	0.16		0.24	0.24	0.25	0.31	0.24	0.06	0.31	0.16	5
Cl	15.7		15.1	13.0	11.7	16.1	14.3	1.9	16.1	11.7	5
NO2-N	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5
Br	0.06		0.07	0.06	0.05	0.04	0.06	0.01	0.07	0.04	5
NO3-N	0.48		0.18	0.22	2.99	0.23	0.82	1.22	2.99	0.18	5
SO4	383		360	371	338	261	343	49	383	261	5
HCO_3 *	342	335	338	335	329	270	325	27	342	270	6
trace (ppb)											
Li	12.0	9.1	8.6	9.2	8.8	8.5	9.4	1.3	12.0	8.5	6
B	43	45	22	40	14	28	32	13	45	14	6
Sc	0.1	4.3	2.5	2.9	2.8		2.5	1.5	4.3	0.1	5
Ti	0.4	6.8	8.7	0.3	10.4		5.3	4.7	10.4	0.3	5
V	0.8	0.0	0.1	0.0	0.1		0.2	0.3	0.8	0.0	5
Cr	4.8	0.8	1.5	12.7	1.5	5.0	4.4	4.4	12.7	0.8	6
Mn		over	over	over	over	over					
Fe		over	474	over	217	131					
Co	2.3	1.4	1.3	1.7	3.6	2.1	2.1	0.8	3.6	1.3	6
Ni	13.8	2.6	2.4	2.7	2.8	4.0	4.7	4.5	13.8	2.4	6
Cu	3.4	1.1	0.4	1.0	0.9	2.9	1.6	1.2	3.4	0.4	6
Zn	39.2	1.3	2.7	18.5	17.6	42.5	20.3	17.5	42.5	1.3	6
As	4.8	0.5	0.1	0.3	0.3	0.9	1.2	1.8	4.8	0.1	6
Se	0.1	0.3	0.0	0.8	0.0	2.3	0.6	0.9	2.3	0.0	6
Br	64	67	61	49	50	57	58	7.1	67	49	6
Rb	6.9	7.0	3.5	7.2	7.4	6.0	6.3	1.5	7.4	3.5	6
Sr	290	301	250	251	224	192	251	41	301	192	6
Mo	1.5	0.5	0.3	0.1	0.2	0.8	0.6	0.5	1.5	0.1	6
Cd	0.16	0.00	0.00	0.22	0.17	0.20	0.13	0.10	0.22	0.00	6
Sn	0.24	0.01	0.01	0.05	0.12		0.09	0.10	0.24	0.01	5
Sb	0.01	0.00	0.00	0.00	0.00		0.00	0.00	0.01	0.00	5
Cs	0.56	0.41	0.40	0.38	0.33	0.29	0.40	0.09	0.56	0.29	6
Ba	43	32	27	26	23	21	29	8.0	43	21	6
W	0.30	0.08	0.01	0.00	0.19	3.25	0.64	1.28	3.25	0.00	6
Pb	1.37	0.08	0.03	0.01	0.01	0.08	0.26	0.54	1.37	0.01	6
U	0.33	0.25	0.25	0.35	0.44	0.92	0.42	0.25	0.92	0.25	6
Nutrients (ppm)											
N			0.42	0.54	2.70		1.22	1.28	2.70	0.42	3
NH3-N			0.72	0.63	0.59		0.65	0.07	0.72	0.59	3
TP				0.27	0.34		0.31	0.05	0.34	0.27	2
BOD (mg/L)											0
COD (mg/L)											0

Notes *reported as ppm $CaCO_3$

**error in T

***electrode froze, pH taken at USX lab

US Steel-East Pit Sump #2

Date	11/21/96	09/09/97	10/10/97	02/05/98	04/09/98	02/11/99	Average	Standard Deviation	Maximum	Minimum	N
Field Parameters											
Temperature	7	9.5 **		6	9	1					
Conductivity	1100	2750	900	1000	950	850					
pH	8.07	7.07	7.11	6.87	7.19	8.30***	7.44	0.59	8.30	6.87	6
Measured Eh	93	177	119	83	85		111.24	39.44	177.00	82.50	5
Corrected Eh	308	390	332	299	299		325.57	38.64	390.25	298.58	5
majors (ppm)											
Al	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.00	6
Si	7.2	7.6	7.8	7.8	7.4	8.0	7.63	0.29	8.00	7.19	6
P	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	6
Fe	0.00	0.02	0.00	0.07	0.00	0.00	0.02	0.03	0.07	0.00	6
Mn	3.32	1.38	1.58	8.59	2.07	1.45	3.06	2.80	8.59	1.38	6
Sr	0.23	0.24	0.23	0.21	0.20	0.20	0.22	0.02	0.24	0.20	6
Ba	0.04	0.03	0.03	0.02	0.03	0.02	0.03	0.01	0.04	0.02	6
Ca	85.8	81.4	82.6	97.7	81.8	84.9	85.7	6.1	97.7	81.4	6
Mg	75.1	70.5	70.6	75.3	64.0	70.7	71.0	4.1	75.3	64.0	6
Na	24.9	19.5	19.1	23.2	22.5	18.3	21.3	2.6	24.9	18.3	6
K	24.9	16.8	16.1	24.5	21.0	12.4	19.3	5.0	24.9	12.4	6
F	0.17		0.22	0.19	0.25	0.16	0.20	0.04	0.25	0.16	5
Cl	5.7		6.6	8.2	8.3	11.1	8.0	2.1	11.1	5.7	5
NO2-N	0.12		0.00	0.56	0.10	0.00	0.16	0.23	0.56	0.00	5
Br	0.04		0.04	0.05	0.05	0.06	0.05	0.01	0.06	0.04	5
NO3-N	11.30		3.99	12.73	5.53	0.74	6.86	5.04	12.73	0.74	5
SO4	333		295	340	270	290	306	30	340	270	5
HCO_3^-*	219	240	254	264	270	238	247	19	270	219	6
trace (ppb)											
Li	10	8.5	8.3	13	10	10	10	1.8	13	8.3	6
B	28	35	42	30	5.9	37	30	13	42	5.9	6
Sc	0.1	3.2	2.2	2.5	2.0		2.0	1.2	3.2	0.1	5
Ti	0.1	1.2	3.9	13.9	12.2		6.3	6.4	13.9	0.1	5
V	0.0	0.0	0.0	0.0	0.1		0.0	0.0	0.1	0.0	5
Cr	4.3	0.2	0.0	8.3	0.3	5.0	3.0	3.4	8.3	0.0	6
Mn		over	over	over	over	over					
Fe	48	86	38	97	31	54	59	27	97	31	6
Co	22.7	1.9	2.2	15.2	3.2	2.5	7.9	8.9	22.7	1.9	6
Ni	3.7	1.9	1.9	5.9	1.1	22.7	6.2	8.3	22.7	1.1	6
Cu	2.2	0.6	1.3	10.9	1.3	0.6	2.8	4.0	10.9	0.6	6
Zn	36.7	0.8	19.8	15.5	13.6	23.3	18.3	11.9	36.7	0.8	6
As	6.6	1.8	1.5	0.4	0.7	1.3	2.1	2.3	6.6	0.4	6
Se	2.5	0.7	0.0	5.5	0.0	2.4	1.8	2.1	5.5	0.0	6
Br	29	44	33	48	44	75	46	16	75	29	6
Rb	27.7	23.5	18.8	35.7	27.6	16.9	25.0	6.8	35.7	16.9	6
Sr	206	278	241	219	223	222	231	25	278	206	6
Mo	5.3	2.5	2.2	0.6	2.1	0.2	2.2	1.8	5.3	0.2	6
Cd	0.00	0.05	0.00	0.04	0.00	0.10	0.03	0.04	0.10	0.00	6
Sn	0.49	0.00	0.00	0.06	0.04		0.12	0.21	0.49	0.00	5
Sb	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	5
Cs	5.98	4.18	3.49	5.44	4.64	2.68	4.40	1.22	5.98	2.68	6
Ba	31	33	30	18	33	19	27	7	33	18	6
W	0.06	0.02	0.00	0.12	0.05	1.22	0.25	0.48	1.22	0.00	6
Pb	0.59	0.00	0.13	0.09	0.12	0.55	0.25	0.25	0.59	0.00	6
U	0.52	0.93	0.76	0.42	1.62	1.43	0.95	0.49	1.62	0.42	6
Nutrients (ppm)											
N			<0.2	2.20	1.80		1.33	1.17	2.20	0.00	2
NH3-N			0.17	2.44	1.94		1.52	1.19	2.44	0.17	3
TP				-0.01	0.01		0.00	0.01	0.01	-0.01	2
BOD (mg/L)											0
COD (mg/L)											0

Notes
*reported as ppm $CaCO_3$
**error in T
***electrode froze, pH taken at USX lab

US Steel-East Pit Sump #1

Date	02/11/99
Field Parameters	
Temperature	
Conductivity	950
pH	8.63***
Measured Eh	
Corrected Eh	
majors (ppm)	
Al	0.00
Si	6.5
P	0.00
Fe	0.00
Mn	0.16
Sr	0.31
Ba	0.02
Ca	[illegible]
Mg	57.2
Na	23.6
K	13.7
F	0.10
Cl	6.7
NO2-N	0.03
Br	0.05
NO3-N	3.50
SO4	259
HCO_3^-*	333
trace (ppb)	
Li	9
B	56
Sc	
Ti	
V	
Cr	4.0
Mn	184
Fe	7
Co	1.3
Ni	3.5
Cu	1.2
Zn	17.1
As	6.7
Se	3.7
Br	69
Rb	11.4
Sr	348
Mo	3.1
Cd	0.00
Sn	
Sb	
Cs	0.40
Ba	29
W	0.75
Pb	0.10
U	2.23

APPENDIX B

DRAFT

HYDROLOGIC CHANGES AFFECTED BY INLAND STEEL'S IN-PIT TAILINGS DISPOSAL PROPOSAL

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January, 1998

Objective: The objective of this hydrologic analysis was to estimate the maximum probable and average annual flow rates for water that could pass through the tailings and ultimately reach the Mesabi Mountain pit, Virginia's municipal water supply. Flow rates were estimated for two development scenarios: 1) "full development" condition, i.e., at maximum tailing deposition with a 35+ foot high containment dike (elevation 1492 feet msl) along the south and east sides of the Minorca pit, and tailings stacked to elevation 1527 feet msl near the north end of the pit, and 2) "reclamation" condition, i.e. after tailings deposition ceases, and achievable reclamation conditions are attained.

Approach: The approach employed was to use existing data to check the reasonableness of basic water balance equations applied to the Minorca pit for "pit empty" (bottom elevation 1325± feet msl) and "present" (pit water elevation 1400± feet msl) conditions, then use the equations to estimate the range of annual flow rates for the two development scenarios. No attempt was made to route water from the Minorca pit to the Mesabi Mountain pit. Rather, it was assumed, given the south-dipping bedrock in the area (HDR Engineering, 1996; Maki, DNR Division of Minerals report, 1998), that all water flowing through the tailings and leaving the Minorca pit via groundwater would eventually reach the Mesabi Mountain pit. Results of this analysis were applied to the water balance of the Mesabi Mountain pit to estimate the maximum probable, and long-term average, percent of water that could come from the Minorca.

WATER BALANCE COMPONENTS FOR "PIT EMPTY" AND "PRESENT" CONDITIONS

General Mine Pit Water Balance Equations

In order to determine the flow rates of water that could potentially pass through the tailings, the different sources of water flowing to the Minorca pit for "pit empty" and "present" conditions were quantified to the extent possible. Two sources of water were quantified, 1) *groundwater inflow* from bedrock, and 2) *precipitation-derived inflow*.

When a pit is totally dewatered, it acts as a hydrologic sink, with no outflow except surface water evaporation. This condition simplifies the water balance analysis since the groundwater component consists solely of *groundwater inflow*, i.e., there is no *groundwater outflow*.

Groundwater outflow will begin to occur only when the pit water level rises above the lowest downgradient water table. In addition, all precipitation which isn't lost to either upland evapotransporation or pit water surface evaporation, will ultimately report to the pit as *net precipitation-derived inflow*. It was therefore only necessary to estimate the evapotransporation and evaporation losses from the Minorca pit's watershed in order to quantify the *net precipitation-derived* inflow to the pit. The water balance for this condition is shown in Equation 1:

Equation 1. Stored Water = Groundwater Inflow + Net Precipitation-derived Inflow

Groundwater inflow will decrease as water accumulates in the pit, because of the decreasing water table gradient which allows groundwater to enter the pit. As the pit water level continues to rise, decreasing *groundwater inflow* and, eventually, increasing *groundwater outflow*, will slow the rate of water rise until it stabilizes at an equilibrium elevation where total outflow equals total inflow. Outflow may occur only as groundwater, or as a combination of groundwater and surface water if the water rises above the runout elevation (lowest rim elevation along the south side of the pit). Surface water outflow will occur if the *groundwater outflow* component is less than the summation of inflows. The water balance for equilibrium condition is shown in Equation 2:

Equation 2. Surface Water Outflow + Groundwater Outflow = Groundwater Inflow + Net Precipitation-derived Inflow

Groundwater Components

Equation 1 was used to quantify the water balance components for the "pit empty" condition. *Groundwater inflow* was estimated using selected Inland Steel winter pumping (pit dewatering) records. During the winter months of December, January, and February, *precipitation-derived inflow* is at or near zero, so that water pumped out of the pit during this time equals *groundwater inflow* to the pit, if changes in the volume of water stored in the pit are accounted for. Limited water level records suggest that the Minorca was pumped dry during winter 1989-1990, by dewatering the adjoining Higgins pit. Monthly pumping records for this period range from 570 gallons per minute (gpm) to 700 gpm. Since the Minorca was dry, there was no *groundwater outflow* from the pit during this time. The *groundwater inflow* component, using Equation 1 with no *precipitation-derived inflow,* was therefore estimated to range from 570 gpm to 700 gpm. The pumping records, however, may reflect the removal of some stored water from the Higgins pit, making the estimate of *groundwater inflow* too high. As a possible check on the reasonableness of these numbers, the Theim Equilibrium Equation was applied to the Minorca using a measured range of hydraulic conductivity (Indeco, 1996) from two locations within the Minorca pit. Results suggest that *groundwater inflow* for "pit empty" condition should be about 400 gpm to 450 gpm. Although application of this equation to mine pits is experimental, it helps support the notion that the 570 gpm to 700 gpm range for *groundwater inflow* is high. Using the lower *groundwater inflow* range maximizes the estimate of *precipitation-derived inflow* for future conditions (discussed later). Figure 1 shows a north-south cross-section of the pit for "pit empty" condition.

Since cessation of mining, intermittent pumping has allowed a significant amount of water to accumulate in the pit, raising the water level about 75 feet to elevation 1400± feet msl for the "present" condition (Figure 1). The higher water level and lack of mining activity in the pit present an opportunity to quantify the water balance components under conditions that are different from "pit empty". The DNR recently installed a data logger in the Minorca to record daily pit water levels (Table 1). A portion of the data logger record was used to estimate the groundwater component. Since water has risen more than half way up the south wall of the pit, it cannot be assumed, without supporting information, that the groundwater component consists solely of *groundwater inflow*. Water could be leaving the pit via *groundwater outflow,* if the pit water level is higher than the lowest downgradient water table. For this reason, the groundwater component for "present" condition is labeled *net groundwater.* However, *groundwater inflow* is obviously much higher than *groundwater outflow,* if it exists, since the pit continues to accumulate a significant amount of water during winter months. Comparing the "present" condition *net groundwater* with "pit empty" *groundwater inflow* gives an indication of whether or not *groundwater outflow* may be occurring at water elevation 1400 feet msl. Water levels in nearby pits, which will be discussed later, also gives an indication of the water table elevation around the Minorca.

Air temperatures dropped during the second week of November, 1997, freezing the pit water surface, eliminating pit water surface evaporation and any significant amount of *precipitation-derived inflow* to the pit. Therefore, water level records from November 15, 1997, through December 18, 1997, were used to estimate the *net groundwater* component for the "present" condition, using Equation 3:

Equation 3. "Present" Condition *Net Groundwater = Pumped water - Change in water storage*
= 1350 gpm - 1012 gpm
= 338 gpm

Net Groundwater for "present" condition, based on this limited data, is less than estimated *groundwater inflow* for the "pit empty" condition, i.e., 338 gpm vs 400 gpm to 700 gpm. The difference could result solely from a reduction in *groundwater inflow*, or from a combination of reduced *groundwater inflow* and the initiation of *groundwater outflow.* If substantial *groundwater outflow* is occurring below elevation 1400 feet (approximately 55 feet below the runout elevation), then the pit is no longer acting as a total sink, rather it is a partial flow-through system. On the other hand, if only diminishing *groundwater inflow* is happening, then the pit is still acting as a total sink. An indication of which scenario is most likely happening can be obtained by comparing water levels in local pits with the 1400 feet elevation in the Minorca. The following table lists pits from nearest to farthest from the rim of the Minorca.

Pit Name	Distance and Direction from Minorca	Water Elevation
Lincoln D	200 feet southeast	1407 feet msl
Unknown	300 feet northwest	1605 " "
Unknown	800 feet west	1535 " "
Lincoln	1000 feet south	1317 " "
Sauntry	2800 feet west	1245 " "
Mesabi Mountain	3700 feet southwest	1220 " "

Concern has been expressed that since the water level in the Mesabi Mountain pit is about 180 feet below that of the Minorca, the apparent, steep water table gradient between the two pits is already facilitating rapid *groundwater outflow* to the Mesabi Mountain pit. If this is correct, *groundwater outflow* would occur during the early years of tailing deposition, when the tailings are well below the rim of the pit, maximizing *groundwater outflow* from the tailings. If this is not correct, *groundwater outflow* would not begin to occur until several years after tailing deposition starts. As noted in the above table, there are three small pits located along the southeast, west, and northwest sides of the Minorca, which have water levels higher than that of the Minorca. This fact suggests that there is higher groundwater around the Minorca, i,e., that the groundwater cone of depression around the Minorca is relatively steep and has a short radius. The Theim Equilibrium Equation, with water elevation 1400 feet msl, predicts a maximum average cone of depression radius of less than 3000 feet from the center of the pit, i.e., only a short distance beyond the pit rim.

One pit which doesn't follow this pattern is the Lincoln pit, located about 1000 feet due south of the Minorca, with a water level more than 80 feet below that of the Minorca. This apparent anomaly hints that *groundwater outflow* could already be occurring in a due south direction toward the Lincoln. Although this is a possibility, it is more probable that there is simply a better hydraulic connection between the Lincoln and the Mesabi Mountain than between the Lincoln and the Minorca. The higher water levels in the three small, closer pits, and the predicted steep cone of depression, suggest that the water table between the Lincoln and the Minorca is higher than the water in either pit. It is therefore concluded that there is no appreciable *groundwater outflow* from the Minorca until the water level rises to at least that of the Lincoln D pit, 1407 feet msl. Pumping from the Minorca was terminated on December 19, 1997, to better define the groundwater component. Water level monitoring will continue for at least the remaining winter months of 1997-1998.

Average Annual Net Inflow

An accurate estimate of *average annual net inflow* can help define *net precipitation-derived inflow.* Ideally, pit pumping records can be used to quantify *average annual net inflow* to the Minorca. Most of the historic pumping records, however, reflect times when the pit dimensions were rapidly changing, or when stored water in the pit was changing to accommodate mining in different parts of the pit. It appears, however, that pumping records for 1990 can be used as an indication of *average annual net inflow* to the pit for "pit empty" condition. Pumping for 1990 averaged 989 gpm. Since precipitation at Virginia for 1989 and 1990 was close to the long term average, it appears that *average annual inflow* for "pit empty" condition should be about 1000 gpm. Pumping records for "present" condition are incomplete, and therefore cannot be used for estimating *average annual net inflow* for this condition.

Net Precipitation-derived Inflow

This component can be estimated for "pit empty" condition by subtracting *groundwater inflow* from *average annual net inflow,* using Equation 4:

Equation 4:

"Pit Empty" *Net Precipitation-derived Inflow* = *Ave. Annual Net Inflow - Groundwater Inflow*
= 1,000 gpm - (400 gpm to 450 gpm)
= 550 gpm to 600 gpm

This *net precipitation-derived inflow* estimate serves as a check on the reasonableness of assumptions used in developing the water balance components for future conditions. *Since the pit is a hydrologic sink for the "pit empty" condition, all precipitation on the watershed that isn't lost to either evapotransporation from the upland area, or evaporation from the water surface, will eventually make it to the pit pond.* Therefore, to make estimates of the potential rates of water flowing through the tailings, the *precipitation-derived inflow* for the "pit empty" condition was also estimated using a range of evapotransporation/evaporation loss figures derived from literature review. The Minorca's surface watershed was delineated and subdivided into relatively homogenous areas that are believed to handle water in a uniform fashion (Figure 2). Watershed areas* for the "pit empty" condition are:

Upland Forest:	258 acres
Pit Proper, rock	668 "
Pit Proper, water	15 "
Total Surface Watershed	941 acres**

* Watershed areas were developed using 1996 elevation maps from Inland Steel.

** Total watershed area was calculated to be the maximum probable; actual watershed area may be as little as 720 acres, depending on the nature of the surface material and bedrock geometry.

Average annual precipitation at the Minorca is about 28 inches. Evapotransporation loss from forested areas was estimated at 11 to 15 inches per year (Baker, 1979). Evapotransporation loss from the pit proper (rock, mostly crushed) and unvegetated tailing surfaces was estimated at 12 to 14 inches per year, (Dave Antonson, DNR Minerals, AMAX study results, 1978-1991). Evaporation from the pit water surface was estimated at 24 inches per year, based on a DNR pit evaporation study at LTV's Dunka pit near Babbitt (Perry and Brooks, 1993). Equation 5 uses these values to estimate *net precipitation-derived inflow*:

Equation 5: *Net precipitation-derived Inflow = (Annual Precipitation - Evapotransporation/Evaporation Loss) x Watershed Area*

Using Equation 5, the range of estimated maximum annual *net precipitation-derived inflow* for “pit empty” condition is:

Upland Forest	28 - (11 to 18) inches per year	x 258 acres	= 133 to 227 gpm
Pit Proper, rock	28 - (12 to 14) “ ” “	x 668 “	= 483 to 552 gpm
Pit Proper, water	28 - 24 “ ” “	x 15 “	= 3 gpm
Annual *Net Precipitation-derived Inflow,* “pit empty” condition			= 619 to 782 gpm

The lower range, using Equation 4, (550 to 600 gpm vs 619 to 782 gpm using Equation 5) suggests that actual evapotransporation loss from the crushed rock surface within the pit, and from the future tailings surface, may be higher than the ranges suggested by literature review. However, in keeping with the objectives of this analysis, the higher range of estimated *net precipitation-derived inflows* will be used for estimating maximum *groundwater outflow* for future conditions.

The maximum surface watershed areas for “present” conditions are:

Upland Forest:	258 acres
Pit Proper, rock	523 “
Pit Proper, water	160 “
Total Surface Watershed	941 acres*

* As for “pit empty” condition, the total watershed area was calculated to be the maximum probable; actual surface watershed area may be as little as 720 acres.

The estimated range of maximum annual *net precipitation-derived inflow* for “present” condition, using Equation 5 is:

Upland Forest:	28 - (11-18) inches per year	x 258 acres	= 133 to 227 gpm
Pit Proper, rock	28 - (12-14) “ ” “	x 523 “	= 378 to 432 gpm
Pit Proper, water	28 - 24 “ ” “	x 160 “	= 33 gpm
Annual *Net Precipitation-derived Inflow,* “present” condition			= 544 to 692 gpm

Maximum estimated *Average Annual Net Inflow* to the Minorca for “pit empty” and “present” conditions is, therefore:

Condition	*Groundwater*	*Precipitation-derived Inflow*	*Ave. Annual Net Inflow*
"Pit Empty"	400 to 450 gpm *In* *	619 to 782 gpm	1019 to 1232 gpm
"Present"	338 gpm *Net* **	544 to 692 gpm	882 to 1030 gpm

* based on Theim Equation; questionable pumping records suggest 570 to 700 gpm

** believed to be all *groundwater inflow*

WATER BALANCE COMPONENTS FOR "FULL DEVELOPMENT" AND "RECLAMATION" CONDITIONS

During the early years of tailing deposition, when the tailing surface is well below the pit rim, all runoff from the tailings will remain in the pit, as previously described for "pit empty" and "present" conditions. Excess water will be discharged to Sauntry Creek. Before the tailings reach the runout elevation of the pit, Inland Steel plans to construct a 35+ foot high containment dike, with a top elevation of 1492 ± feet msl, along the south and east sides of the Minorca (Figure 3). This dike will allow stacking tailings up to about 40 feet above their contact with adjacent topography to the northwest, north, and northeast of the Minorca. Tailings will be stacked in a circular pattern with the highest elevation located near the north end of the pit. Tailing thickness will very from more than 150 feet at the deepest part of the pit (south end), to about 30 feet near the north end of the pit (Figure 4). The tailing surface will slope down in all directions from the proposed, highest elevation of 1527 feet msl near the north end of the pit. Tailings will be spigotted into the basin via a 4000 gpm slurry containing nearly 3000 gpm water. Reclaim water will be pumped out of the clearwater pond at the south end of the basin at about 2900 gpm (Noramco, 1997). This continuous, large inflow of water will keep the water table near the surface of the tailings. Once the tailing surface rises above the south rim of the pit, the groundwater mound formed within the tailings should begin to eliminate *groundwater inflow* into the tailings from outside the basin. When spigotting ceases, the groundwater mound within the tailings will undoubtedly drop to a lower elevation. However, because of infiltrating precipitation, low vertical hydraulic conductivity*, underlying, impermeable quartzite bedrock, and presence of the dike along the south side of the basin, the groundwater mound is expected to remain above the tailings contact with adjacent topography. The water table in National's inactive tailing basin ranged from 5 to 25 feet below the tailing surface. Under these conditions, USGS estimated *groundwater inflow* to National's tailing basin at less than 0.1 % of the total inflow to the basin, even with higher, natural ground (glacial drift) adjoining about 25% of the basin; virtually all inflow was precipitation-derived. Assuming a similar pattern develops at the Minorca basin, this condition should eliminate most, if not all, *groundwater inflow* to the tailings from outside the pit area. To help-evaluate this conclusion, an estimate of the Minorca pit's static water level (without tailings) was

* USGS, 1991, estimated vertical hydraulic conductivity in National Steel's inactive tailing basin at 0.00004 feet per day

made using the Theim Equation. Estimated static water level was 1450± feet msl, compared with the minimum probable water table within the tailings, after reclamation, of 1470+ feet msl. It is therefore likely that the ultimate tailings water table will be at least 20 feet above the static water table in the area.

The USGS study also concluded that there was very little surface runoff from National's tailing basin. Most of the precipitation, which wasn't lost to evapotransporation or pond water evaporation, infiltrated the tailings and left the basin as *groundwater outflow*. Although there is a logical explanation for this (discussed later), it was assumed that all *net precipitation-derived inflow* will infiltrate the tailings and be lost as *groundwater outflow* for "full development" condition.

Surface watershed areas and water balance components for "full development" and "reclamation" will be the same, except that "full development" condition will include a maximum additional 100 gpm *net slurry water inflow* (Noramco, 1997). Watershed areas for both conditions are:

Upland Forest	191 acres	
Pit Proper, rock	334 "	
Tailings	336 "	(includes 31 acres course tailing dike area)
Tailings Pond	80 "	
Total Surface Watershed	941 acres	

The estimated maximum range of annual *net precipitation-derived inflow* for "full development" condition, using equation 5, is:

Upland Forest	28 - (11-18) inches per year	x	191 acres	= 99 to 168 gpm
Pit Proper, rock	28 - (12-14) " " "	x	334 "	= 242 to 276 gpm
Tailings (unvegetated)	28 - (12-14) " " "	x	336 "	= 243 to 278 gpm
Tailings Pond	28 - 24 " " "	x	80 "	= 17 gpm
Annual *Net Precipitation-derived Inflow* for "full development" condition				= 601 to 739 gpm

These figures can be assumed to simulate maximum *groundwater outflow* **only** if there is no surface water discharge from the tailings pond. Whether or not excess water will be available from the tailings pond (to be discharged to Sauntry Creek) will depend on the rate of *groundwater outflow* from the tailings. The minimal surface water outflow at National's tailing basin, less than 10% of total precipitation (USGS, 1991), was probably due to the fact that the pond's runout elevation was about three feet above the bottom of the pond. During dry periods, seepage loss from the pond would drop the water level below the runout elevation, creating storage for subsequent snowmelt and storm runoff. Therefore, much of the potential surface water outflow was captured in the pond and infiltrated, increasing *groundwater outflow*. Excess runoff to the Minorca tailings pond may be substantial during active tailing deposition because of the artificially high water table maintained by constant slurry inflow. However, for purposes of this analysis, it was assumed that no water would be discharged to Sauntry Creek by the time the basin reaches "full development". Under this assumption, *net precipitation inflow,* plus the 100 gpm *net slurry water* must leave the basin as *groundwater outflow.* Therefore, the estimated, temporary, maximum range of annual *net groundwater outflow* for "full development" condition is 701 to 839 gpm.

POTENTIAL EFFECTS ON INFLOW TO MESABI MOUNTAIN PIT

A water balance analysis for Virginia's drinking water supply, the Mesabi Mountain pit, for 10/31/91 to 11/17/95, showed *average annual net inflow* of about 2135 gpm (HDR Engineering, 1996). During this time period, there was no outflow (groundwater or surface water) from the Minorca pit to the Mesabi Mountain pit. As a result, the estimated 2135 gpm inflow to the Mesabi Mountain pit does not include any inflow from the Minorca pit, making this number smaller than it would be if the Minorca watershed had been contributing.

Theoretically, if the Minorca is filled with tailings, all *groundwater outflow* could eventually reach the Mesabi Mountain, increasing its *net inflow* and potentially altering its water quality. The volume of water coming from the Minorca will be an important consideration in determining how much the Mesabi Mountain's water could be altered. The maximum estimated range of annual *net groundwater outflow* from the Minorca tailings basin at "full development", 701 to 839 gpm, could, theoretically, increase **temporary** *total inflow* to the Mesabi Mountain pit by 33% to 39%.

It is important to note that **these figures were intentionally calculated to reflect temporary, "worst case" conditions**, including:

1) maximizing watershed area for *precipitation-derived inflow,*
2) assuming no surface water discharge from the tailings pond at "full development",
3) unvegetated tailings and pit rock surfaces, and
4) minimal estimates for evapotransporation losses.

In reality, even if all the "worst case" conditions occurred, the predicted maximum *groundwater outflow* would occur for only a few years. *Groundwater outflow* is not expected to begin until the tailings pond reaches at least elevation 1407 feet msl, and may not begin until the pond approaches the predicted static water level of 1450± feet msl. As tailings are stacked higher, *groundwater outflow* will gradually increase until it peaks, temporarily, at "full development". After reclamation, at least two factors will work to significantly reduce long-term, average annual *groundwater outflow.* Vegetating tailing and pit rock surfaces with grasses would increase evapotransporation loss by at least 3 inches per year, reducing *groundwater outflow* by at least 104 gpm. Any surface water outflow from the tailings pond will further reduce *groundwater outflow.* Noramco, 1998, estimated that post-mining surface outflow from the tailings pond would average 440 gpm (9 inches). This figure may be high, given the low surface water outflow (approximately 2 inches) measured by USGS at National. However, as previously discussed, the relatively high elevation of the outlet control at National's tailing basin minimized surface water outflow. The future Minorca tailings pond outlet channel could be designed to maximize surface water outflow (to Sauntry Creek) by constructing it at the lowest possible elevation. For example, if an outlet channel were constructed with a bottom elevation near the lowest tailings elevation in the pond (1470± feet msl), a significant portion of potential *groundwater outflow* would be captured as surface water outflow. Maximizing surface water outflow, however, would limit the possibility of creating permanent wetlands on the tailings. However, this may prove to be more desirable than attempting to create wetlands (which maximize seepage loss to groundwater). An added benefit would be maximization of surface water outflow to Silver and Virginia Lakes, which is desired for water quality reasons. For the purpose of this analysis, it was assumed that a minimum of 4 inches of surface water outflow will be achieved, reducing *groundwater outflow* by an estimated 194 gpm. **Consequently, vegetating bare surfaces with grasses, and achieving minimal surface water outflow of 4 inches per year from the tailing pond, would reduce the estimated maximum long-term *groundwater outflow* by 298 gpm, to 301 to 439 gpm, or 14% to 21% of the Mesabi Mountain's inflow. With an achievable, increased evapotransporation loss of 5 inches per year by establishment of forest vegetation (preferably conifer) on bare areas, and an achievable surface water outflow of 6 inches per year, the estimated long-term, average *groundwater outflow* from the Minorca would drop to 136 to 274 gpm, or 6% to 13% of the Mesabi Mountain's inflow.**

CONCLUSIONS

1) Runout elevation (lowest elevation along the south rim) for the Minorca pit is approximately 1455 feet msl.

2) Lowest elevation in the Minorca pit is approximately 1325 feet msl.

3) When totally dewatered, the pit is a hydrologic sink, i.e., there is no *groundwater outflow.*

4) Net process water will add a maximum of 100 gpm continuous inflow to the pit during active tailing deposition (Noramco, 1997).

5) The estimated maximum range of *average annual net inflow* to the pit, assuming average hydrologic conditions, varies from 1019 to 1232 gpm for "pit empty" condition, to 882 to 1030 gpm with the pit water level at 1400 feet msl.

6) *Groundwater inflow* for "pit empty" condition is estimated at 450 to 500 gpm using the Theim Equation, and 570 to 700 gpm using questionable pumping records.

7) *Net groundwater* was calculated at 338 gpm for "present" condition, using limited water level data from November and December, 1997. This figure is believed to consist solely of *groundwater inflow,* i.e., no *groundwater outflow* is believed to be occurring at or

below water elevation 1400 feet msl.

8) *Groundwater inflow* from outside the Minorca is expected to diminish to zero as the tailings are stacked above the pit rim, creating an oblong, mounded water table within the tailings. After "full development", the water table in the tailings is expected to remain at least 20 feet above the natural, static water table in the area

9) *Groundwater outflow* will begin to occur when the water level in the pit rises above the lowest downgradient water table elevation, which is unknown, but appears to be higher than the present Lincoln D water elevation of 1407 feet msl. *Groundwater outflow* will increase as tailings are stacked above the pit rim, and will peak at an estimated maximum (temporary) range of 701 to 839 gpm at "full development". Termination of spigotting, vegetating bare surfaces with grasses, and achieving minimal surface water outflow from the tailing pond of 4 inches per year, will reduce the range of estimated maximum annual *groundwater outflow* to 301 to 439 gpm. Estimated, achievable, long-term, average annual *groundwater outflow,* assuming forest vegetation of bare areas (preferable conifer), and 6 inches per year surface water outflow from the tailing pond area, is 136 to 274 gpm.

10) Average annual *net inflow* to the Mesabi Mountain pit is estimated at 2135 gpm (HDR Engineering, 1996).

11) One hundred percent of the *Groundwater outflow* from the Minorca pit is assumed to reach the Mesabi Mountain pit. *Groundwater outflow* from the Minorca is estimated to make up a temporary, maximum of 33% to 39% of the Mesabi Mountain inflow at "full development". Estimated **maximum** annual inflow to the Mesabi Mountain pit, with minimal reclamation and normal weather conditions, is 14% to 21%. Estimated, long-term, achievable, **average** annual inflow, with conifer forest vegetation establishment, and surface water runoff of 6 inches per year, is 6% to 13%.

12) Because the Minorca pit is presently a hydrologic sink, it will "make water" during early years of tailing deposition, requiring Inland Steel to discharge excess surface water to Sauntry Creek. Average annual discharge may exceed 1000 gpm initially, depending on the elevation of the tailings pond in the pit. Discharge is assumed to drop to zero by "full development" in order to maximize estimated *groundwater outflow.*

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TABLE 1. Minorca Pit Daily Water Level Readings

JDATE	DATE	WATER ELEV. FEET ABOVE MSL
209	7/28/97	1401.73
262	9/19/97	1401.11
272	9/29/97	1400.75
286	10/13/97	1400.5
290	10/17/97	1400.4
291	10/18/97	1400.3
292	10/19/97	1400.3
293	10/20/97	1400.3
294	10/21/97	1400.1
295	10/22/97	1400.1
296	10/23/97	1400.1
297	10/24/97	1400.1
298	10/25/97	1400
299	10/26/97	1400
300	10/27/97	1400
301	10/28/97	1400
302	10/29/97	1400
303	10/30/97	1400
304	10/31/97	1400
305	11/1/97	1400
306	11/2/97	1400
307	11/3/97	1400
308	11/4/97	1400
309	11/5/97	1399.9
310	11/6/97	1399.9
311	11/7/97	1399.9
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337	12/3/97	1399
338	12/4/97	1399
339	12/5/97	1399
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342	12/8/97	1398.9
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345	12/11/97	1398.9
346	12/12/97	1398.7
347	12/13/97	1398.7
348	12/14/97	1398.7
349	12/15/97	1398.7
350	12/16/97	1398.7
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352	12/18/97	1398.7
353	12/19/97	1398.6
354	12/20/97	1398.6
355	12/21/97	1398.6
356	12/22/97	1398.6
357	12/23/97	1398.6
358	12/24/97	1398.6
359	12/25/97	1398.7
360	12/26/97	1398.7
361	12/27/97	1398.7
362	12/28/97	1398.7
363	12/29/97	1398.7
364	12/30/97	1398.7
365	12/31/97	1398.7
1	1/1/98	1398.7
2	1/2/98	1398.7
3	1/3/98	1398.7
4	1/4/98	1398.7
5	1/5/98	1398.7
6	1/6/98	1398.7
7	1/7/98	1398.7

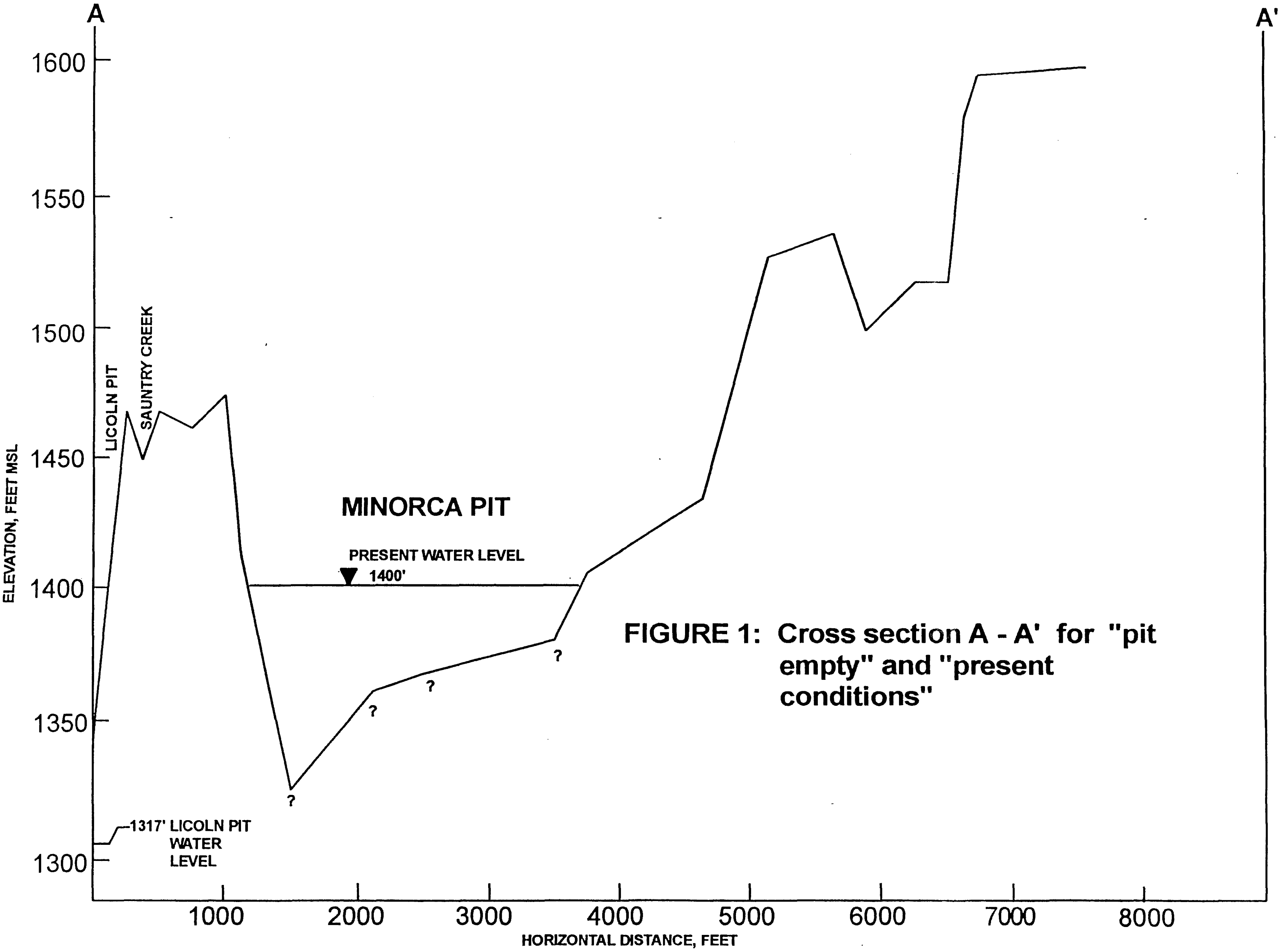


FIGURE 1: Cross section A - A' for "pit empty" and "present conditions"

- ▭ Forested Areas within the Minorca Pit Watershed (F)
- ▭ Minorca Pit Water Boundary at Elev. 1402 - feet msl (W)
- Minorca Watershed Boundary
- ⬚ Higgins Pit Outline (H)
- (R) Unvegetated Rock

N
W E
S

1000 0 1000 Feet

Scale 1" = 1000'

Figure 1a. Minorca Pit Cross-Section A to A'

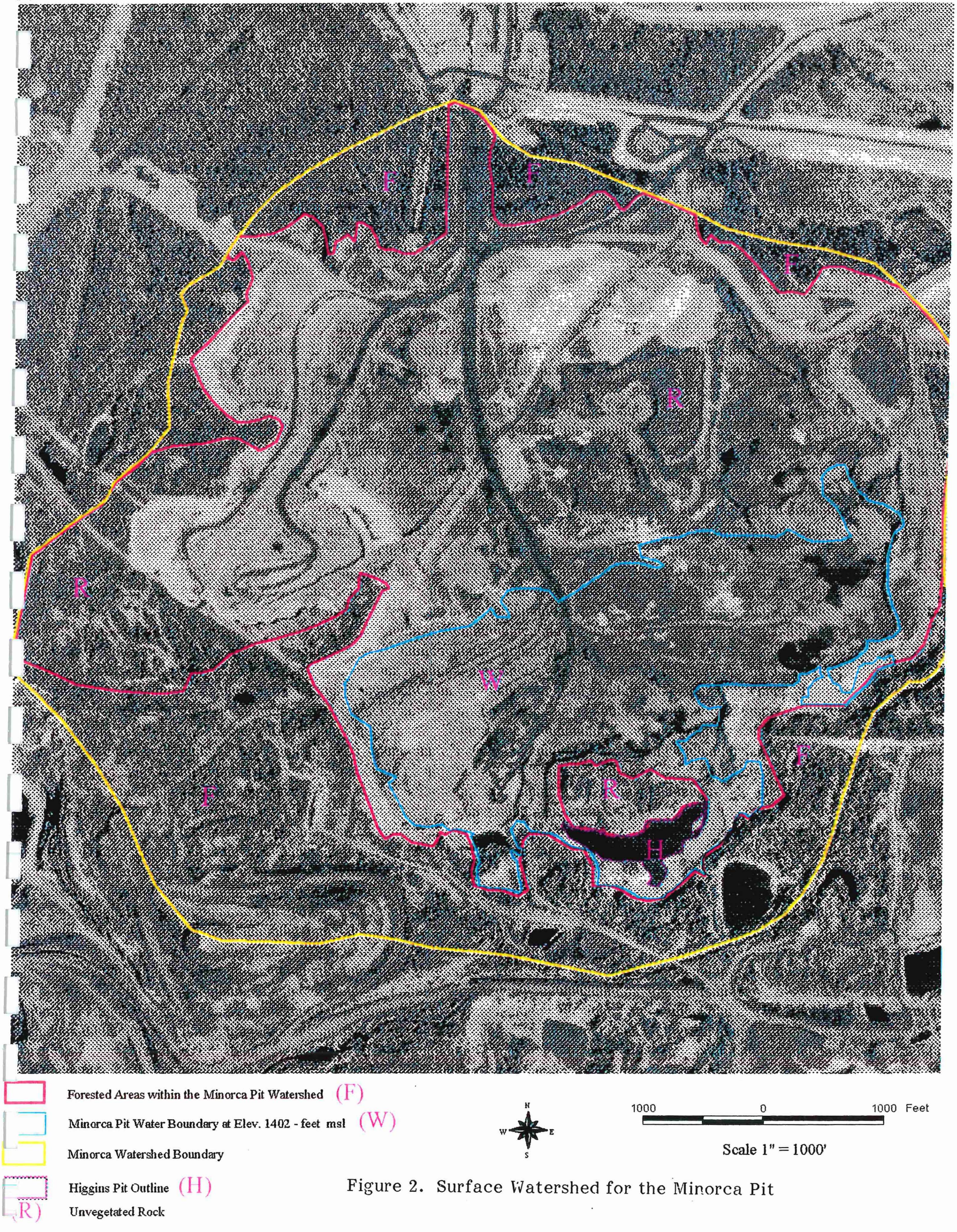
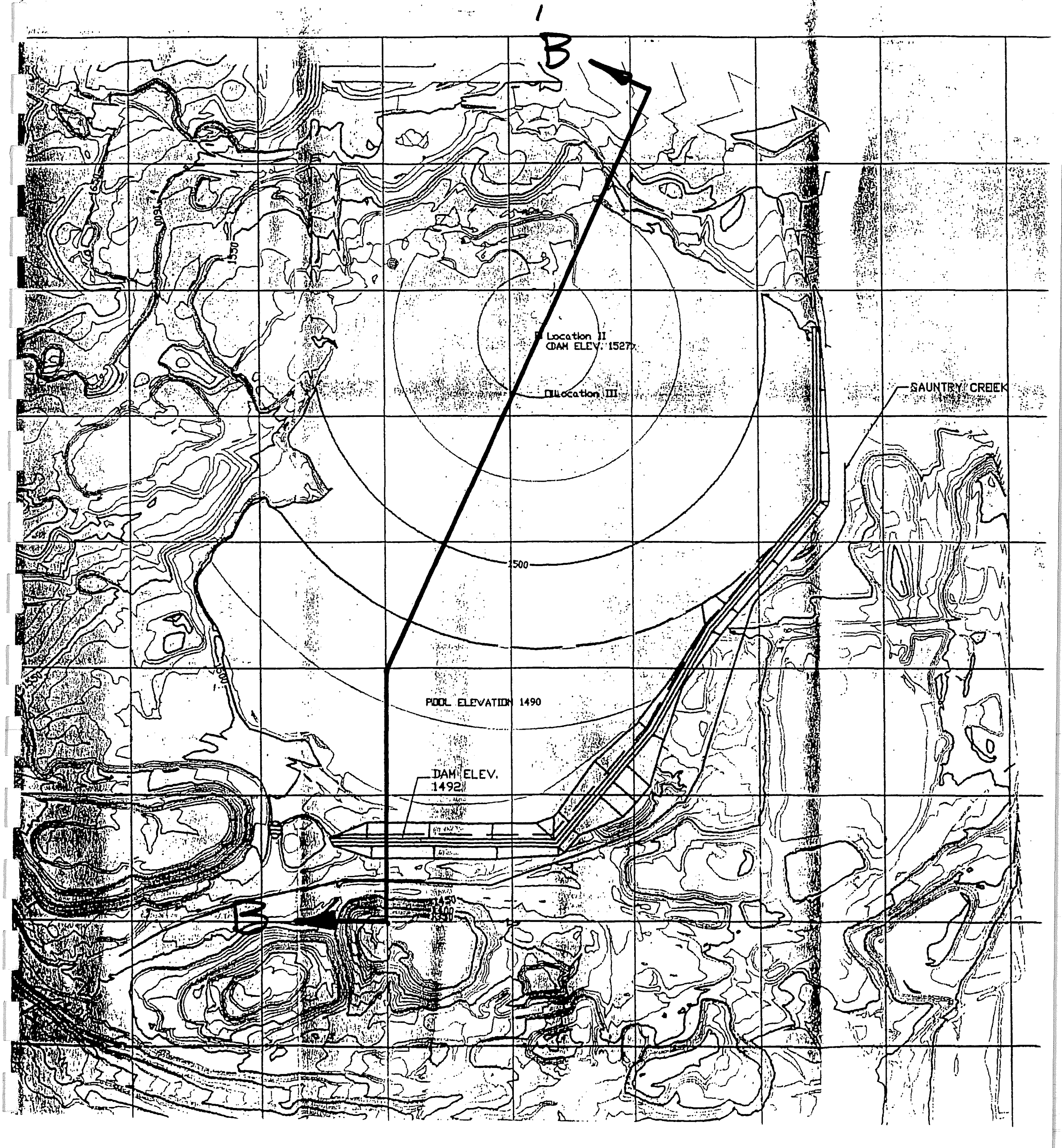


Figure 2. Surface Watershed for the Minorca Pit

FIGURE 3. FINAL DEPOSITION PLAN (FROM INDECO, 1997)



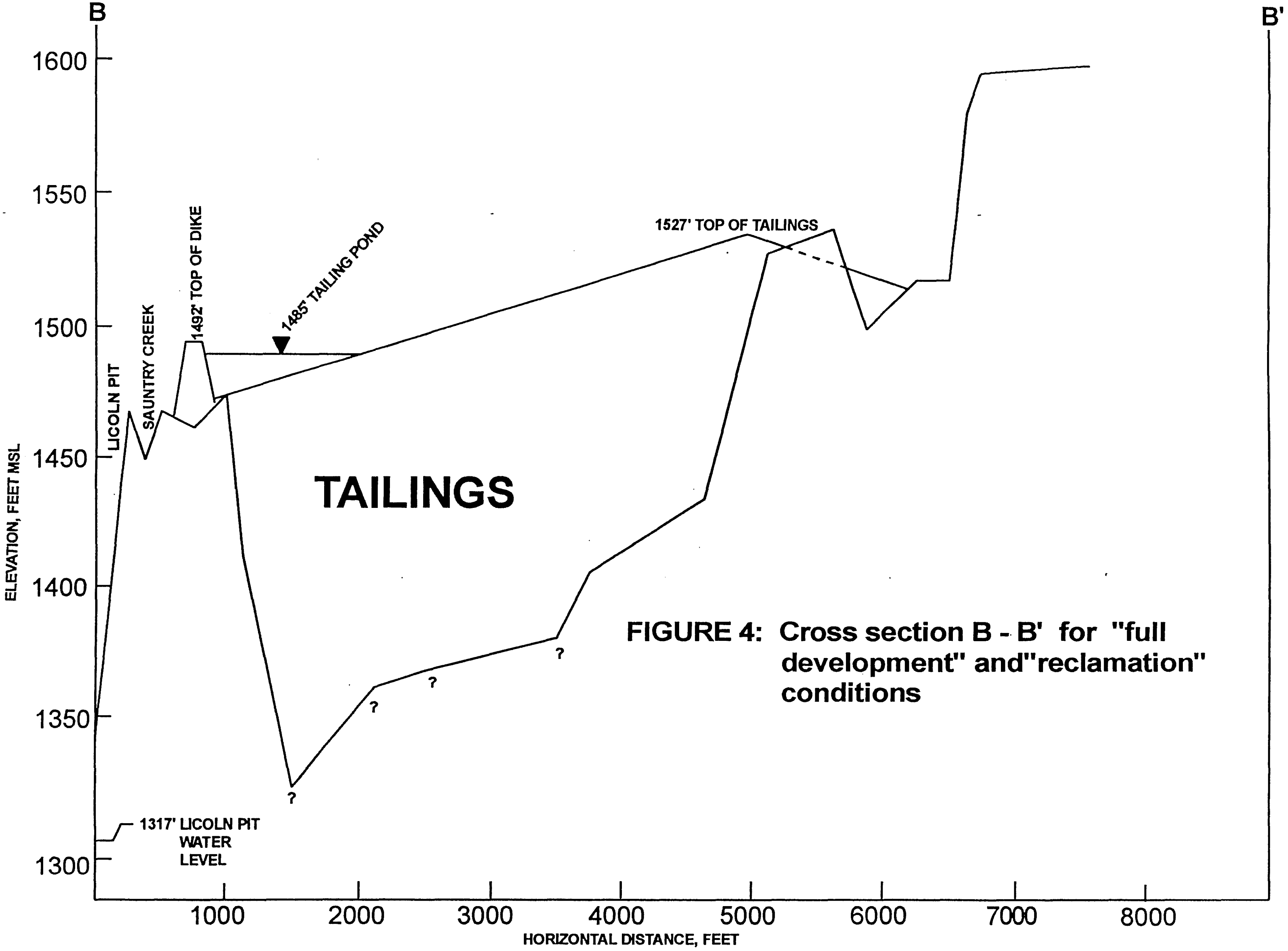


FIGURE 4: Cross section B - B' for "full development" and"reclamation" conditions

APPENDIX C

Health Risk Assessment
for the
Proposed Minorca In-Pit Tailings Disposal Project

September 25, 1998

Prepared by the Minnesota Department of Health

EXECUTIVE SUMMARY

Inland Steel Mining Co. (ISMC) requested approval from the State of Minnesota to deposit fine taconite tailings into the Minorca Pit, a mined-out taconite pit owned by the company. Proposed action such as this requires completion of a supplemental Environmental Impact Statement and a Risk Assessment to "demonstrate that deposition of the tailings will not pose an unreasonable risk of pollution or degradation of groundwater" (Minnesota Statutes, Taconite Deposition, 1996, Chapter 407, Section 56). The Minnesota Department of Health agreed to conduct a health risk assessment for the proposed project. The assessment focused on the potential for contamination of the principal water supply (the Missabe Mountain Pit) for the city of Virginia. It was conducted as an open process allowing input from private citizens and representatives from Virginia, ISMC, state and federal agencies.

The health risk assessment addressed potential risk to the drinking water of the citizens of Virginia. For the purpose of the health risk assessment, the following assumptions were made:

1. a direct hydrologic connection exists between the Minorca Pit and Missabe Mountain Pit;
2. water from the Minorca Pit will migrate to and mix with water in the Missabe Mountain Pit; and
3. the water chemistry of the present tailings basin will be similar to the water chemistry in the Minorca Pit, if the proposed action is implemented.

Chemical analyses of water samples from natural sources (wells and water-filled mine pits) were compared with analyses of water samples associated with processing taconite (processing plant discharge, tailings basin, seeps, monitoring wells, process water in the plant, and laboratory column experiments). Four elements, arsenic, fluoride, manganese, and molybdenum were selected as elements and compounds of concern (ECCs). Because of agency concern, a fifth ECC, organic process chemicals, was added to the list.

Ongoing DNR research into mine pit hydrology in the Iron Range aided in the assessment of the potential for migration of contaminants. Assuming revegetation and reclamation of the pit following tailings disposal, water leaving the Minorca Pit would provide an estimated 20 percent of the total groundwater entering the Missabe Mountain Pit. A worst case estimate of 40 percent contribution representing a temporary maximum prior to reclamation is also included. Mixing is assumed to occur under these conditions resulting in a 5-fold dilution of the ECCs in the Missabe Mountain Pit (20 percent contribution), or a 2.5-fold dilution (40 percent contribution) as a worst case maximum.

The fate of the ECCs with migration in the groundwater was estimated using hydrogeochemical modeling and comparative analysis of the water chemistry at different sites. During movement of the ECCs in groundwater from the Minorca Pit to the Missabe Mountain Pit, several conservative assumptions intended to overestimate the risk were made. First, the levels of ECCs would not decrease due to dilution from other groundwater sources. Second, the water available for diluting ECC-bearing groundwater included only groundwater flowing into the Missabe Mountain Pit. The effects of dilution from surface runoff and precipitation were not included. Last, the effects of oxidation and biologic processes on ECCs within the Missabe Mountain Pit were not included in the estimates.

Of the five ECCs, arsenic and organic process chemicals were predicted to reach levels that would be equal to or most likely below natural water levels in the Missabe Mountain Pit. The remaining ECCs, fluoride, manganese, and molybdenum were predicted to occur at levels of potential human health concern. The projected concentrations of the ECCs in the Missabe Mountain Pit were each compared with a site-specific health based value or drinking water standard. The sole exposure route expected, based on the characteristics of all the ECCs, was through drinking water. Inhalation and dermal exposure were not considered to be viable exposure routes. The results from risk characterization were as follows:

Arsenic

Projected Drinking Water Standard: 2-5 μg/L

Projected maximum concentration using a 5-fold dilution: Less than1 μg/L

Projected maximum concentration using a 2.5-fold dilution: Less than 1 μg/L

Fluoride

Drinking Water Standard: 4,000 μg/L

Projected maximum concentration using a 5-fold dilution: 900 μg/L

Projected maximum concentration using a 2.5-fold dilution: 1,800 μg/L

Manganese

Site Specific Health-Based Value: 1,300 μg/L

Projected maximum concentration using a 5-fold dilution: 1,200 μg/L*

Projected maximum concentration using a 2.5-fold dilution: 2,400 μg/L*

* Values exclude the effects of oxidation and biologic processes that decrease levels of manganese in surface waters.

Molybdenum:

Site Specific Health-Based Value: 30 μg/L

Projected maximum concentration using a 5-fold dilution: 10 μg/L

Projected maximum concentration using a 2.5-fold dilution: 20 μg/L

Organic Process Chemicals

Site Specific Health-Based Value: Will vary depending on organic compound (see text)

Projected maximum concentration using a 5-fold dilution: None

Projected maximum concentration using a 2.5-fold dilution: None

All predicted levels of ECCs calculated for the Missabe Mountain Pit were below drinking water limits for the 5-fold dilution factor. For the worst case scenario of a 2.5-fold dilution, predicted levels for arsenic, fluoride, molybdenum, and organic process chemicals also fell below the standards. However, the projected level for manganese exceeded the 1,300 μg/L site-specific health based value. The predicted values for manganese did not include the effects of natural processes common in surface water. These processes would aid in limiting development of higher levels of manganese in the Missabe Mountain Pit.

Based on the outcome of the health risk assessment, MDH concluded that the implementation of the proposed project would pose negligible risk to the population of the city of Virginia. However, certain activities were recommended to monitor the quality of water both during and after tailings disposal.

The activities recommended are as follows:

- install monitoring wells or sites between the two pits to determine changes in water quality over time;
- continue periodic sampling of natural and recycled pit waters for changes in chemistry and increases in levels of ECCs;
- conduct periodic limnologic profiles in the Missabe Mountain Pit to determine the degree of mixing of pit waters and the possible development of low oxygen layers;
- prevent disposal of quantities of organic material or other substances that could decrease pH and make the waters more reducing;
- develop a Source Water Protection Program for the Missabe Mountain Pit to protect the water quality in the pit from the effects of multiple development in the area.

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1.0 Introduction and Scope

Purpose: *Provide background information on the proposed Inland Steel Mining Company's (ISMC) taconite deposition project and discuss the scope of the health risk assessment.*

1.1 Introduction

According to the 1996 Minnesota Statutes, Chapter 407, Section 56 - Taconite Deposition the Minnesota Pollution Control Agency (MPCA) may issue a permit for deposition of fine tailings into taconite mine pits "...provided the proposer demonstrates through an **environmental impact statement**[1] (EIS) and risk assessment that the deposition will not pose an unreasonable risk of pollution or degradation of groundwater." In 1993, ISMC requested approval from the State of Minnesota to develop a procedure for depositing fine taconite tailings into the Minorca Pit[2]. The Minnesota Department of Natural Resources (MDNR), as the responsible government unit for the proposal, was required to conduct a supplemental EIS prior to an evaluation of the proposed permit request. In addition, in December 1996, the Health Risk Assessment (HRA) Unit of the Minnesota Department of Health (MDH) agreed to conduct a health risk assessment as the stipulated risk assessment for the proposed project. This document will describe the health risk assessment as it relates to the proposed request made by ISMC. The health risk assessment will focus on an evaluation of the potential risk of contamination of groundwater flowing into the Missabe Mountain Pit by the proposed deposition of fine **taconite ore tailings** into the Minorca Pit.

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[1] Words or phrases in bold are defined in the Glossary of Terms - Appendix A.

[2] The Minorca Pit is a mined taconite pit located near the city of Virginia, Minnesota and owned by the Inland Steel Mining Company. It is the focus of discussion regarding the proposed taconite deposition.

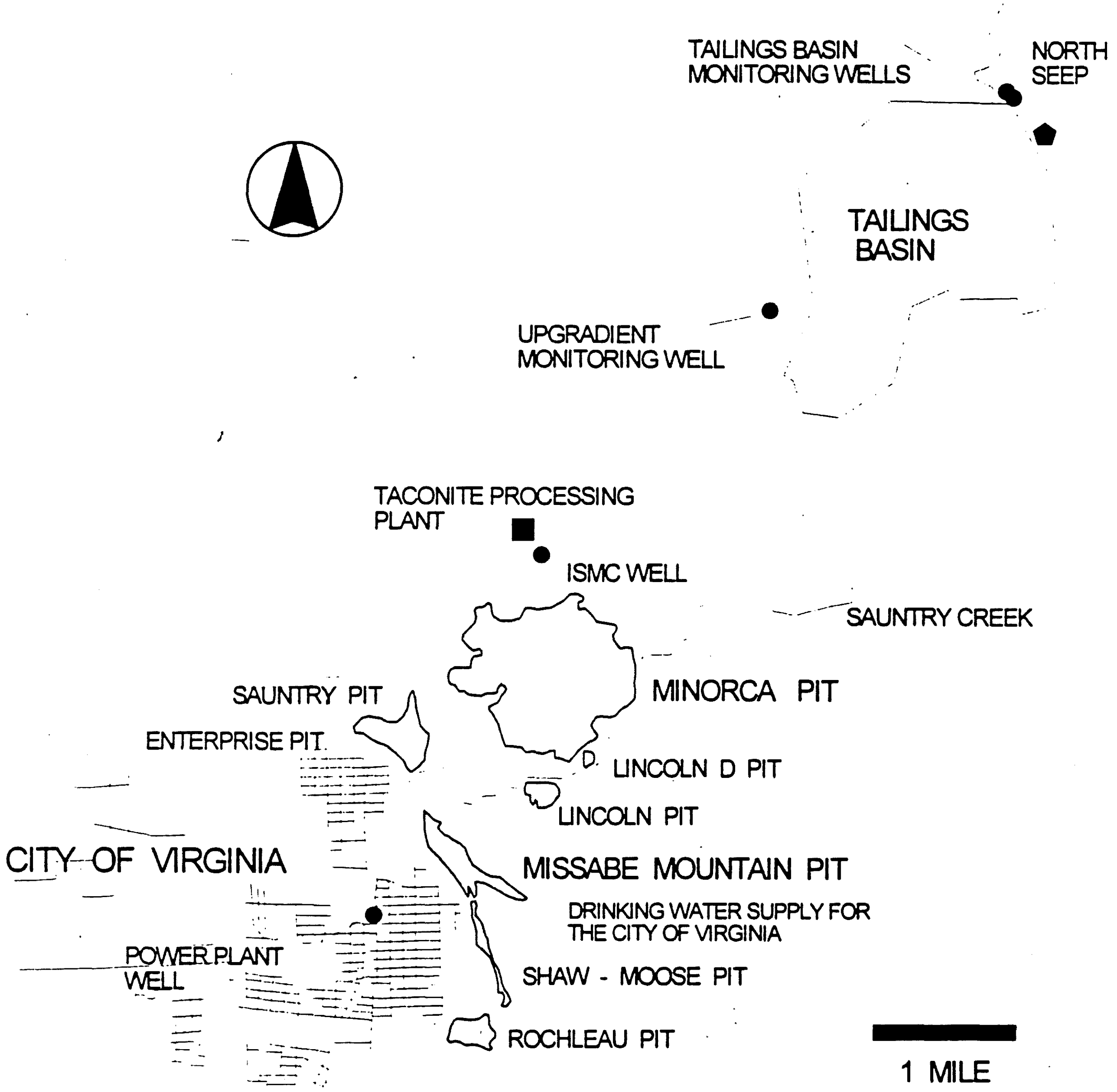
1.2 Background Information

The Missabe Mountain Pit along with several natural iron ore pits including Sauntry, Enterprise, Shaw-Moose, and Rochleau comprise a north-trending linear depression to the east-northeast of the city of Virginia, Minnesota. It is the primary drinking water reservoir servicing the residents of the city of Virginia (see Figure 1). Due to the hydrogeology of this region, many of the abandoned pits are filling with water over time. At present, the surface water bodies in the separate pits are not connected. However, with a continued rise in water level, an eventual surface-hydrologic connection between the water bodies is likely to occur. The Minorca Pit (located approximately one mile northeast of the Missabe Mountain Pit) is the site for the proposed disposal of fine taconite tailings by ISMC.

ISMC mines taconite ore from the Laurentian Pit located approximately four miles southeast of the city of Virginia. The first step in **ore processing** involves transporting the crude ore to the taconite-processing facility. The ore is crushed and subjected to magnetic separation and flotation processes that remove the iron leaving residual tailings. The processing facility combines the tailings with water to create a slurry that is pumped to a tailings basin located approximately three miles northeast of the processing plant (see Figure 1). Once in the basin, the tailings settle out of the water and the resultant clarified water is available for reuse by ISMC for future ore processing. Water from the tailings basin can also be intermittently discharged into Wuori Creek, located north of the tailings basin. An intermittent average discharge of 4.1 million gallons per day with a maximum rate of 9.6 million gallons per day is allowed several times per year (during snow-melt and heavy rain) until water levels in the tailings basin have decreased to an acceptable level. The amounts of discharge and water quality requirements are specified in **NPDES/SDS** permit number MN0055964 issued to ISMC. Before discharge, water quality must meet criteria stipulated in the permits.

Estimates indicate that, at present levels of production, the existing tailings basin will reach its holding capacity in five years. The MDNR permit to mine currently held by ISMC allows for an

Figure 1. Generalized map of the study area



expansion of the basin. However, due to the high costs associated with pumping slurry to the tailings basin and the destruction of the natural wetlands of the area, ISMC is proposing to deposit the tailings-slurry into the Minorca Pit.

1.3 Proposed Action

As an alternative to expansion of the present tailings basin, ISMC proposes to use the Minorca Pit as a permanent disposal site for the tailings. The proposed action calls for pumping the tailings-slurry through a pipeline connecting the ISMC ore processing facility to the Minorca Pit. The tailings will be deposited in the northern, central, and southern parts of the pit. The tailings will not be deposited in the western part of the pit. As with the tailings basin, the tailings will settle out of suspension in the pit and the remaining water will flow into the Lincoln D Pit (see Figure 1). From the Lincoln D Pit, the clarified water will be pumped through a pipeline to the processing facility for reuse in ore processing. Projections indicate that the Minorca Pit will be filled with tailings to an elevation of approximately 1,470 feet above sea level after ten years. After the first five years, a dike approximately 32 feet high and 6,000 feet long will be constructed at the south end of the pit to provide additional storage capacity for the tailings and prevent water from leaving the Minorca Pit.

Sauntry Creek will also be diverted when the dike is constructed. After tailings disposal ends, a canal and spillway will be built at the lowest possible elevation in the Minorca Pit to collect surface runoff from the reclaimed basin and divert it into Sauntry Creek. The diversion will minimize the amount of water seeping into and moving through the tailings into groundwater. If the permit is approved, it is expected that tailings will be placed in the Minorca Pit for approximately ten years. Following ISMC's tailings disposal, the pit will be mitigated to MDNR mine land reclamation rules.

Because of the proximity of the plant to the Minorca Pit, and its downhill location from the plant, the proposed project would result in savings for ISMC due to decreased pumping costs. It will also prevent the loss of wetlands that would be destroyed if the present tailings basin was expanded. However, a potential risk of contamination of the drinking water exists due to the Minorca Pit's close proximity to the Missabe Mountain Pit. The main objective of the health risk assessment is to determine whether the proposed action has the potential to pollute the city of Virginia's drinking water supply, and likewise, present a danger to the health of the residents.

1.4 Scope of the Health Risk Assessment

The Minorca Pit is located approximately one mile northeast of the Missabe Mountain Pit. The scope of the health risk assessment is to determine the potential risk of contamination to the drinking water supply of the city of Virginia if the proposed tailings disposal project is permitted and implemented. Therefore, the MDH's HRA Unit is conducting this health risk assessment in conjunction with the supplemental EIS drafted by the MDNR. The health risk assessment is designed to screen for human health risks and provide input for regulatory decision making. Due to data limitations, a set of conservative assumptions was established to assure that the process would yield a health risk assessment that is sufficiently protective of the public. The assumptions were as follows:

1. The health risk assessment focuses on groundwater migrating from the Minorca Pit to the Missabe Mountain Pit. The principal aquifer considered in the health risk assessment is the Biwabik Iron Formation.
2. A direct hydrologic connection is assumed to exist between the Minorca Pit and the Missabe Mountain Pit. All groundwater leaving the Minorca Pit is assumed to enter the Missabe Mountain Pit. Data on direction and controls on groundwater flow are not available to determine actual flow paths, so a direct connection between the two pits cannot be proved or disproved.
3. Results are based on the present process outlined by the company. The findings of this health risk assessment may not be valid if the process used to extract iron from taconite ore is changed or modified.

4. The potential effects of the proposed action under normal conditions are considered. It does not address the effects of surface spills or failures that may cause a direct interaction of tailings with surface waters in the study area.
5. The health risk assessment addresses human health issues associated with the drinking water for the city of Virginia. Based on the location of the proposed project and land use, drinking water safety is the most immediate issue associated with the project. Ecological issues are not addressed.

In a scoping document released in November 1997, a health risk assessment comprised of eleven basic steps was proposed. Several of the key steps are as follows:

- conduct an analysis of the water quality data and finalize the list of elements and compounds that will be evaluated in the health risk assessment;
- evaluate the toxicity of given elements;
- determine the potential for migration of contaminants from the Minorca Pit to the Missabe Mountain Pit and assess the potential for reaction within the groundwater and pits that would increase or decrease the levels of elements in the water;
- assess the potential for exposure; and
- characterize the potential human health risk from exposure that would be expected if water from the Minorca Pit migrated to and mixed with groundwater from the Missabe Mountain Pit.

1.5 Participants in the Heath Risk Assessment

Chief participants in the development of the health risk assessment were scientists from MDH, and scientists and regulators from MDNR, MPCA, University of Minnesota (U of M), ISMC, and the city of Virginia. In addition, U.S. Geological Survey (USGS) staff participated in the process by serving as reviewers of the data. Specialists from the Minnesota Geological Survey (MGS) and Natural Resources Research Institute (NRRI) also provided data and background information.

1.6 Communications

The health risk assessment was conducted as an open public process. Four community meetings were held at the Virginia City Council Chambers during completion of the project. Discussions focused on issues associated with the proposed in-pit tailings disposal project (June 1997), scope of the health risk assessment (August 1997), an interim status report on progress of the health risk assessment (December 1997), and presentation of the findings (July 1998). Each meeting allowed time for questions and public comments. Several of the meetings were televised on a local cable channel.

In addition to the open public meetings, scientists, regulators, and stakeholders met frequently to discuss the methods used in data evaluation. Five meetings were held between October 1997 and June 1998. Representatives of the city of Virginia were briefed on the results of the meetings.

Informal communication was also maintained with representatives from the ISMC and the city of Virginia. Louise Grams from WHLB Radio in Virginia also held an interview with MDH staff to discuss drinking water issues.

2.0 Assessment of the Hydrogeology of the Study Area

Purpose: *Assess the impact of the geology and hydrology of the study area on the potential transport of elements from the Minorca Pit through the Biwabik groundwater aquifer to the Missabe Mountain Pit.*

2.1 Physical Characteristics of the Study Area

The study area for the health risk assessment includes the land containing the Minorca and

Missabe Mountain Pits. The Sauntry, Enterprise, Lincoln, Shaw-Moose and Rochleau Pits, as well as smaller pits in the area are also included (see Figure 1). The primary research focus was on the land between the city of Virginia and the northern and eastern boundaries of the St. Louis River Watershed (see Figure 2).

2.2 Background Geologic and Hydrologic Research

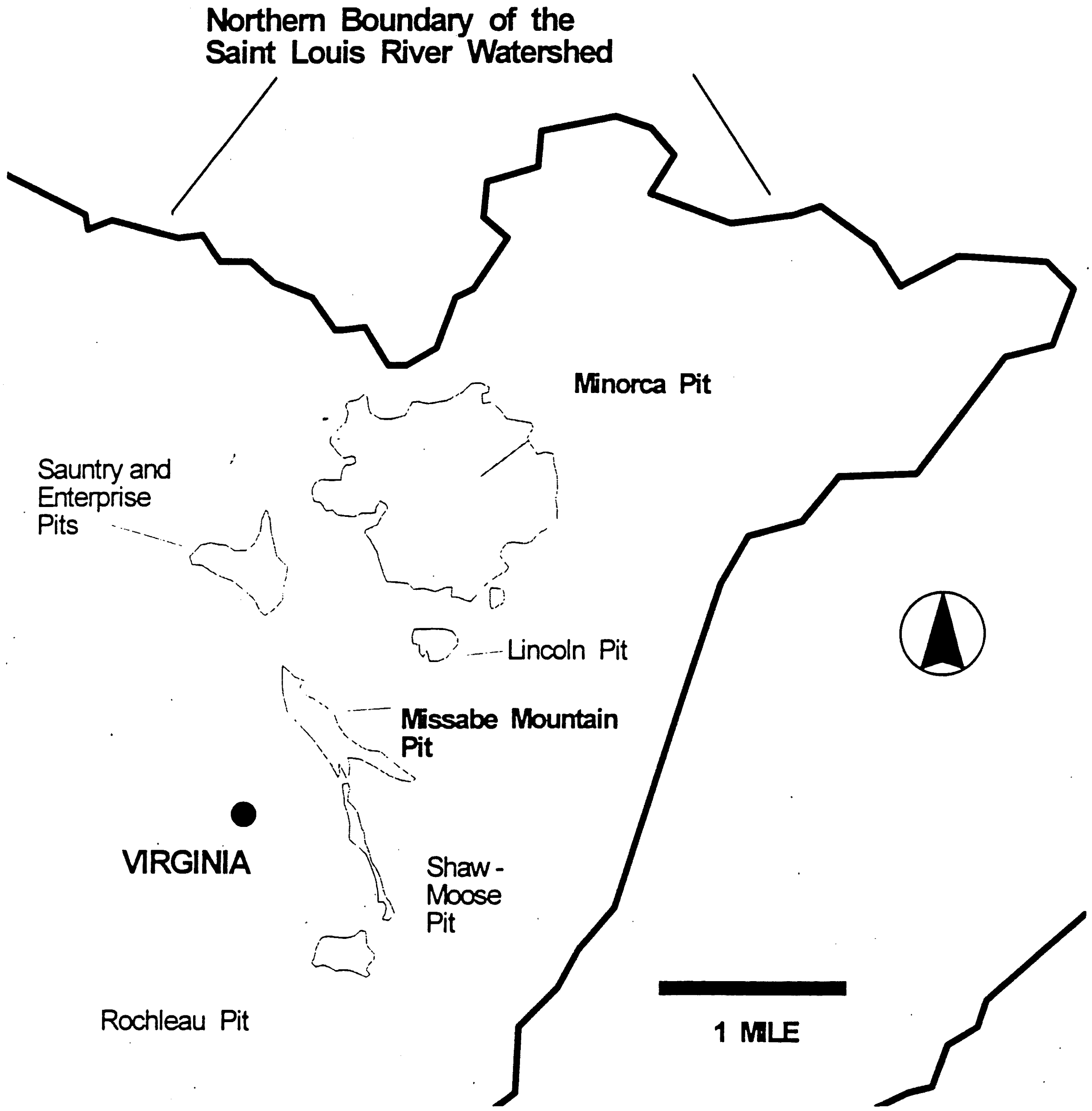
Published research and personal communication with scientists working in the study area provided the majority of the geologic and hydrologic background information. Additional information was obtained from ISMC, MGS, NRRI, and the USGS. Citations for published data and personal communications are included in Table 1 of Appendix B.

Useful data on groundwater flow are limited for the study area. This is largely due to the complexity of the hydrology of groundwater around mine pits. The Biwabik Iron Formation has a particularly complex structural geology with rocks folded, fractured, and faulted in the area. These characteristics create a potentially significant effect on groundwater flow. In addition, the development, maintenance, and abandonment of the mined pits complicate the groundwater hydrology.

Prior to preparation of the health risk assessment, available hydrologic information was gathered for the Minorca Pit. HDR Engineering Incorporated, under contract with ISMC, obtained a history of water levels of the pits, a list of known water wells, and general information for a hydrologic assessment of the study area. As part of their ongoing research into pit hydrology, the MDNR conducted a water balance study for the Minorca Pit. The USGS also provided additional hydrologic information.

The health risk assessment was developed under the worst-case assumption that all water leaving the Minorca Pit will eventually migrate to the Missabe Mountain Pit. Accordingly, an important part of this hydrologic assessment is to determine the **limnologic** characteristics of the Missabe

Figure 2. Map showing study area, location of main mine pits, and northern boundary of the Saint Louis River Watershed.



Mountain Pit as the receiving pit. Information about thermal gradients and changes in oxygen saturation with depth in the Missabe Mountain Pit was provided by NRRI, U of M, and HDR Engineering Incorporated. Table 1 of Appendix B lists general references for hydrology. Appendix C contains limnologic information on the Missabe Mountain Pit.

2.3 Geologic Assessment of the Study Area

The primary geologic rock formations found in the study area include the Biwabik Iron Formation, the underlying Pokegama Quartzite, and the overlying Virginia Formation (see Figure 3). A layer of Quaternary glacial drift is also present in the area. The Biwabik Iron Formation is the primary focus of the health risk assessment.

The Biwabik Iron Formation and the underlying Pokegama Quartzite are primarily **metasedimentary** rocks. Both are known to be depositionally complex. Their thickness may change significantly over a short distance, and in some places, the formations may not be present at all. Only a thin layer of the Biwabik Iron Formation is present in the area where the Minorca Pit was developed. During development, a 40- to 200-foot section of the Biwabik Iron Formation was intercepted by mining. However, to the south and west of the pit, the thickness is reported to be more than 750 feet.

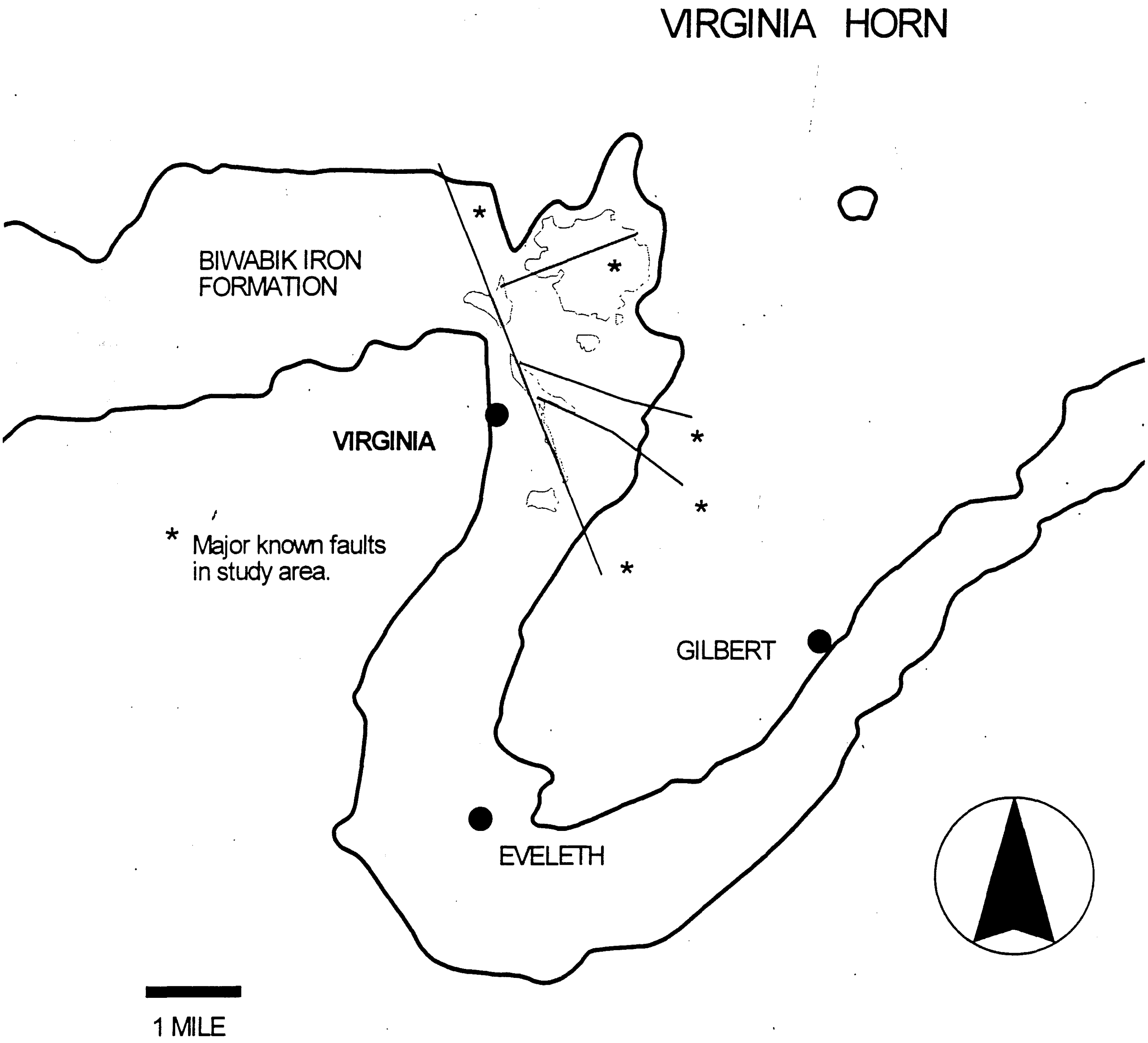
The Biwabik Iron Formation is the major groundwater aquifer for the study area. Water flow through the Biwabik Iron Formation will be affected by faults and zones of fracturing and oxidation present in the formation. These zones are located primarily along structural features such as the **Virginia Horn** (see Figure 4). The faults, folds, and other structures associated with the Virginia Horn affect water flow in the study area. A significant north-south trending structure, believed to be a highly oxidized fault, is associated with the presence of natural iron ore pits, specifically the Sauntry, Enterprise, Missabe Mountain, Shaw-Moose, and Rochleau Pits. The presence of other subsidiary features, predominately faults, are correlated with the presence of natural iron ore pits east of the Missabe Mountain Pit.

Figure 3. Generalized geologic description of the rock formations and unnamed rock units in the study area.

Formation or Rock Unit	Reported Thickness in the Study Area	Description of the Rock
Drift (Surficial glacial deposits)	Less than 100 feet	Described as rubble (discontinuous thin drift overlying bedrock) in the north part of the study area and as a red clayey till south of the Minorca Pit
Virginia Formation	Absent over exposed Biwabik Iron Formation and existing mines	Interbedded carbonaceous shale , mudstone, argillaceous siltstone, and fine-grained feldspathic graywacke
Biwabik Iron Formation (Mined for taconite and natural iron ore. Principal aquifer for the study area.)	750 feet reported	Thick bedded granular units of chert, iron silicates, magnetite, and hematite interbedded with thin bedded units of iron silicates, carbonates, magnetite, and hematite
Pokegama Quartzite	Thickness unknown in study area. HDR Engineering (1997) reported a thickness of 350 feet	Quartzite with locally interbedded conglomerate, quartz wacke, and quartz rich siltstone and shale

Compiled from HDR Engineering Inc. (1997), Geologic Map of the Mesabi Iron Range (1993), and Lindholm et. al. (1979).

Figure 4. Generalized map of the Virginia Horn showing the study area, outcrop of the Biwabik Iron Formation, and other geologic features



2.3.1 Geologic Assessment of the Minorca Pit

The Minorca Pit was created during mining activity on the Virginia Horn and is located near the northern edge of the St. Louis River Watershed (see Figure 2). Because of its location on the Virginia Horn the rock mined in the Minorca Pit is structurally complex. The layers of Biwabik Iron Formation slope to the southeast in the Minorca Pit, while south of the pit, the layers slope to the south. At the same time, the thickness of the formation increases to the south and west. Adding to its complexity, a fault (shown in Figure 4) was reported to have cut through the rock in the Minorca Pit (Geologic Map Missabe Iron Range, Minnesota 1993).

Miners produced relatively unoxidized taconite ore from the Minorca Pit. Several sections of the pit were not mined; however, since the ore had been oxidized to the point that it could not be processed in the ISMC's pellet plant. Prior to taconite mining, small sections of **oxidized** natural iron ore were mined resulting in development of the Higgins, Sullivan, Lincoln D, and several unnamed pits in and around the present extent of the Minorca Pit. The presence of these oxidized zones was expected due to the following:

- the Minorca Pit was developed on a major geologic fold (the Virginia Horn);
- faults and/or fracture zones are common in the rock in and near the Minorca Pit; and
- the Biwabik Iron Formation is relatively shallow in the study area.

Limited data are available regarding the portion of the Biwabik Iron Formation between the Minorca Pit and Missabe Mountain Pit. Much of the surface in this area is covered by drift or with tailings from previous mining operations.

MDH staff conducted two studies to characterize the structural geology of the study area and delineate potential locations of fracturing between the two pits. The first was a lineament/fracture trace analysis using aerial photos. Lineaments or fracture traces appear as conspicuous lines on aerial photos. They are believed to represent fracture zones or faults in the earth's crust that can be delineated more easily from an aerial perspective. The lines are assessed to ensure that they are not associated with manmade activity (roads, power lines, irrigation canals, fence lines) or other non-geologic features. There is a high potential for error in selecting fracture traces from an aerial photograph. Visiting the site and checking for signs of fracturing on the earth's surface is necessary to validate each fracture trace. From the study, signs of well developed fracture zones were not evident in the area between the Minorca Pit and the Missabe Mountain Pit.

The second study focused on an analysis of aeromagnetic point data. Fetter (1980) defined the cause of magnetic readings as distortions in the earth's magnetic field by materials in the earth's crust. The anomalies give a general indication of the type of rocks in a formation. Since the Biwabik Iron Formation is by nature composed of magnetic rock, this procedure was used to characterize the general structure of the area. Results from the analysis were qualitative and required field checking. Although the data, in general, confirmed the locations of known structural features and natural ore pits, resolution was insufficient to delineate local zones of intense fracturing that could affect flow between the Minorca Pit and other pits.

Based on the analytical techniques used in the studies, zones of increased fracturing in the Biwabik Iron Formation between the Minorca Pit and the Missabe Mountain Pit could not be verified. However, the presence of small pits mined for natural iron ore occurring on a line between the Minorca and Sauntry Pits suggest a possible interconnection between the two pits. Table 1 of Appendix D contains a summary of results and specific information on data sources used in the two studies.

2.4 Hydrologic Assessment of the Study Area

The hydrologic assessment is limited since little is known about groundwater flow in and around the study area. Hydrology data for the study area are limited as follows:

1. Only a few water wells have been drilled in the area, so verification of heads and potential flows through the aquifer have not been possible.
2. Many of the major pits have been pumped and the pumping has impacted water levels in pits and nearby water wells.
3. At the time the health risk assessment was conducted, there were no monitoring wells in the Biwabik Iron Formation near the Minorca Pit. Aquifer tests were conducted on two test wells drilled into the floor of the Minorca Pit. Although **hydraulic conductivity** was determined from the test results, recovery curves and supporting data were not available. In addition, **tracer tests** were not conducted on the wells.
4. The above mentioned wells were drilled in an area where the remaining Biwabik Iron Formation was estimated to be 30 to 40 feet thick. The hydraulic conductivity determined from the wells is representative of a small section of the total aquifer. No data are available in the study area for a thicker sequence of the Biwabik Iron Formation.
5. Groundwater from the Biwabik Iron Formation flows along fractures in the rock. No evidence exists to support the hypothesis that the aquifer can be analyzed or treated in the same manner as a sandstone aquifer would be treated (e.g., as a porous or permeable media).
6. The area is covered by a blanket of glacial drift material (see Figure 3). The extent of hydraulic interconnection of aquifers in the drift and the Biwabik Iron Formation has not been determined.

2.4.1 Descriptive Regional Hydrogeology

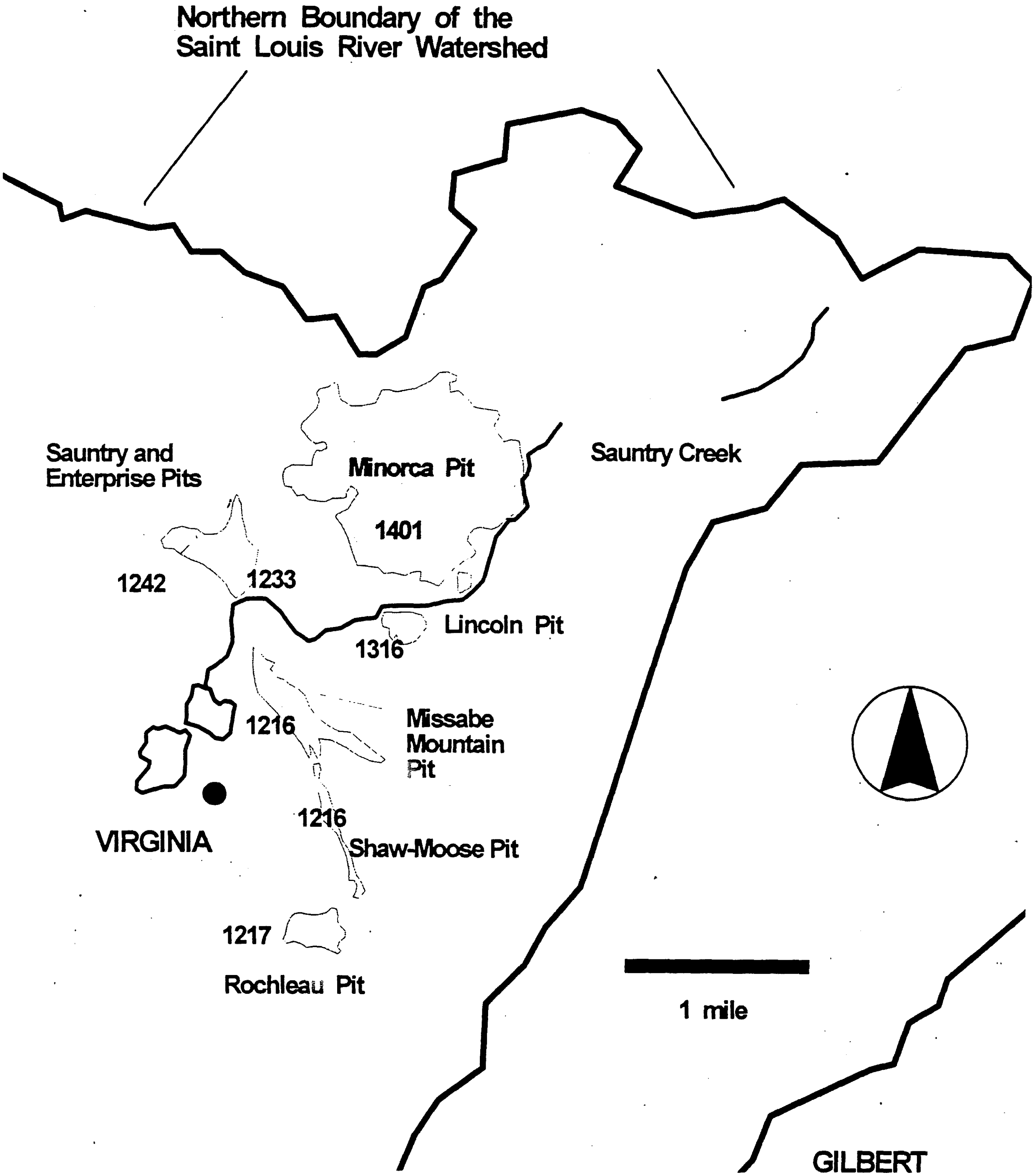
An important aspect of the hydrogeology of the study area is surface water drainage east and north of the city of Virginia. The main control on surface water drainage in the study area is the presence of the northern boundary of the St. Louis River Watershed. The boundary marks a topographic high that acts as a divide for surface water drainage. Rivers and creeks to the north of the boundary, such as the Pike River (east of the study area) and Wuori Creek (north of the present tailings basin) flow to the north and east away from the boundary. To the south, rivers such as the St. Louis River and East Two River flow to the south and west away from the northern boundary of the St. Louis River Watershed. In the study area, surface water will tend to flow toward the south and west. The Sauntry Creek, flowing to the west, is the only feature draining the study area.

Water-filled pits are the most significant surface water features in the study area, although natural lakes also occur in the area. Many of the pits, as shown in Figure 5, are slowly filling with water from groundwater sources as well as surface runoff and precipitation (rain and snow). As they fill, the water level rises in each pit. The water levels recorded in November 1996 by HDR Engineering Incorporated for pits in the study area are presented in Figure 5 (HDR Engineering Incorporated, 1997b).

The two main groundwater aquifers in the study area are the layers of glacial drift (Drift) and the Biwabik Iron Formation. The Drift is comprised of red clay till and rubble (Lindholm et.al., 1979). The rubble occurs in the northern portion of the study area where it is reported to be a discontinuous thin drift overlying the bedrock. Drift thicknesses are reported to be less than 100 feet in the northern section of the St. Louis River Watershed. Common yields for wells drilled in the glacial drift are less than 10 gallons per minute (gpm), although yields of over 500 gpm have been reported in some areas. The Biwabik Iron Formation varies in thickness throughout the region. Common yields for wells producing in the Biwabik Iron Formation range from 5 to 15 gpm (Lindholm et al., 1979). Well yields have been recorded as high as 1000 gpm. The Pokegama Quartzite, located underneath the Biwabik Iron Formation, is not considered an aquifer in the region. Unless it is highly fractured, the presence of the Pokegama would limit downward flow of water from the overlying Biwabik Iron Formation.

Permeability is generally defined as how easily water flows through a porous material. Certain geologic materials such as sandstones (rock), sands, and gravels possess high primary permeability. The Biwabik Iron Formation, composed mainly of chert, iron silicates, and iron oxides has low primary permeability. However, due to fracturing, oxidation and the creation of

Figure 5. Surface water features in the study area.



more permeable layers in the rock where in-place minerals have been dissolved by water, certain zones of the Biwabik Iron Formation are more permeable than they originally were. This is referred to as secondary permeability. Because of secondary permeability, groundwater is assumed to flow more readily through the rock connecting the Missabe Mountain Pit and north-south trending natural iron ore pits. Flow through relatively unoxidized rock, such as that found in the Minorca Pit, could occur only through fractures or bedding planes cutting through the rock. The available data do not conclusively indicate a connection between the Minorca Pit and Missabe Mountain Pit. In order to provide an adequate margin of safety, however, the health risk assessment is conducted under the assumption that it such a connection exists.

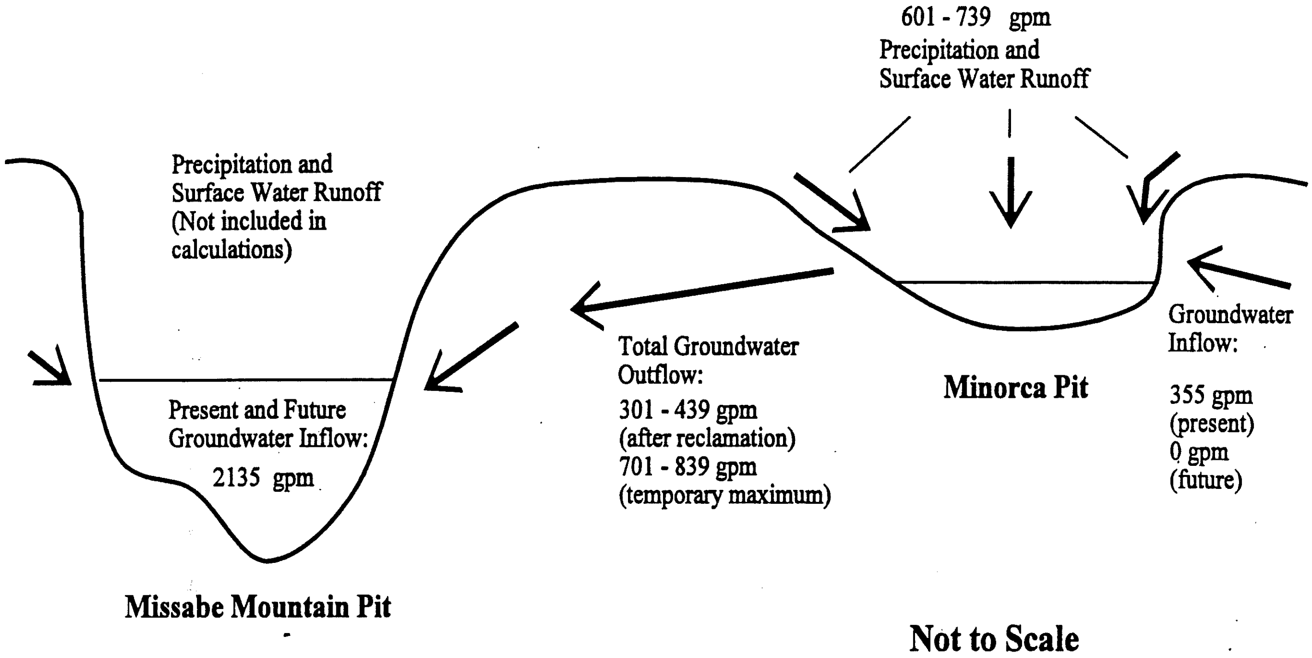
MDH staff evaluated the possibility that underground mining activities created conduits for water movement between the Minorca Pit and Missabe Mountain Pit. Oxidized sections of natural iron ore in the Biwabik Iron Formation were mined utilizing underground methods prior to surface mining. Analysis of available mine maps revealed three locations of abandoned mine **shafts**. The first shaft was reported in the Lincoln D Pit directly southeast of the main Minorca Pit. The second shaft was noted north of the abandoned Commodore Pit (south of the Lincoln Pit). The map showed a potentially abandoned mine passageway looping northward and then returning back to the shaft. Based on the archived map, mine passageway development was limited to a small section north of the abandoned Commodore Pit. A third shaft was found in a pit southeast of the Norman Pit outside the area of concern. The historic shafts and mine passageway were constructed in oxidized ore. As such, historic underground mine development is expected to be found primarily in oxidized ore. According to ISMC personnel, abandoned underground workings were intersected and mined out during the development of the surface mine pits (ISMC, personal communication, 1998). Although available information does not confirm that abandoned mine workings created a connection between the Minorca Pit and Missabe Mountain Pit, MDH staff assumed a direct connection exists (see Section 1.4).

2.4.2 Hydrogeology of the Minorca Pit and Adjacent Pits

The Minorca Pit, mined until 1993, currently acts as a sink for precipitation and runoff from the surrounding area (John Adams, personal communication, 1998). The present water elevation in the pit is approximately 1,400 feet above sea level. Recent research conducted by the MDNR estimated that groundwater flow into the pit is relatively low; 355 gpm compared with a net precipitation derived inflow of 601 gpm to 739 gpm (see Figure 6). In addition, research indicated that the Minorca Pit is currently not losing water to the surrounding Biwabik Iron Formation and that net water loss will not occur until the static water level rises to an elevation estimated by MDNR (using the Theim Equation) at about 1,450 feet. Ongoing MDNR studies on mine pits show that groundwater outflow occurs when the water level in the pit rises to within 10-15 feet of its pre-mining static water level. Therefore, ground water outflow could conceivably begin to occur from the Minorca Pit at between 1,435-1,440 feet (Adams, 1998). At that point, anticipated groundwater flow away from the pit will range from 701 gpm to 839 gpm (see Figure 6). These worst-case values do not reflect reclamation of the site that is predicted to maximize surface runoff and minimize groundwater outflow. After reclamation, the values are expected to drop to 301-439 gpm (see Figure 6).

Current and previous water levels in the various pits, the power plant well, and additional wells in the area indicate that groundwater lost from the Minorca Pit may flow to the Missabe Mountain, Lincoln, and Sauntry Pits (see Figure 5). However, water levels in the pits also indicate that water leaving the Lincoln and Sauntry Pits will eventually reach the Missabe Mountain Pit. Therefore, water that does not directly flow to the Missabe Mountain Pit has the potential to reach it through alternate flow paths. Based on a water balance study on the Missabe Mountain Pit conducted by HDR Engineering Incorprated (HDR Engineering Incorporated, 1997b), groundwater inflow into the pit was calculated at 2,135 gpm. This value agrees with inflow volumes determined by engineers from the city of Virginia (city of Virginia Public Utilities, 1998, personal communication).

Figure 6. Values used in calculations for hydrologic assessment of study area.



Issue Addressed	Calculated Present Value (gpm)	Anticipated Future Value (gpm)	Comments	Sources
Calculated Groundwater Inflow into the Minorca Pit	355	0	Decrease based on assumption that with filling, all flow will be away from pit.	John Adams (1998) personal communication
Calculated Inflow into the Minorca Pit from Precipitation and Runoff	601-739	601-739	Values assumed to remain the same.	John Adams (1998) personal communication
Projected Groundwater Outflow from the Minorca Pit with reclamation	0	301-439	Based on precipitation and runoff plus 100 gpm from tailings disposal.	John Adams (1998) personal communication
Projected Groundwater Outflow from the Minorca Pit prior to reclamation	0	701-839	Temporary Maximum. Based on precipitation and runoff plus 100 gpm from tailings disposal.	John Adams (1998) personal communication

Issue Addressed	Calculated Present Value (gpm)	Anticipated Future Value (gpm)	Comments	Sources
Calculated Groundwater Inflow into Missabe Mountain Pit	2135	2135	Value assumes no change in inflow into the receiving pit.	HDR Engineering, Inc, (1996)

Assumptions:

- All groundwater leaving the Minorca Pit will eventually migrate to the Missabe Mountain Pit.
- Value of 2135 gpm excludes precipitation and any surface runoff for the Missabe Mountain Pit.
- Groundwater utflow will not occur until water level in Minorca Pit rises to within 10-15 feet of pre-mining static water level.

Due to the nature of water flow between the pits, the Minorca Pit will not be the sole source of recharge water for the Missabe Mountain Pit. Precipitation, runoff and groundwater from the other pits and surrounding aquifer(s) contribute to recharging the Missabe Mountain Pit. The total projected outflow from the Minorca Pit constitutes an estimated 39 percent of total inflow into the Missabe Mountain Pit. This assumes no net increase in groundwater inflow (a stable value of 2,135 gpm) and excludes the contributions of precipitation and surface runoff into the Missabe Mountain Pit. The value is a temporary maximum since the volume of water collected in the Minorca Pit will decrease when a ground cover is established during reclamation. In addition, ISMC proposes to build an outlet structure at the lowest elevation during reclamation to maximize capture of surface water runoff and minimize groundwater outflow. After reclamation, the values are expected to decrease with total projected outflow from the Minorca Pit constituting 20 percent of the total inflow into the Missabe Mountain Pit.

3.0 Comparison of the Geochemistry of Natural Waters and Process Waters in the Study Area

Purpose: *Compare the geochemistry of the natural waters and process waters.*

3.1 Description of Data Used in the Geochemical Assessment

For purposes of the health risk assessment, **natural water** is defined as water samples taken from the pits and three wells (power plant well, ISMC well, and up-gradient well). Also included in the 'natural water' category are samples from the MPCA's Ground Water Monitoring and Assessment Program (GWMAP) database. Water quality analysis from GWMAP was used to determine concentrations of elements in groundwater on a regional basis and to approximate background water quality for elements where data from the study area were not available (see Table 2, Appendix B for a compilation of data sources).

Process water is defined as water samples that were in contact with taconite tailings. Process water includes samples taken from the discharge pipe into the tailings basin (plant discharge), the discharge from the tailings basin (tailings basin), monitoring wells outside of the tailings basin (shallow and deep monitoring wells), a seep at the northern edge of the basin (seep), and laboratory column experiments (process water test columns 1 and 2). See Figure 1 for approximate locations of natural and process water sampling sites.

Several ongoing studies are being conducted by ISMC, MDNR and U of M. The ISMC research included analyses of both natural and process water samples from the study area. The samples were drawn from a total of nine natural water sites and three process water sites. After collection, the samples were not filtered prior to acidification (sample preservation) and analysis, resulting in potentially higher values for many elements in the samples. The analyses were still used in the geochemical assessment, although it is noted in the body of the report where analyses of unfiltered samples were used.

Research conducted by MDNR and the U of M examined the chemistry of process waters from four active taconite mining operations located on the **Mesabi Iron Range**. ISMC was one of the four mining operations investigated. Samples were taken periodically from six process water sites. The ISMC sites include the taconite processing plant, the pipe that discharges tailings water from the processing plant, the tailings basin, a seep at the northeast corner of the tailings basin, and two monitoring wells north of the basin (Berndt and Lapakko, 1997).

Research staff also conducted a series of laboratory column experiments where tailings from ISMC processing plant were placed in 2-inch-diameter vertical columns. The objective of the experiments is to identify reactions that occur when tailings are in contact with process waters. These experiments were not intended to precisely simulate the quality of water in the field. Water from the ISMC processing plant was added to the columns and allowed to filter continuously through the tailings. Water samples were periodically collected from a port at the base of the column and analyzed. The experiments, conducted over a period of 216 days (approximately 31 weeks), monitored changes in the concentrations of different elements over time. Column experiments were also conducted on the tailings using groundwater produced from the Biwabik Iron Formation (groundwater test column -- Keewatin No. 1 Well, located near Keewatin, Minnesota) . An additional experiment used distilled water as a surrogate for rainwater precipitation into a tailings basin (rainwater test column). The results from these experiments were used qualitatively in the health risk assessment to verify expected changes in concentrations of a given element after interaction with the tailings.

3.2 Geochemical Assessment of Natural Water Sources in the Study Area

Water from the wells and pits in the study area are hydrochemically classified as 'bicarbonate-type', with the bicarbonate anion making up greater than 50 percent of the major anions in solution (Fetter, 1980). Calcium and magnesium are the dominant cations (see Figure 7). The **pH** of the water ranged from 7.4 to 9.2 with an average of 7.9 (see Table 1).

In general, natural waters from the wells and pits meet Minnesota and federal drinking water quality standards. Several elements with high concentrations across the region, however, were found in the study area at levels below the regional levels. For instance, the iron content of the water in the Minorca Pit is lower than the federal secondary drinking water standard of 0.3 milligrams per liter (mg/L), although the iron content in waters outside of the study area has been known to exceed this secondary drinking water standard (MPCA's GWMAP database, 1998). In some areas in the region, manganese can also occur in the natural water supplies at levels above present drinking water standards (MPCA's GWMAP database, 1998).

Figure 7 displays the chemical characteristics of the natural water samples (shaded shapes). The clustering effect seen in the diagram is strong indication that the natural water sources are similar in chemical makeup. In some cases, water quality differences can aid in determining whether water bodies are interconnected and one water body is a source of recharge for another. In the case of the Missabe Mountain Pit, however, identification of sources of recharge is difficult due to the low variability in water chemistry among the surrounding pits.

Figure 7. Piper diagram comparing samples from the different mine pits, tailings basin (2 samples) and column experiments (41 day and 216 day). (Definition of water classification from Fetter (1980, p338))

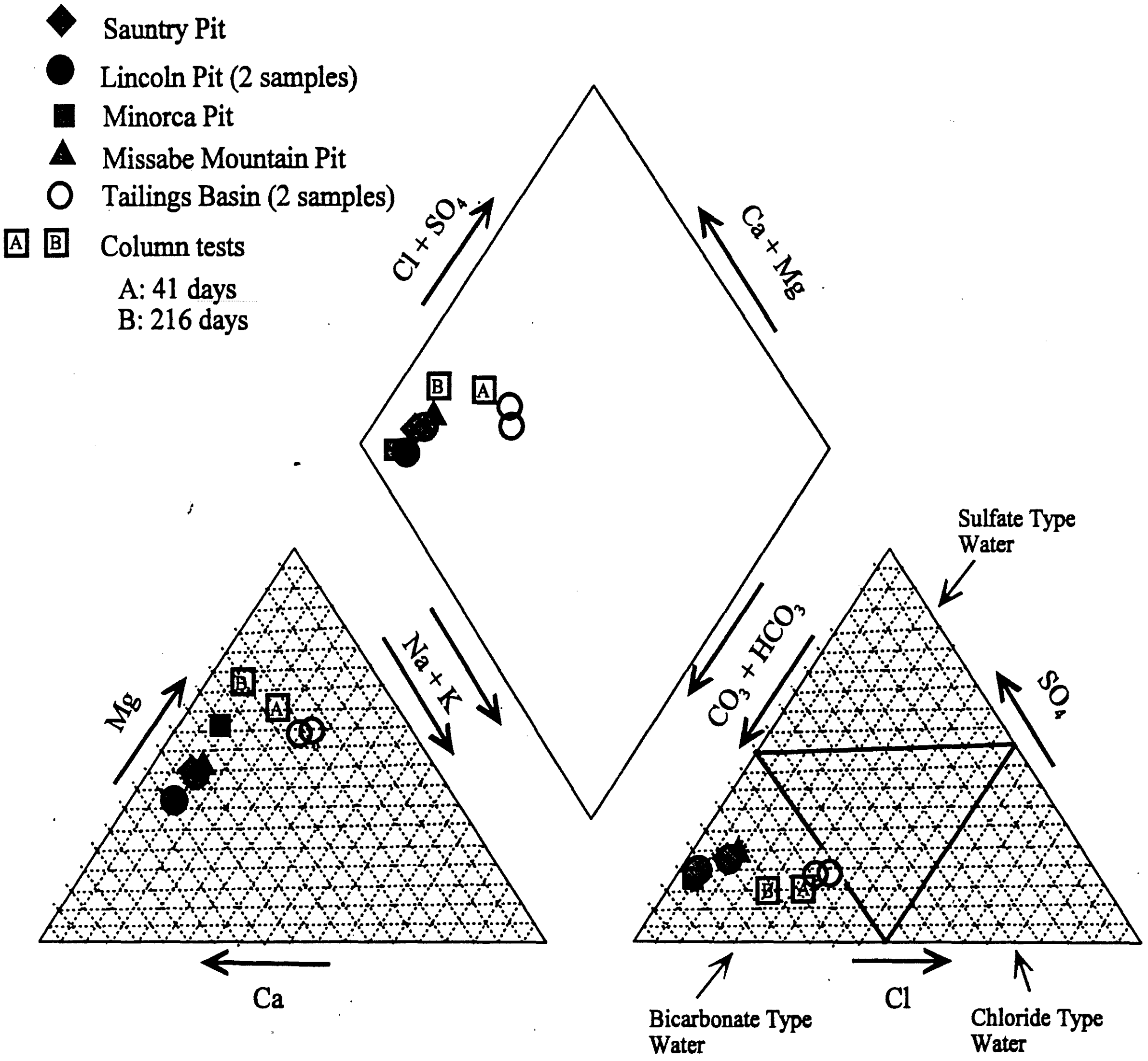


Table 1. Average and range of values for pH in natural and process waters

Sampling Site	Number of Samples	Average Value (Standard Units)	Range (Standard Units)
Natural Waters			
All Sites	27	7.9	7.4 - 9.2
Process Waters			
Plant Discharge	5	8.4	8.2 - 8.6
Tailings Basin	6	8.6	8.2 - 8.8
North Seep	3	7.7	7.4 - 7.8
Shallow Monitoring Well	4	7.1	6.9 - 7.3
Deep Monitoring Well	4	7.0	6.7 - 7.2

Similarity among the natural waters was also found in the isotopic data collected by Alexander and Alexander (1997). They concluded that the isotopic ratios could not be used to differentiate water sources. As the isotopic composition of the water bodies change over time, however, the isotopic ratios may become more effective in determining water sources.

A secondary goal of the isotope study was to determine age of the natural water. The **tritium** values for water samples in the study area varied from 10 to 21 TU (Tritium Units). Comparing these values to recorded levels of precipitation indicated that the majority of the water was precipitation falling less than 25 years ago with some possibly falling less than 5 years ago. Sources for the deeper water were not identified for the study area.

3.3 Geochemical Assessment of Process Water from the Study Area

The health risk assessment assumes that the geochemistry of the present tailings basin will be representative of the geochemistry of the water in the Minorca Pit when filled with tailings. By analyzing the plant discharge and tailings basin waters, it is possible to determine changes in water quality due to interactions with the tailings and dilution from precipitation and surface runoff. Water in the seep is assumed to be representative of the quality of water that would leave the Minorca Pit tailings basin and enter the groundwater. The water has been separated from the atmosphere and the effects of high oxygen levels during migration through the tailings. Monitoring well water chemistry is similar to that from the seep although it exhibits decreased pH and oxidation/reduction potential (**Eh**) and an increase in the levels of constituents such as iron, manganese and arsenic.

Low pH and Eh in the monitoring wells may be partly due to the reaction of the process water with minerals in the tailings. This is similar to the reaction that the water undergoes in the seep and test columns. However, buried organic material nearby the monitoring wells may also contribute to the change in reducing conditions. Appendix F contains a letter written by the MDNR that discusses the characteristics of the monitoring wells and the possible influence of organic material on pH and different elements.

Known pH values varied for the different process waters (see Table 1). Values from the seep (7.4-7.8) and basin monitoring wells (6.7-7.3) are lower than values for the tailings basin (8.2-8.8 with an average of 8.6). The lower pH in monitoring wells may be partly due to the presence of organic material or to reactions taking place between water and minerals in the tailings.

To further evaluate the quality of the process waters, it is necessary to separate the waters sampled at the surface of the tailings basin from those sampled at the seep. Seep water is isolated from the atmosphere and shows the effects of a closed, low-oxygen environment with lower pH and Eh and more **reducing conditions**. When compared to tailings basin surface samples, samples from the seep water have lower sulfate, molybdenum, arsenic, and pH. However, increases in the concentrations of manganese, iron, and calcium are also noted (Berndt, 1998).

3.4 Comparison of the Geochemistry of Natural Water with Process Water

All natural and process waters in the study area are hydrochemically classified as 'bicarbonate-type' since bicarbonate is the major anion present (see Figure 7). Water from the tailings basin and seeps tend to be slightly higher in sodium and chloride than the natural waters. The concentration of sodium in process waters ranges from 12 to 48 mg/L (sodium levels in natural waters range from 7 to 12 mg/L). Those for chloride range from 20 to 85 mg/L (chloride levels in natural waters range from <1 to 17 mg/L).

The column experiments determined that time is an important factor in determining chemistry and levels of different elements in water exposed to tailings. Over time, the pH and Eh decrease slightly in water seeping through the in-place tailings. Consequently, process water chemistry changes and levels of different elements either decrease or increase (see Figure 7).

The changes are the result of dissolution of silicate and carbonate minerals and cation exchange occurring within the tailings. The effects of exposure of process water to tailings for specific elements will be discussed in Section 4.2.2. Further discussion is found in Berndt and Lapakko (1997).

As noted previously, the pH values for the process waters vary depending on whether the samples were collected from the tailings basin or the seep and monitoring wells. When comparing the natural and process waters and assessing the range in values for each group, the variation is greater within the process water group than between the process waters and natural waters. Values for Eh qualitatively suggest a less reducing environment in the tailings basin, the seep, and deep monitoring well than is found in the shallow monitoring well. Eh values for the tailings basin, seep, and deep monitoring well range from 280 to 418 millivolts (mV). In comparison, values for the shallow monitoring well are the lowest recorded for the study area ranging from 154 to 189 mV. The lower Eh may indicate the presence of organic material[3].

Alkalinity and sulfate levels are additional parameters used to evaluate water quality. Process waters from the seep and monitoring wells tend to have a higher alkalinity [expressed as mg/L calcium carbonate ($CaCO_3$)] than natural waters and water from the tailings basin. The average alkalinity values for the seep and monitoring wells is 224 mg/L. The average alkalinity values for the plant discharge, tailings basin, and natural waters are 189, 167, and 187 mg/L, respectively. Sulfate levels for the plant discharge are higher (average values of 56 mg/L for plant discharge) than for the tailings basin and natural waters (average values of 41 and 42 mg/L, respectively). Sulfate levels for the seep and monitoring wells are lower than either the process and natural waters. As noted by Berndt (1998), reaction of water with the tailings

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[3] These values are relative measurements and should be used qualitatively to determine whether an environment is oxidizing or reducing. Differences in values between the natural and process waters may have also been due to measurement error and differences in equipment and calibration.

results in a decrease in sulfate along with reduction in pH. The shallow monitoring well tends to be lower in sulfate (from 12 to 23 mg/L) than both the seep (from 20 to 42 mg/L) and the deep monitoring well (31 to 73 mg/L). The majority of the major and trace elements in the process water did not occur at levels that exceeded those of the natural waters (to be covered in Section 4.2).

A concern was raised that the addition of more acidic rainwater to the tailings could increase levels of potentially harmful elements in the process water. Research conducted by the MDNR and U of M expanded the column experiments to include placing simulated rainwater (pH of 5.5, alkalinity of 0) in contact with tailings (Berndt, 1998). The resulting effluent possessed a similar pH to the seep and natural waters. The alkalinity was higher than both natural and process waters. Results from the column tests indicate a buffering of the water's chemistry that may prevent significant changes in water quality when the tailings are exposed to rainwater. In addition, effluents from the rainwater and groundwater column experiments contained many of the constituents at levels close or equal to values seen in the column experiments using process water. This is apparent, despite the fact that the tailings material had been previously exposed to process water for a year. The results suggest that various elements will be released from the tailings for an indefinite period of time.

4.0 Human Health Risk Assessment

Purpose: *Determine the potential for an impact of the proposed project on human health.*

4.1 Introduction

In 1994, the National Research Council outlined a four-step process for determining whether a particular situation could potentially pose a risk to human health. The four steps of this risk assessment process are as follows: 1) hazard identification, 2) dose response assessment, 3) exposure assessment, and 4) risk characterization (National Research Council, 1994). For the current health risk assessment, hazard identification was addressed by developing a list of elements and compounds that were present in process waters in concentrations above background levels. Consideration was also given to elements and compounds of concern to the citizens of the city of Virginia.

The dose response step of the analysis was also examined. A basic tenet of toxicology asserts that the dose of a chemical defines whether or not it is a poison (i.e., all chemicals are poison if present in high enough concentrations). Conversely, the most toxic chemicals will be harmless if they are not present in high enough concentrations to produce effects. Therefore, the risk assessor must determine whether or not a chemical concentration is or will be high enough to exert a toxic effect.

Assessment of exposure and risk characterization are the final steps in the risk assessment process. Humans must be exposed to a chemical either internally or externally for it to exert a toxic effect. All possible routes of entry into the body must be considered since even the most toxic chemicals occurring at high concentrations will be harmless as long as there is no route for exposure. In the risk characterization phase, evidence accumulated during the first three steps is combined and explained, and risk assessment decisions are presented and defended. In addition, the risk characterization should contain the information that was not used and reasons for why it did not receive additional consideration.

Because of limitations in geological and hydrogeological information, the health risk assessment used a very conservative default assumption, i.e., anything that goes into the Minorca Pit will ultimately end up in the groundwater that feeds the Missabe Mountain Pit. The logic behind this approach is that health risks to the citizens of the city of Virginia will be minimized if the project is judged safe through conservative assumptions regarding hazard identification. In addition, using a conservative approach will help to ensure minimal impact on future generations by anticipating changes in conditions that may increase risks posed by the process.

4.2 Hazard Identification: Selection of Elements and Compounds of Concern

During hazard identification, a list of chemicals of concern was developed by examining available data from a number of sources as well as examining tailings basin chemicals that occurred at concentrations above area background levels. Organic chemicals added during the taconite processing were also added to the list. Each chemical was evaluated for potential toxicity at the level found. The potential for observing higher concentrations of each chemical was also considered. Through this process the list of chemicals of concern was shortened to arsenic, fluoride, manganese, molybdenum, and the organic process chemicals.

4.2.1 Water Quality Research

The MDNR and U of M research on the tailings chemistry (discussed in Section 3.1) provided pertinent information needed to define the **elements and compounds of concern** (ECC). At MDH's request, U of M researchers conducted geochemical modeling to predict the fate of the ECCs. Other data sources included files of state and local government agencies as well as published research. A listing of water chemistry data sources is shown in Table 2 of Appendix B.

Water sampling and analysis described in Section 3.1 aided in determining the potential for inorganic and organic compounds becoming a public health problem. Five elements, manganese (Mn), arsenic (As), fluoride (F), molybdenum (Mo), and beryllium (Be), were found in the tailings or process water at concentrations of potential regulatory concern. The possible presence of organic process chemicals in the water was also a concern. Input from stakeholders and scientists familiar with the proposed project prompted MDH staff to focus on the possibility that changes in water chemistry over time could result in a mobilization of elements (see **mobility** in Appendix A). Mobilization of the elements could potentially lead to increases in concentrations within the study area to levels of public health concern.

4.2.2 Determination of Elements and Compounds of Concern (ECCs)

Water quality data for process water samples were compiled and compared to current and proposed drinking water standards. The comparisons included an evaluation of a total of 56 elements and compounds. The criteria for selection of the ECCs were as follows:

- elevated by taconite processing to levels above present or proposed state or federal drinking water standards;
- elevated by the process to levels above natural background water quality;
- that could increase to potentially harmful levels if the geochemistry of the waters in the study area changed; and
- that are of public concern.

The criteria for selection excluded elements or compounds that were naturally high in the groundwater and/or were not elevated because of processing taconite ore. Elements listed in Table 2 were eliminated from consideration since they fell at or below background levels of natural water in the study area and below applicable drinking water standards. The elements enriched in the process water compared to the surrounding natural water were subjected to additional evaluation (see Table 3). A number of the elements and compounds in Table 3 were subsequently eliminated since available information indicated that the levels fell below those considered harmful to human health.

In addition, citizens raised concern during the town meetings that asbestiform minerals, radon, and manganese could potentially cause harm if found in the tailings basin. These constituents were given additional consideration, although two were eliminated. Asbestiform minerals and radon were eliminated since they were either not present in groundwater or did not meet the criteria for selection as an ECC (see Table 3). The ECCs were selected based on their behavior in the present geochemistry of the water as well as the potential for increased mobilities resulting from changes in water chemistry (e.g., lower pH, reducing conditions, changes in the presence of other elements). The latter was evaluated by geochemical modeling and comparative analysis of

Table 2. Elements and compounds evaluated during selection process

Below background and/or below Regulatory Standards
Aluminum, Antimony, Barium, Beryllium, Boron, Cadmium, Cerium, Chloride, Chromium, Cobalt, Copper, Gallium, Iron, Lanthanum, Lead, Lithium, Magnesium, Mercury, Nickel, Niobium, Phosphorus, Potassium, Rhenium, Rubidium, Selenium, Silicon, Silver, Sodium, Strontium, Tellurium, Thallium, Thorium, Tin, Uranium, Vanadium, Yttrium, Zinc, Zirconium. Sulfate, Amines, Surfactants, Nitrates, Total Residual Petroleum Hydrocarbons, Cyanide, Asbestiform minerals.
Above background. Not considered to be of regulatory or health concern.
Bromide, Cesium, Germanium, Scandium, Tungsten, Oil and Grease.
Background unknown. Not considered to be of regulatory or health concern
Radon.
Above background and considered to be of regulatory or health concern. Selected as ECC.
Arsenic, Fluoride, Manganese, Molybdenum.

Table 3. Breakdown of elements or compounds exceeding background level

Element or Compound	Concentration in Process Water (mg/L)	Background Level if Known (mg/L)	Comments
Arsenic	<0.002 - 0.008	<0.0001 - 0.015	Selected as ECC. See text.
Bromide	0.16 - 0.63	0.02 - <0.20	Used as a tracer in groundwater studies.
Cesium	0.0002 - 0.002	0.00001 - 0.0004	Concentration is below level of concern.
Fluoride	1.3 - 7.6	0.2 - 0.9	Selected as ECC. See text.
Germanium	0.0001 - 0.0005	Undetected	Concentration is below level of concern.
Manganese	Tailings samples = <0.001 - 0.1 Seep, monitoring wells, and laboratory columns = 0.11 - 6.6	<0.0001 - 1.02	Values given for background level were from analyses of unfiltered samples. Tailings samples were at or below 0.1. Samples from the seep and monitoring wells were greater than background. Selected as ECC. See text.
Molybdenum	Seep and monitoring wells = 0.002-0.014. Tailings basin = 0.015-0.090	0.0041- 0.018	Values associated with seeps and wells are <0.015. Values associated with tailings basin are > 0.015. Selected as ECC. See text.

Element or Compound	Concentration in Process Water (mg/L)	Background Level if Known (mg/L)	Comments
Oil and Grease	<1 - 1.4	Unknown	A general and qualitative EPA-required test inclusive of many organic materials. Organic process chemicals were selected as ECC.. See text.
Radon	Unknown	Unknown	Is not found in surface waters. An inhalation hazard .
Scandium	<0.0001 - 0.004	Unknown	Concentration is below level of concern
Tungsten	<0.0001 - 0.002	Unknown	Concentration is below level of concern

water samples obtained from geochemically different sites adjacent to the present tailings basin.

The ECCs chosen for evaluation in the health risk assessment were arsenic, fluoride, manganese, and molybdenum. Some reported levels for fluoride, manganese, and molybdenum exceeded the primary and/or secondary drinking water standards. Reported levels of arsenic fell below present drinking water standards, although the standards under revision are projected to be lowered by the year 2001. Water samples tested for organic process chemicals provided little or no evidence for their presence in the system. However, due to staff's limited knowledge of the specific organic compounds in the patented products and their concern regarding the analytical detection limits, the organic process chemicals were included as an ECC.

4.2.2.1 Arsenic

Arsenic exists in the natural waters (unfiltered samples) in concentrations ranging from < 1 μg/L (detection limit) to 4 μg/L with the majority of the values below the detection limit (see Table 4). Values for arsenic in the process waters ranged from <1 to 8.1 μg/L. Average arsenic values for filtered samples (Berndt, 1998) were 3.0 μg/L for plant discharge water and 4.8 μg/L for tailings basin water. Water from the monitoring wells had average values of 6.4 μg/L (shallow monitoring well) and 2.3 μg/L (deep monitoring well). In comparison, samples from the seep had an average value of < 1 μg/L. In the process water test columns, arsenic levels decreased from a starting value of 8 to < 3 μg/L over the 216-day- experiment. The arsenic values taken from the laboratory column experiments are also presented in Appendix E for comparison.

Figures 8a and 8b display graphical representations of changes in arsenic levels over time for the process water and column experiments. Figure 8a illustrates changes in arsenic levels in process waters over a 1.5 year period. Figure 8b illustrates the changes in arsenic levels over a 216-day-period in the column experiments. In Figure 8b, arsenic levels decrease in column samples with increased water/tailings reaction time. Arsenic levels for both process water test columns were highest at 14 days. By 95 days, the levels reached a minimum. The cause of this observed trend

Table 4. Summary statistics for arsenic levels in natural and process waters

Sampling Site	Number of Samples	Average Value (µg/L)	Range (µg/L)
Natural Waters			
All Sites	11	1.5 *	<1 - 4.1
Process Waters			
Plant Discharge	5	3.0	1.9 - 3.8
Tailings Basin	6	4.8	3.1 - 7.4
North Seep	3	0.7	0.5 - 0.8
Shallow Monitoring Well	4	6.4	4.5 - 8.1
Deep Monitoring Well	4	2.3	2.2 - 3.3

* Note: Values of <1 were considered equal to 1 in calculating the overall average. This assumption will have an effect of potentially overestimating the true average.

Figure 8a. Arsenic levels in process waters

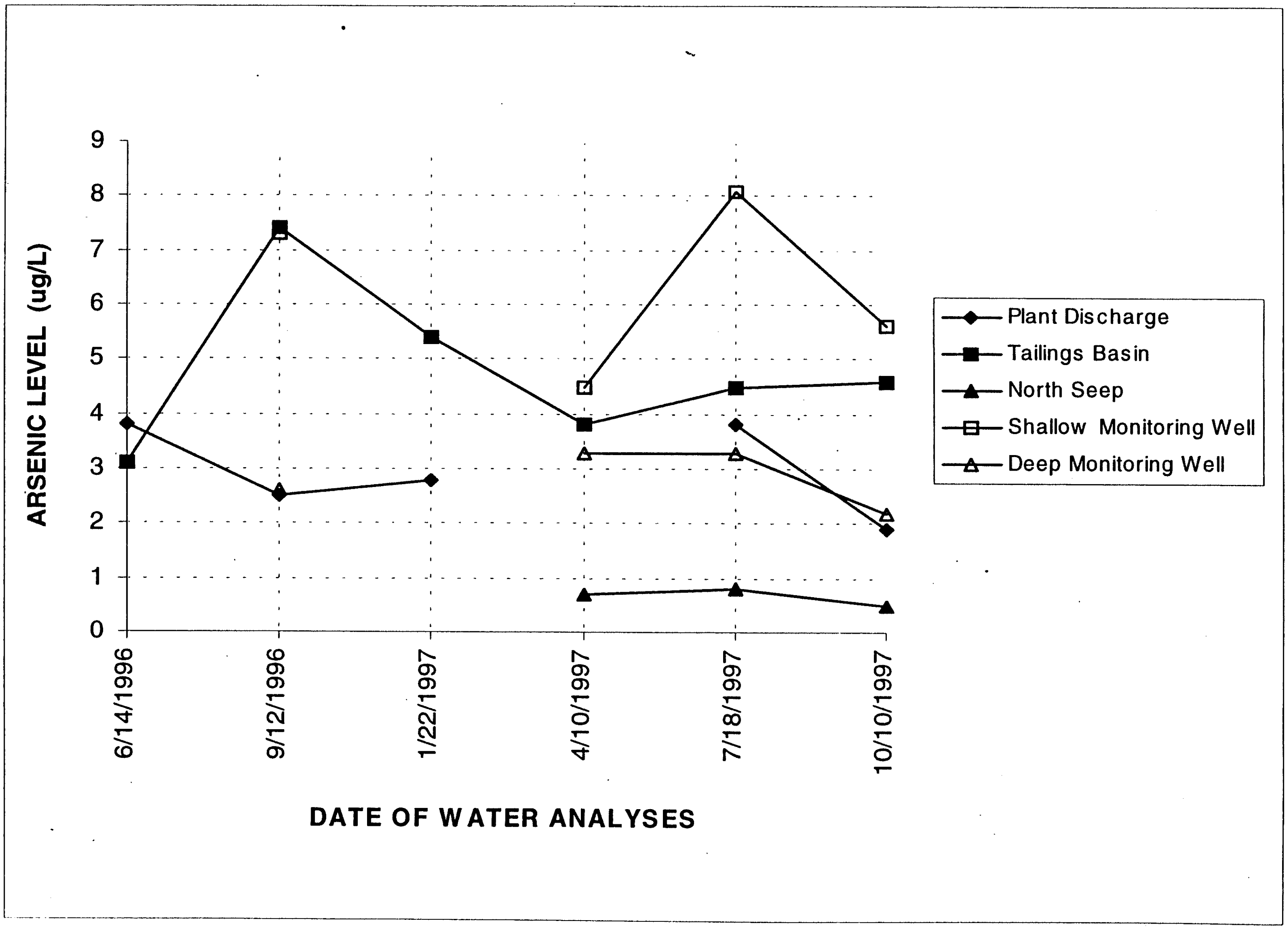
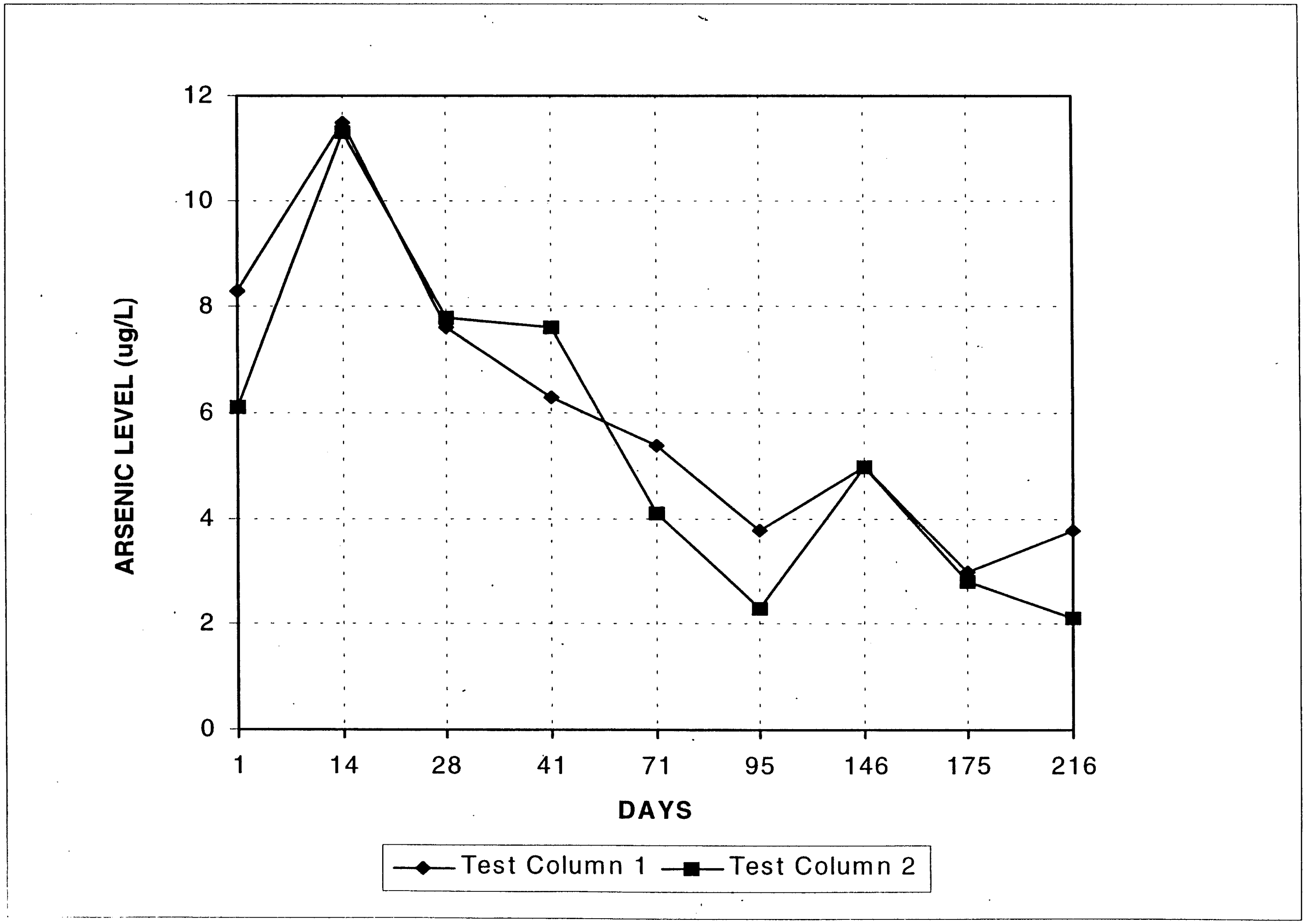


Figure 8b. Arsenic levels in process water test columns



is presented in Section 4.3.3.1.

4.2.2.2 Fluoride

Fluoride occurs naturally in water in the study area at concentrations ranging from 0.3 to 0.5 mg/L. These fluoride concentrations are enriched in the process water during production of taconite pellets (See Table 5). Average values for filtered samples (Berndt 1998) are 4.2 mg/L for plant discharge and 2.4 mg/L for tailings basin water. Fluoride values for the seep were similar to those for tailings basin water with an average value of 2.4 mg/L. Fluoride concentrations in the shallow and deep monitoring wells varied with an average value of 3.3 mg/L for the shallow monitoring well and 1.3 mg/L for the deep monitoring well. The fluoride levels for samples from the column tests varied from a starting value of 3.7 mg/L to an ending value of 2.8 mg/L (see Appendix E).

Changes in fluoride levels over time are presented in Figures 9a and 9b. Figure 9a compares levels of fluoride in the tailings basin, seep, and monitoring wells over a 1.5-year-sampling period. The fluoride levels in the tailings basin, seep, and monitoring wells remain relatively constant. The fluoride levels in the two samples drawn from the plant discharge water exceeded the other water samples. The reason for this difference is not known. A decrease in fluoride is noted in samples from the tailings basin and seep collected in April 1997. During this time, increased surface runoff entering the basin during spring thaw resulted in dilution of the process waters. Figure 9b illustrates fluoride levels in the column experiments over a 216-day-period. Although there is some drop in fluoride levels with time, the decrease is not as noticeable as the drop in arsenic levels (see Figure 9b).

4.2.2.3 Manganese

Manganese levels in the natural waters (unfiltered samples) within the study area ranged from 0.01 to 1.0 mg/L with an average value of 0.26 mg/L (see Table 6). For process waters, all analyses for manganese in plant discharge water (Berndt 1998) were < 0.1 mg/L. The average of

Table 5. Summary statistics for fluoride levels in natural and process waters

Sampling Site	Number of Samples	Average Value (mg/L)	Range (mg/L)
Natural Waters			
All Sites	11	0.5	0.3 - 0.5
Process Waters			
Plant Discharge	5	4.2	2.3 - 7.6
Tailings Basin	6	2.4	1.3 - 2.9
Seep	3	2.4	1.8 - 3.0
Shallow Monitoring Well	4	3.3	3.1 - 3.4
Deep Monitoring Well	4	1.3	0.6 - 1.6

Figure 9a. Fluoride levels in process waters

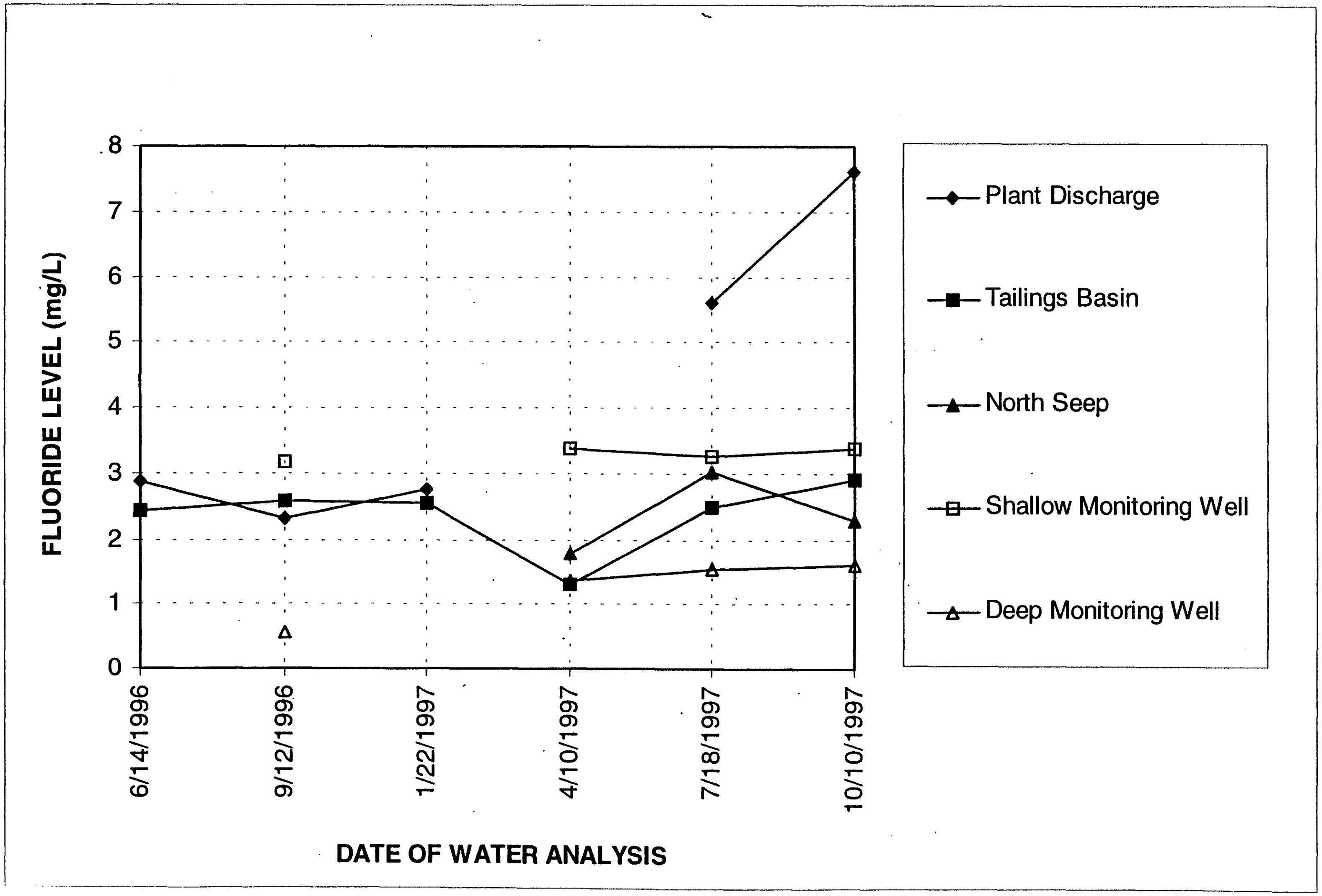


Figure 9b. Fluoride levels in process water test columns

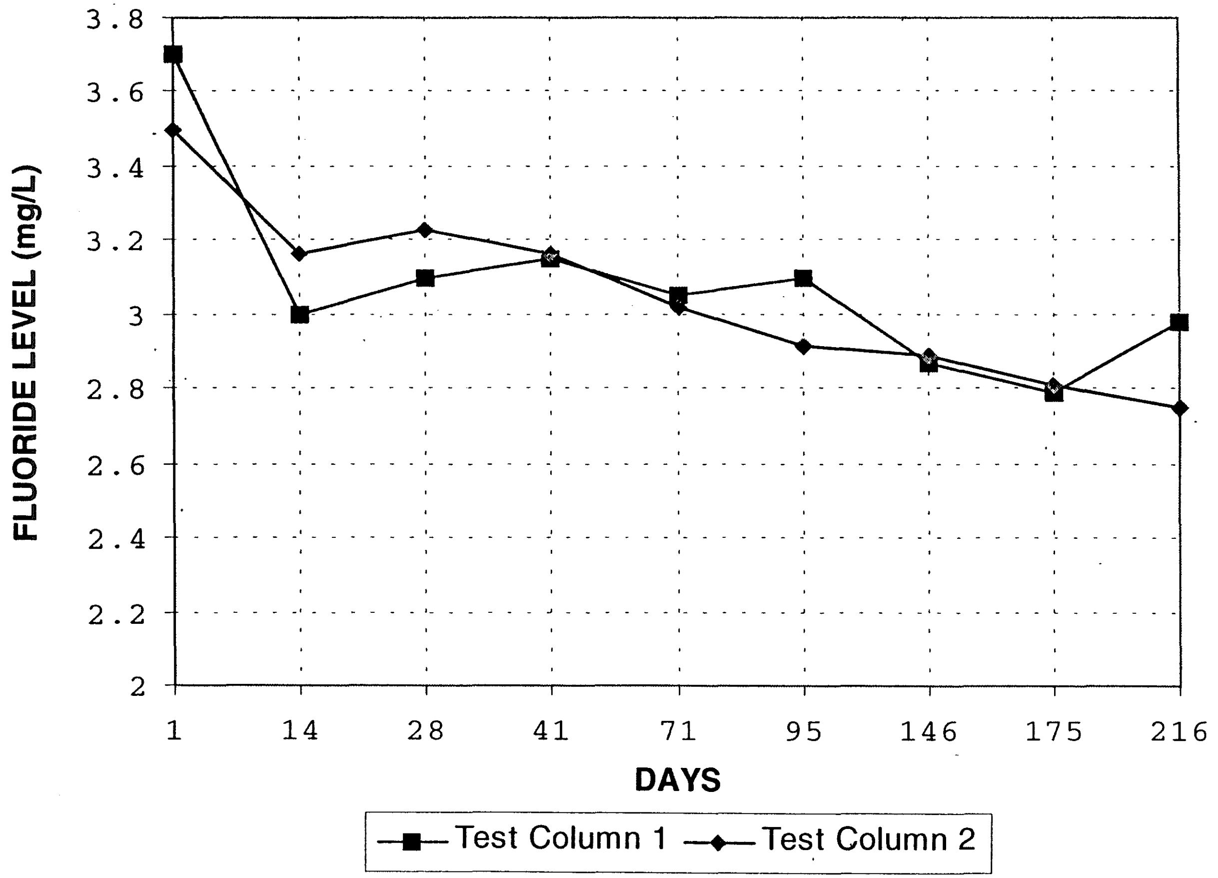


Table 6. Summary statistics for manganese levels in natural and process waters

Sampling Site	Number of Samples	Average Value (mg/L)	Range (mg/L)
Natural Waters			
All Sites	11	0.26	0.01 - 1.02
Process Waters			
Plant Discharge	5	0.1	0.10 - 0.10
Tailings Basin	6	0.02	0.00 - 0.10
North Seep	3	3.03	1.70 - 3.80
Shallow Monitoring Well	4	4.15	4.00 - 4.30
Deep Monitoring Well	4	5.60	4.40 - 6.60

samples from the tailings basin water was 0.02 mg/L. An increase is apparent from sample analyses of seep and monitoring well water. The average manganese value for the seep is 3.03 mg/L. The average manganese values for the monitoring wells are 4.15 mg/L for the shallow well and 5.60 mg/L for the deep well. The levels of manganese were lower in the laboratory experiments. The values from the process water test column varied from a starting value of 0.1 mg/L to an ending value of 0.6 mg/L (see Appendix E).

Changes in manganese levels over time are illustrated in Figures 10a and 10b. There is a large difference in manganese values between plant discharge and tailings basin waters, and waters from the seep and monitoring wells (see Figure 10a). The manganese levels in the plant discharge and tailings basin water of the basin are negligible; whereas the seep and monitoring wells have increased levels due to the interaction of process water with the tailings. Such an increase is evident in the column experiments (see Figure 10b).

4.2.2.4 Molybdenum

Molybdenum is reported to occur in the natural waters of the study area at values ranging from the detection limit (<5 μg/L) to 10 μg/L (unfiltered samples). The majority of the values are at 5 μg/L. Molybdenum is present in process waters at levels above the natural background water quality (see Table 7). Average values for filtered samples (Berndt 1998) are 78 μg/L for the plant discharge water, 35 μg/L for tailings basin water, and 6 μg/L for seep water. The molybdenum level values for both experimental process water test columns varied from a starting value of 100 μg/L to an ending value of 15 μg/L over the 216-day-experiment. For comparison, average molybdenum values for test columns with rainwater and groundwater were approximately 7 μg/L (Berndt, 1998). Observations show that molybdenum levels in process water can also vary significantly over time (see Figures 11a and 11b). Similar to arsenic, the molybdenum values for water that has interacted with the tailings are lower than levels for plant discharge and tailings basin samples (see Figure 11a). Molybdenum concentrations for tailings basin water are lower than for plant discharge; whereas, concentrations in seep and well water are

Figure 10a.. Manganese levels in process waters

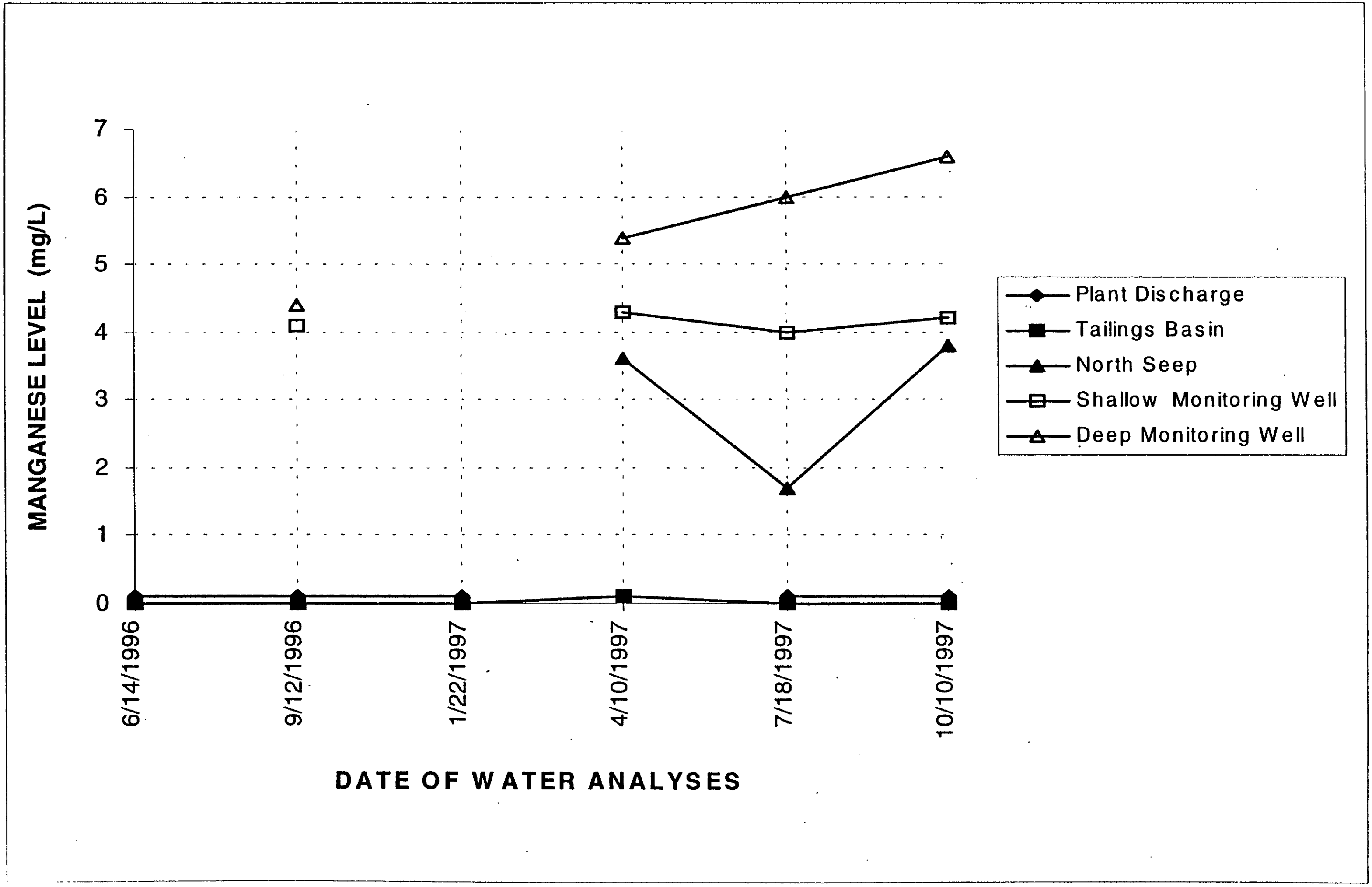


Figure 10b. Manganese levels in process water test columns

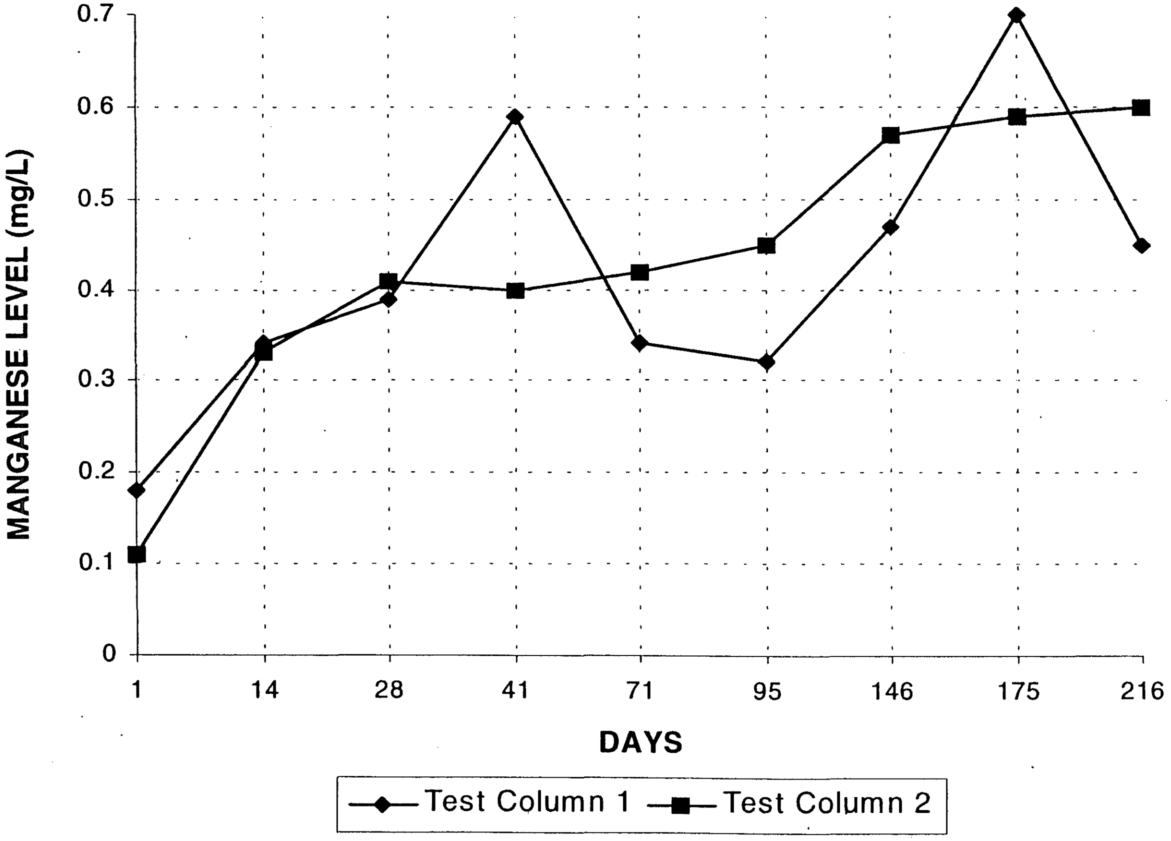


Table 7. Summary statistics for molybdenum levels in natural and process waters

Sampling Site	Number of Samples	Average Value (µg/L)	Range (µg/L)
Natural Waters			
All Sites	11	5.5	<5 - 10
Process Waters			
Plant Discharge	5	78	68 - 86
Tailings Basin	6	35	16 - 49
North Seep	3	6	2 - 14
Shallow Monitoring Well	4	7	6 - 8
Deep Monitoring Well	4	6	3 - 8

Figure 11a. Molybdenum levels in process waters.

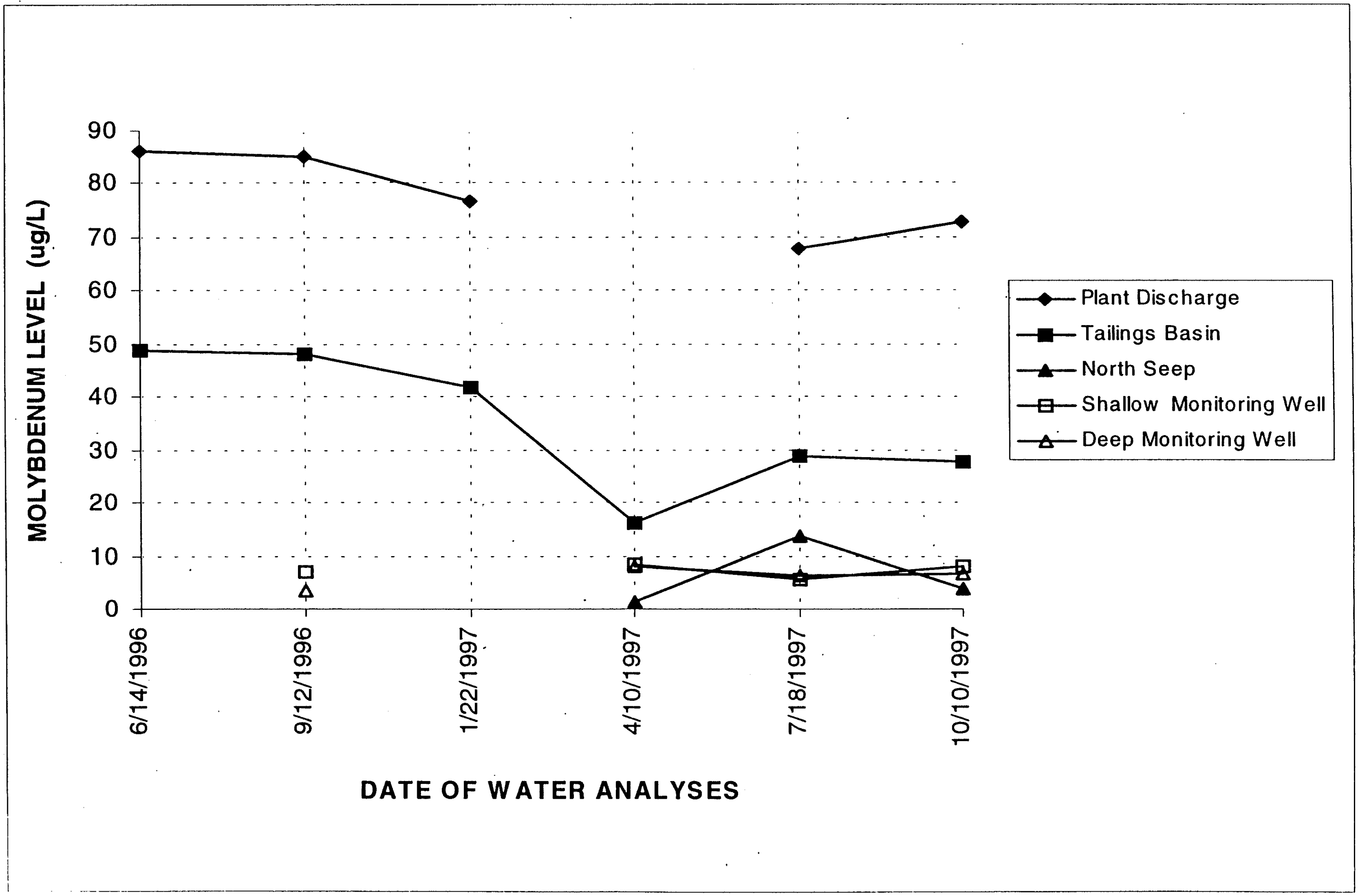
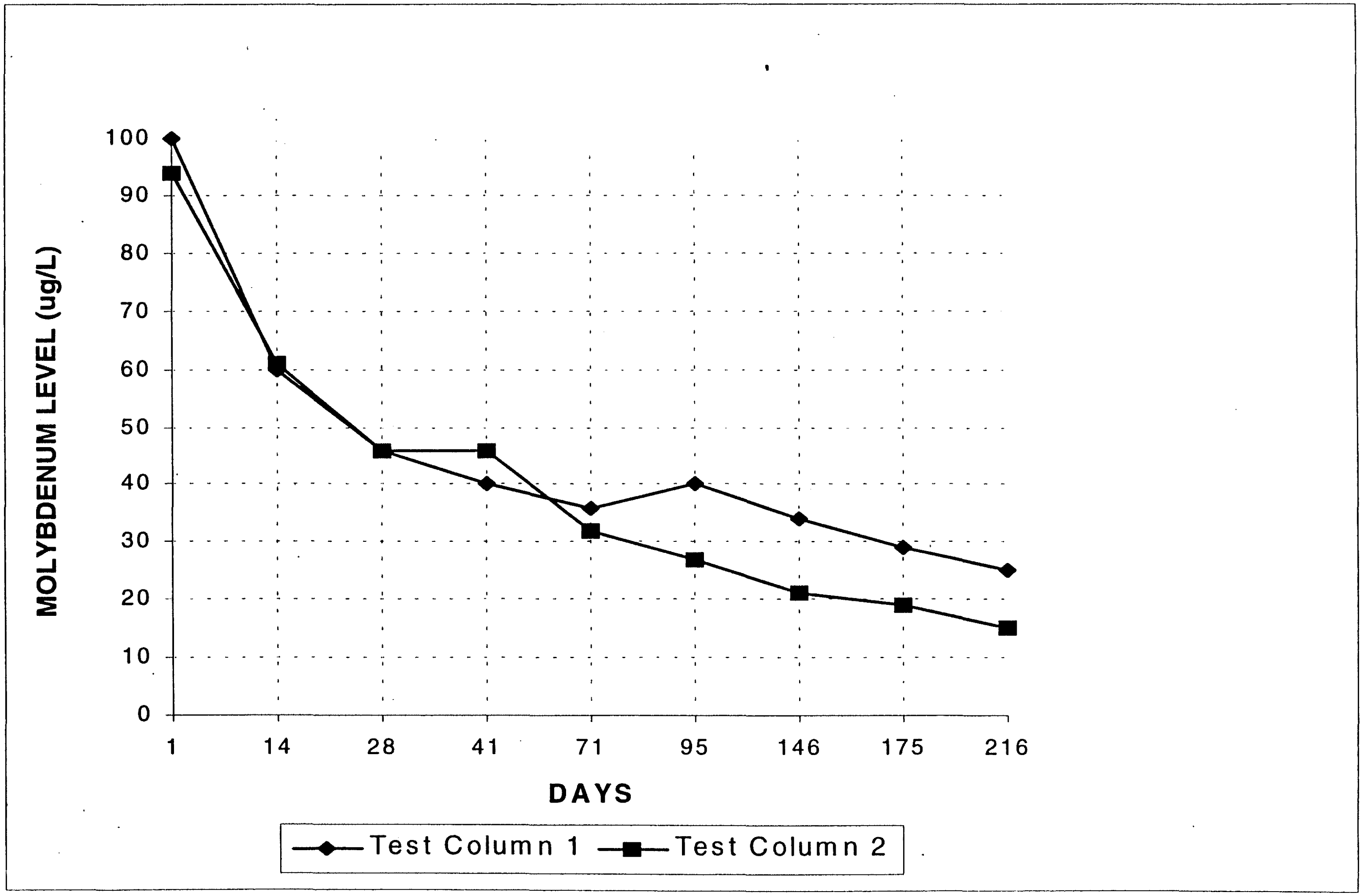


Figure 11b. Molybdenum levels in process water test columns



lower than tailings basin water. Although dilution is responsible for some of the fall in the molybdenum levels, the decrease is also related to tailings-water interaction. In the process water column experiments, molybdenum levels decreased by 75 to 85 percent of their initial levels during the 216-day-experiment period (see Figure 11b).

4.2.2.5 Organic Process Chemicals

Organic process chemicals, or those chemicals intentionally added during the production of taconite pellets, are the final group of elements and compounds of concern. Flotation aids (isododecyloxypropylaminopropylamine), frothers (C4-C18 alcohols, aldehydes and esters, butyric acid, 2-ethylhexanol, 2-ethylhexanal, trimethylnonanol), defoamers (straight run middle distillates, polyglycol acid ester, ethoxylated tall oil acid), and flocculants (hydrotreated light petroleum distillate, fatty acid ester, acrylamide/acrylate, ethoxylated alcohol, polydimethyldiallyl ammonium chloride) are added to the tailings water mixture to aid in the enrichment of iron in the pellets. The production of taconite pellets requires large amounts of water and low amounts of process chemicals, generally in the low parts per million (ppm) range (i.e., 2.6 ppm for total added process reagents). Since the process chemicals are biodegradable, initial analyses conducted on samples from the tailings basin and adjacent monitoring wells failed to detect any of the hydrocarbons added during taconite processing.[4] Process water samples were also analyzed for other organic compounds (see Table 8). The only organic contaminants found in the analyses were "oil and grease" at 1 mg/L for three samples from the basin and seep and trichlorofluoromethane at 1 μg/L for one sample from the basin.

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[4] Additional work, conducted by U of M and MDNR researchers, examined samples of the specific organic reagents used in the taconite processing. This research was conducted to determine if the analytical method used was sensitive to the reagents present. Results indicated that the method was sensitive to all reagents except amines. Amines are known to have an affinity for clays and would likely adsorb onto clays in the tailings.

Table 8. Values for organic compounds from analyses of natural and process waters *

Sampling Site	Number of Samples	Values
Natural Waters - All sites		
Anionic Surfactants[1]	11	All values <0.25 mg/L
Volatile Organic[1] Compounds	11	Not Detected
Process Waters - Tailings Basin/Seep/Monitoring Wells		
Anionic Surfactants [1]	3	All values <0.50 mg/L
Anionic Surfactants	6	5 values <0.10 mg/L, one sample not determined due to problems encountered during analysis
Volatile Organic Compounds[1]	3	Not Detected
Volatile Organic Compounds	6	5 samples Below Detection Limits, one sample: 1.2 µg/L trichlorofluoromethane
Organic Processing Chemicals	4	Not Detected
Amines	3	All values <0.02 mg/L
Oil and Grease	3	0.9 - 1.4 mg/L
Semivolatile Organic Carbon (also called Base Neutral Acids)	3	Below Detection Limits
Cyanide	3	All values <0.02 mg/L
Other organic carbon parameters in process waters		
Total Organic Carbon	8	1.3 - 7.9 mg/L
Biological Oxygen Demand	6	All values <1 mg/L

Chemical Oxygen Demand	8	2 - 17 mg/L

* Unless otherwise noted, samples were collected by scientists from DNR and UofM on a quarterly basis (6/96,9/96,1/97,4/97). Analyses are presented in Berndt and Lapakko (1997), Table 2.5.

[1] Samples were collected by HDR Engineering Incorporated in September 1996. Analyses are presented in HDR Engineering, Inc. (1997), Table 13.

4.3 Exposure Assessment: Assessment of the Potential for Migration of Contaminants from the Minorca Pit to the Missabe Mountain Pit

All possible routes of exposure must be anticipated when conducting the health risk assessment. Ingestion of a contaminant present in food or drinking water, inhalation, and/or **absorption** through the skin are all possible routes of exposure. Chemical and physical characteristics of an ECC indicate the potential for volatility that could result in a loss of material to the atmosphere leading to respiratory exposure. On the other hand, if the ECC entered the groundwater, the potential exists for it to be transported into the municipal water supply of the city of Virginia. This could lead to oral exposure through the use of the water for cooking and drinking purposes and dermal exposure through the use of the water for bathing and washing.

Inhalation and dermal absorption were ruled out as potential routes of exposure after examining the chemical and physical properties of all the ECCs. For example, given arsenic's non-volatility, it is unlikely that humans will be exposed by inhalation. Likewise, dermal exposure is also unlikely since it exists primarily in a charged state (tri-pentavalent) making it difficult to cross the skin. Thus, ingestion of arsenic through water consumption is the most realistic route of exposure.

Duration and intensity of exposure are additional factors to consider. An important consideration is whether or not short-term, high-dose exposure is more likely than long-term, low-dose exposure. Assuming the water contained in the Minorca Pit is dilute, a greater potential exists for long-term exposure to relatively low concentrations of the chemicals.

4.3.1 Assumptions Made in Modeling the Fate of ECCs in Groundwater

The assumptions made for conducting the fate and transport analysis are based on the quality and availability of data on the hydrology and water geochemistry of the study area. Because of the sparse of information on the hydrology of the Biwabik Iron Formation, the primary focus for the fate and transport analysis is on the known chemistry of the ECCs and waters. Findings from the project contracted by MDH to geochemically model the fate of the ECCs (Berndt, 1998) were incorporated with the results of work completed by MDNR, U of M, and ISMC. This research base provided the information framework used for the modeling. Assumptions and/or conditions for the model are as follows:

1. Changes in the concentration of an ECC can occur from **adsorption**, precipitation, or other geochemical activity. Dilution in the aquifer by other groundwater sources is not assumed to occur.
2. Natural water sources will not become significantly acidic or reducing over time. The assessment will address conditions for pH ranges of 6.5 to 8.5 and Eh values representative of what is currently seen in the tailings, seep, and natural waters.
3. No estimate is made of time of travel for ECCs migrating in the groundwater. This assessment assumes the ECC-bearing water will migrate directly to the Missabe Mountain Pit within an undetermined time period.
4. The percent contribution of groundwater from the Minorca Pit to the Missabe Mountain Pit will be 20 percent (representative of reclaiming the tailings with a grass cover). For comparison, 40 percent (representative of no reclamation of the tailings pile) is also included.
5. Mixing will occur in the Missabe Mountain Pit sufficient to dilute the incoming Minorca water to 20 percent and 40 percent of the total volume. The effects of chemical and biologic processes in the Missabe Mountain Pit are also considered.
6. Precipitation and watershed runoff contributions to the Missabe Mountain Pit were excluded. Only groundwater contributions were considered.

4.3.2 Projected Quality of Water Generated from Tailings Disposal

Levels of ECCs and additional constituents are equal to or below the primary and secondary drinking water standards for all but two elements, fluoride and manganese. Where standards do not exist, the concentration of elements or compounds in the tailings water is typically equal to or below the levels found in the natural groundwater. Some non-ECC elements found at higher levels in the process waters are not considered a health risk (see Section 4.2).

4.3.3 Potential for Migration of Five ECCs

Four elements (arsenic, fluoride, manganese, and molybdenum) and organic compounds (chemical additives) were analyzed for their fate and potential for transport. Geochemical calculations (Berndt, 1998) were computed using Geochemist's Workbench, Version 2.0, a program useful for performing fluid speciation, mineral reaction, and adsorption calculations. More specific information on the geochemical modeling and thermodynamic data sources are found in Berndt (1998). The results of the modeling and laboratory work for each of the ECCs are presented below.

4.3.3.1 Arsenic

Arsenic is expected to adsorb onto iron oxides in the tailings and along fractures in the Biwabik Iron Formation. Based on results from geochemical modeling, arsenic present in the tailings and groundwater is likely to bind to hematite or other iron oxides (i.e., under conditions expected in the pit and fractured Biwabik Iron Formation). Analyses of arsenic in the process waters also shows this effect (see Figures 8a & 8b). High concentrations of arsenic in water often occurs simultaneously with high iron concentrations under reducing conditions. This was seen in the monitoring well water where both arsenic and iron concentrations were elevated. When in the presence of oxygen, however, arsenic will likely precipitate out of the water along with iron. Mixing in the Missabe Mountain Pit will also provide oxygenated water. It is unlikely that arsenic will reach the drinking water supply in levels higher than natural background under these conditions. Predicted concentrations for arsenic leaving the Minorca Pit are < 1 to 8 μg/L. Predicted levels for arsenic entering the Missabe Mountain Pit are < 1 μg/L.

Because arsenic is sensitive to changes in pH and Eh, higher concentrations may occur in the tailings water if organic matter or other materials that cause reducing conditions are added to the system in significant amounts (amount undefined). See Appendix F for further discussion of the effects of organics on the development of a reducing environment.

In order to examine the potential for arsenic to become mobile in the waters, several predictive models were created under varying conditions. The first models assumed temperatures of 25°C and an alkalinity of approximately 180 mg/L (3.0 milliequivalents). Excluding the addition of organics and other reducing materials, the lowest calculated Eh ranged from 100 to 150 mV in the taconite tailings pore fluids (Berndt, 1998). Likewise, the expected pH level was between 6.5 and 7.5 in the tailings water. For the models assuming 5°C and the same level of alkalinity, the expected Eh was moderately higher while the pH was lower. Measured Eh values for natural waters (surface and groundwater) in the study area exceeded 100 mV and are not expected to fall below this level. Under these conditions, arsenic is not expected to desorb from the tailings. Therefore, arsenic levels are not expected to increase in waters flowing from the Minorca Pit.

4.3.3.2 Fluoride

Average fluoride levels within the process waters were higher than those found in the natural waters (see Table 5). Assuming conditions in the Minorca Pit are similar to those in the tailings basin, geochemical modeling predicts that fluoride is capable of reaching a peak concentration of 4.5 mg/L (Berndt, 1998). Fluoride concentrations are affected by temperature and calcium levels, i.e., the higher the calcium at 25° C, the lower the fluoride level. Based on calcium levels in the process, rainwater and groundwater, predicted maximum values of fluoride varied from <3 to 4.5 mg/L. Unlike arsenic, fluoride is not expected to be removed from the groundwater by reacting with minerals in the Biwabik Iron Formation. Dilution, however, is expected to be a major factor in lowering fluoride concentrations. Evidence of dilution is displayed in Figure 9a. Lower fluoride levels are found in the tailings basin and seep compared to the plant discharge in samples collected during Spring 1997.

4.3.3.3 Manganese

Manganese occurs naturally within the study area at levels of 0.01 to 1.02 mg/L (See Table 6). Average manganese levels in the water samples drawn from the seep and monitoring wells were all higher than 3 mg/L. Levels of manganese in the tailings basin were significantly lower (0.0 to 0.1 mg/L).

The large difference in values is a result of a combination of physical (dilution), geochemical (oxidation and reduction), and biologic processes (use of dissolved manganese by naturally-occurring microorganisms). Initially, water coming from the processing plant is low in dissolved manganese causing levels in the tailings basin to remain low. The low levels are likely due to oxidation of manganese in the water and dilution in the tailings basin. Water that percolates through the tailings is exposed to a different geochemical environment resulting in a lower pH and more reducing conditions than in surface waters. The changes increase the solubility of manganese causing higher concentrations in water. Therefore, manganese levels in the seep and monitoring wells are much higher than surface water in the tailings basin. The presence of organic material may further increase manganese levels.

The solubility of manganese in water increases as alkalinity and temperature decrease. Since alkalinity and temperature are lower in natural waters, manganese is expected to remain high in the groundwater. Unless the manganese-bearing groundwater is exposed to oxygen-bearing water from the surface or mixes with large amounts of water from other areas within the aquifer, the manganese levels will not change significantly. Based on values from the seeps and monitoring wells and on hydrogeochemical modeling, manganese values of up to 6 mg/L are possible in water migrating from the Minorca Pit (Berndt, 1998).

When manganese-bearing groundwater reaches the Missabe Mountain Pit, mixing with waters within the pit are expected to decrease levels of manganese in the water. Limnologic profiles indicate that the upper 144 feet of water in the Missabe Mountain Pit has been oxygenated.

Oxygen in the water reacts with the manganese resulting in formation of insoluble manganese oxide particles. Manganese will not be re-released into the water until manganese oxide particles encounter reducing conditions such as those commonly found at the bottom of a lake (Davison, 1993). Micro-organisms which utilize the manganese in water as a nutrient and catalyze oxidation of the element to a solid manganese oxide are also believed to respond to high levels of manganese dissolved in the water. Although the values of manganese in incoming groundwater may be high, the levels within the pit are expected to decrease by oxidation and biologic processes. The phenomena is expected to occur as long as the Missabe Mountain Pit water is mixing and higher oxygen levels predominate in the lake (Davison, 1993).

4.3.3.4 Molybdenum

In general, molybdenum levels in the taconite plant and surface waters from the tailings basin exceed the site-specific health-based value (**HBV**) of 30 μg/L established by the MDH. Molybdenum levels dropped to below 10 μg/L for process water reacting with tailings (see Table 7 and Figures 11a and 11b). If higher pH levels exist in the groundwater flowing through the Biwabik Iron Formation, molybdenum would not be expected to precipitate out of the water during transport. Dilution, therefore, is the primary method by which molybdenum concentrations will decrease in the waters.

Unlike the natural waters, molybdenum in the process waters behaves similarly to arsenic. Although arsenic is adsorbed more readily onto iron oxide, molybdenum adsorption increases when lower pH levels are present during tailings water interaction (Berndt, 1998). However, molybdenum will tend to remain in solution outside the tailings basin if the pH of the natural groundwater is higher.

The levels of molybdenum in water from the seep and monitoring wells are considered representative of that which will enter the Biwabik Iron Formation from the Minorca Pit. To reflect that assumption, a molybdenum level of 10 μg/L is used in the health risk assessment. In contrast, a level of 50 μg/L is also used. During the active phases of tailings disposal, process water is pumped into the pit with the tailings. The majority of the pit water is then pumped to the processing plant for reuse. For daily operation, the water remaining in the pit is assumed to react with the tailings resulting in lower levels of molybdenum. The 50 μg/L value is included to represent a situation where some of the process water does not have time to fully react with the tailings and is circuited into the fractured aquifer. This scenario is not expected to occur under normal conditions during deposition of the tailings, nor does it reflect what is expected after tailings disposal is completed. Therefore, the range proposed for the health risk assessment varies from 10 to 50 μg/L to reflect water that has not fully reacted with the tailings.

4.3.3.5 Organic Process Chemicals

Regulatory agencies have expressed concern regarding the presence and potential effect of process chemicals in the disposed tailings water. The chemicals used in the tailings disposal process are biodegradable and expected to break down quickly in the environment. Analyses conducted on water samples taken from the basin, seep, and monitoring wells were negative for surfactants, amines, and other organic constituents resulting from taconite processing and disposal. Additional analyses indicated that no organic chemicals of concern are initially present in the additives. This research indicates that chemicals added to waters during the processing of taconite ore do not persist in the tailings basin.

4.3.4 Qualitative Description of Groundwater Flow and Projected Levels of ECCs in the Missabe Mountain Pit

The assumptions and rationale used in the fate and transport analysis were discussed in Section 4.3.1. As noted in that section, maximum relative contributions to the Missabe Mountain Pit are estimated to range from 20 percent (reclaimed with grass cover) to 40 percent (prior to reclamation). The 40 percent value is considered a conservative default (i.e., worst-case scenario), since the Minorca Pit's contribution is calculated at < 10 percent if forest growth is successfully established on the tailings pile (John Adams, 1998, personal communication).

Although the potential for mixing of waters in the Missabe Mountain Pit is not known, some degree of it is assumed. Mixing of water layers will help to prevent higher concentrations of ECCs from forming in localized areas within the pit. The quality of the water leaving the Minorca Pit is not expected to change substantially over time. Based on analyses of the process waters, an increase in salinity is expected; however, bicarbonate will remain as the predominate anion in the groundwater.

Of the five ECCs, three are projected to remain in groundwater at levels of potential human health concern during migration through the Biwabik Iron Formation and into the Missabe Mountain Pit. These elements are: 1) fluoride modeled at 3 to 4.5 mg/L, 2) manganese modeled at 0.01 to 6 mg/L, and 3) molybdenum modeled at 10 to 50 μg/L. Arsenic and organic process chemicals are projected to be at levels far below concern (arsenic) or not present at all (organic process chemicals). Dilution is expected to occur when other sources of water migrating into the Missabe Mountain Pit are mixed. Assuming that 20 to 40 percent of the water flow into the Missabe Mountain Pit is from the Minorca Pit, a 5-fold and 2.5-fold **dilution factor** is estimated. The maximum expected values for all ECCs are displayed in Table 9.

4.4 Dose Response Assessment

In order to set safe levels of chemicals in drinking water, the MDH used a reference dose approach for chemicals that are not carcinogenic. This is a conservative approach that uses available toxicological information to estimate the amount of a chemical that may be safely consumed on a daily basis for a lifetime. The reference dose approach assumes there is a threshold level of the chemical below which no effects are experienced. Reference doses are calculated by using experimental data to first determine a level at which no or very low responses are seen. This level is then divided by uncertainty factors to account for such variables as individual sensitivity, data deficiencies, and extrapolations. Daily consumption of a chemical at

Table 9. Estimated concentrations of ECC's in the Missabe Mountain Pit (These values do not include the effects of oxidation and biologic processes that are expected to occur in the pit)

ECC	Range of Modeled or Predicted Concentrations of ECCs	Based on 20% contribution to the Missabe Mountain Pit 5-fold dilution factor	Based on 40% contribution to the Missabe Mountain Pit (worst case scenario) 2.5-fold dilution factor
Arsenic	< 1 - 8 µg/L	Less than 1 µg/L	Less than 1 µg/L
Fluoride	3 - 4.5 mg/L	0.6 - 0.9 mg/L	1.2 - 1.8 mg/L
Manganese	0.1 - 6 mg/L	0.02 - 1.2 mg/L	0.04 - 2.4 mg/L
Molybdenum	10-50 µg/L	2.0 - 10.0 µg/L	4.0 - 20.0 µg/L
Organic Compounds	Low to not detected	None	None

or below the calculated reference dose is presumed safe. Due to the conservative nature of the reference doses, consumption of a chemical at a higher level than the calculated reference dose will not necessarily be toxic. Less information, however, is available to estimate safety. Once a reference dose is obtained, it may be used to calculate the quantity of the particular chemical that can safely be consumed through drinking water.

Reference Dose (**RfD**) = No Observed Effect Level ÷ Uncertainty Factors

No thresholds are assumed for cancer causing compounds. In the case of carcinogens, the assumption is that exposure to any amount of carcinogenic materials will cause some increased risk of developing cancer in an individual's lifetime. For the establishment of drinking water values by MDH, an increased risk of 1 in 100,000 is assumed to be negligible.

4.4.1 Arsenic

Arsenic is a metal that has long been considered toxic when consumed. Chronic ingestion of arsenic causes hyperpigmentation of the skin, keratosis and adversely affects the peripheral circulation. Chronic exposure to inorganic arsenic compounds may lead to neurotoxicity of both the peripheral and central nervous systems. Arsenic has also been shown to be carcinogenic in humans.

Arsenic levels in the tailings basin are elevated above background levels, but fall below the current United States Environmental Protection Agency (USEPA) developed drinking water standard or maximum contaminant level (**MCL**) of 50 μg/L. However, the USEPA recently received a mandate to review the available toxicologic data and develop a new MCL for arsenic by the year 2000. Projections for the new MCL for arsenic range from 2 to 20 µg/L, but the final level is likely to fall between 2 and 5 µg/L. The concentrations of arsenic currently reported for the tailings basin exceed the projected MCL. Because arsenic levels may exceed the new MCL when promulgated, the MDH is proceeding conservatively by assuming that the new MCL will be set at 2 μg/L.

4.4.2 Fluoride

The USEPA has established a primary drinking water standard (MCL) for fluoride of 4 mg/L that is based on the ability of fluoride to disrupt normal bone formation causing a crippling skeletal fluorosis when consumed on a chronic basis. A secondary, non-enforceable standard of 2 mg/L is based on the ability of fluoride to cause discoloration in children's teeth.

4.4.3 Manganese

The USEPA has recently established a safe consumption level for the general population of 10 milligrams per day (mg/day) [RfD = 0.14 milligrams per kilogram per day (mg/kg/day)] for chronic consumption of manganese from all sources. However, intakes over this reference dose are not necessarily toxic. In fact, many individuals may consume a diet containing more than 10 mg/day without cause for concern. In general, an individual consumes 2 to 5 mg/day in their diet suggesting that 5 to 8 mg of manganese per day could be safely consumed from the drinking water. Assuming an average consumption level of two liters of water per day implies that 1 to 4 mg/L would be a safe drinking water level. However, because of questions concerning health effects of lifetime consumption of drinking water containing 2 mg/L manganese, differences in absorption of manganese for infants and neonates, and the fact that manganese is more rapidly absorbed by fasting individuals, the USEPA has recommended the use of a modifying factor of 3 when considering drinking water as the source of manganese. To calculate a site specific health based value (**HBV**) for manganese, MDH followed the advice of the USEPA and applied a modifying factor of 3 for the RfD. Using the USEPA prescribed relative source contribution of 0.8 indicates that 2.6 mg of manganese may be safely consumed from a drinking water source. Since an average adult consumes 2 liters of water per day, levels of 1.3 mg/L manganese in drinking water may be consumed without concern for health effects.

Further qualifications of this risk estimate are needed since **homeostatic** mechanisms to regulate uptake and elimination of manganese exist. The implications of this qualification are that a wide range of dietary values of manganese may be considered safe.

4.4.4 Molybdenum

Molybdenum is an essential element that acts as a co-factor for the enzymes xanthine oxidase and aldehyde oxidase. The average daily human intake in food is 350 μg and approximately one-third of all freshwater supplies contain molybdenum. Prolonged consumption of high levels of molybdenum (10 to 15 mg/day) may result in an increase in serum uric acid concentrations that, in turn, can cause gout-like symptoms such as pain, swelling, inflamation, and deformities of the joints. The reference dose for molybdenum, based on its effects on serum uric acid levels, is 0.14 μg/kg/day. This reference dose was used to calculate a site-specific HBV of 30 μg/L, a water concentration of molybdenum that can safely be consumed on a daily basis for a lifetime.

4.4.5 Organic Process Chemicals

A number of organic chemicals are added to process water during the production of taconite pellets. In addition, organic materials such as "oil and grease" from machinery may be inadvertently added to the process water. Analyses of organic compounds indicated the presence of low levels of "oil and grease" (1 mg/L). All other organic compounds fell below the limits of detection. All attempts to detect process organic chemicals in water samples taken from the pit were unsuccessful indicating that these chemicals are rapidly degraded once they enter the environment. In addition, limited toxicological information indicates that adverse effects should not be expected from the presence of low concentrations of these materials in the pit.

The data set for the toxicology of commercially used organic process chemicals is limited. Much of the available data are based on short-term, high-concentration occupational exposures to a particular chemical. In addition, the identities of many of the components of the mixtures of process chemicals are either unknown or classified as proprietary. The major concern from a risk assessment standpoint is that most of these organics are added as poorly defined mixtures and limited amounts of toxicological data available exist for mixtures. For the purposes of this risk assessment, the available toxicological literature was surveyed for information about classes of organics and, in the cases where specific toxicological data were not available, conservative HBVs based on **surrogate** compounds were developed (see Table 10).

4.4.5.1 HBVs for Chemicals with Specific Data

Specific data for several process chemicals were available. Data for 2-ethylhexanol indicate a safe consumption level of 1.1 mg/L while those for butyric acid suggest that 0.35 mg/L can be safely consumed. Both of these chemicals are added in maximum amounts of 0.012 mg/L. Trifluoromethane, found at a concentration of 1 µg/L in tailings basin water, has a safe consumption level of 2,000 µg/L.

4.4.5.2 HBVs for Chemicals Developed using Surrogate Values

4.4.5.2.1 Petroleum Distillates

Petroleum distillates are mixtures of numerous compounds used in a number of industrial settings. A number of reference doses, based on the chain lengths of principle components, have been developed for this group of organics (Total Petroleum Hydrocarbon Criteria Working Group, 1996). For this risk assessment, MDH has selected the most restrictive reference dose (0.1 mg/kg/day) for total petroleum hydrocarbons as a surrogate for the group as a whole and estimated a safe consumption level of 0.7 mg/L for drinking water.

4.4.5.2.2 Polyglycol Compounds

Few data are available for the chronic toxicity of the polyglycol compounds that are used as anti-

Table 10. Site Specific values for organic components of tailings basin

Chemical or Chemical Class	Site Specific Health Based Value (mg/L)
2 - ethylhexanol	1.1
Butyric acid	0.35
Total petroleum hydrocarbons	0.7
Polyglycols	3.5
Medium and Long Chain Alcohols	0.7
Esters	ND*
Aldehydes	1.4
Aliphatic Amines	3.5
Polydimethyldiallyl-ammonium chloride	1.4
Acrylamide/Acrylate Polymers	3,500

* Not determined

foaming agents. However, feeding studies on rats and dogs indicate that polyglycols are not very toxic when administered on a long-term basis (Gingell et al., 1994). For example, in a two-year feeding study a dose of 500 mg/kg/day caused only a slight decrease in growth in the treated animals. Using these data and a conservative uncertainty factor of 1,000, a safe consumption level of 3.5 mg/L of drinking water was estimated.

4.4.5.2.3 Medium- and Long-Chain Length Alcohols

Medium- and long-chain length alcohols are mildly toxic on a chronic oral basis (Lington and Bevin, 1994). The lowest observed adverse effect was at 100 mg/kg/day for any of the alcohols examined. Using this number as a default and a conservative uncertainty factor of 1,000 equates to a safe consumption estimate of 0.7 mg/L for drinking water. Alcohols are added to the process water in concentrations up to about 0.08 mg/L.

4.4.5.2.4 Esters

Nearly all common aliphatic and aromatic esters are considered biologically inert (Bisesi, Patty's, 1994). In general, it has been impractical to determine toxicity values for them since they are rapidly hydrolyzed in the body and excreted. Esters are added to the process waters in concentrations of up to 0.08 mg/L.

4.4.5.2.5 Aldehydes

Aldehydes, particularly higher molecular weight forms, have a low toxicity level (Bisesi, 1994). However, using the lowest available reference dose of 0.2 mg/kg/day as a surrogate, a safe drinking water value for aldehydes is estimated at 1.4 mg/L. Aldehydes are added to the process water in concentrations up to approximately 0.08 mg/L.

4.4.5.2.6 Aliphatic Amines

Aliphatic amines are highly fat soluble and are highly alkaline. They are used extensively in industrial settings, but tend to break down very rapidly in the environment (Benya and Harrison, 1994). Because aliphatic and alicyclic amines are highly alkaline, they tend to be acute irritants when in contact with the skin. Most aliphatic amines are characterized by distinctly unpleasant odors and for the most part become toxic through inhalation exposure. Some questions exist regarding the conversion of these compounds to nitrosamines and the subsequent carcinogenicity resulting from this conversion. The limited information regarding the toxicological properties of this group of compounds tends to deal with respiratory exposures. Higher molecular weight alkyamines such as the isododecyloxypropylaminopropylamine used in the taconite process tend to have lower chronic toxicities than the shorter chained amines. A two-year feeding study where rats received octadecylamine indicated a no observed adverse effect level (**NOAEL**) of 500 mg/kg/day. Using a conservative uncertainty factor of 1,000 gives a reference dose of 0.5 mg/kg/day suggesting a safe consumption level of 3.5 mg/L in the drinking water. Little information is available for flocculents such as polydimethylallylamonium chloride. Toxicity for the allylamine group tends to decrease as the length of the molecule is increased. Using toxicity data for diallyamine should, therefore, provide a conservative surrogate for a long-chained molecule. Long-term inhalation studies in rats yielded a NOAEL of 200 mg/kg/day. Using an uncertainty factor of 1,000 yields a reference dose of 0.2 mg/kg/day and, consequently, a safe drinking water consumption level of 1.4 mg/L.

4.4.5.2.7 Acrylamide/Acrylate Polymers

Acrylamide/acrylate polymers have a low toxicity level (Harris and Sarvadi, 1994). Feeding mixtures of 1 percent polyacrylamide/polyacrylate polymers to rats and 5 to 6 percent mixtures to dogs for two years caused no ill effects. Using the 1 percent dietary level as the basis for estimating a NOAEL (assuming a consumption rate of 5 percent of the body weight per day) and an uncertainty factor of 1,000 gives a reference dose of 0.5 grams per kilogram per day (g/kg/day). These values equate to a safe drinking water concentration of 3.5 grams per liter (g/L). Unlike the other chemicals used in the taconite process, these polymers are resistant to degradation and are therefore very stable in the environment. Little chance exists, then, for breakdown into their monomeric forms shown to cause skin irritation in occupational settings. See Table 10 for site-specific HBVs.

4.5 Risk Characterization: Characterization of Human Health Risk from the ISMC's Proposed Taconite Tailing Project

A health risk assessment was conducted to determine whether ISMC's proposal to dispose of taconite tailings into the Minorca Pit would pose an unacceptable risk to public health. To accomplish this, exposure levels of the ECCs were estimated and compared to safe exposure levels established by current state HBVs and federal standards. For arsenic, the safe exposure levels were estimated by using the current USEPA projected values.

The fate and transport analysis determined that three ECCs (fluoride, manganese, and molybdenum) had the potential to successfully migrate from the Minorca Pit to the Missabe Mountain Pit at levels of public health concern. As was noted in Sections 4.4.1 and 4.4.5, neither arsenic nor the organic process chemicals will be transported via groundwater to the city of Virginia's drinking water supply.

The safe consumption level for fluoride is based on the MCL developed by the USEPA. The HBVs for manganese and molybdenum were developed by the MDH using data from the USEPA Integrated Risk Information System (IRIS) database. HBVs are the concentration of chemicals that may be safely consumed on a daily basis for a lifetime. These numbers are developed using conservative techniques. The more uncertainty that exists, the more conservative the resultant values. This conservative approach ensures an adequate level of safety, and is necessary to allow for a range of uncertainties in the numbers. It also ensures that, despite extrapolations, the safe exposure levels developed are protective. However, a conservative approach may also result in a situation where consumption of a chemical at levels above its HBV may not be harmful. These values are presented in Table 11. Also presented in Table 11 are the projected worst-case scenario values for concentrations of these chemicals in the Minorca Pit and worst-case projections for the amounts of each chemical that might eventually reach the Missabe Mountain Pit. Hydrologic monitoring (see Section 2.4.2) indicated that the predicted maximum worst-case contribution of the water from the Minorca Pit to the Missabe Mountain Pit is 40 percent. This implies that any chemical in the water from the Minorca will be diluted by a factor of at least 2.5 times before it enters the Missabe Mountain Pit. As the tailings in the Minorca Pit are vegetated, the contribution of the Minorca Pit to the Missabe Mountain Pit will decrease to a maximum of 20 percent. In other words, a 5-fold dilution of ECCs in water flowing from the Minorca Pit is expected.

Arsenic is expected to precipitate out of the water when it is exposed to iron oxides on the tailings and fracture surfaces in the Biwabik Iron Formation. If values are elevated to maximum levels found in the monitoring wells (8 μg/L), the final values in the Missabe Mountain Pit are predicted to be low. Values of arsenic based on a 5-fold and 2.5-fold dilution are expected to be below the 2 μg/L projected drinking water standard.

Hydrogeochemical modeling predicts that the maximum fluoride concentration in the Missabe Mountain Pit would be 900 µg/L with a 5-fold dilution and 1,800 µg/L with a 2.5 fold dilution. These values are well below the primary MCL of 4,000 µg/L and, therefore, will not pose a significant risk to human health.

The MDH has calculated a site-specific HBV for manganese of 1,300 mg/L (Table 11). Based on hydrogeochemical modeling, the maximum possible manganese concentrations in the Missabe Mountain Pit are 1,200 μg/L with a 5-fold dilution and 2,400 μg/L with the worst-case situation of a 2.5-fold dilution. The potential manganese concentrations in the Missabe Mountain Pit would, therefore, be below the HBV of 1,300 μg/L for the 5-fold dilution, but exceed this value with the 2.5-fold dilution scenario. Such a worst case predicted value would present a long-term concern for public health. However, it is anticipated that the physical and biological processes that naturally limit the levels of dissolved manganese in surface waters will keep manganese concentrations low in the oxygenated portion of the Missabe Mountain Pit (estimated as the upper 144 feet). The levels of manganese expected to occur in the Missabe Mountain Pit will not pose a health risk to the citizens of the city of Virginia.

The concentration of molybdenum in the tailings basin is 50 µg/L (Table 11). This is assumed to be the highest concentration of molybdenum that could leave the pit under normal circumstances. Since the projected concentrations (10 µg/L at a 5-fold dilution or 20 µg/L at a 2.5-fold dilution) are lower than the MDH-derived HBV of 30 µg/L, molybdenum levels in drinking water from the Missabe Mountain Pit also should not pose a health risk to the citizens of the city of Virginia.

Organic process chemicals were not found in analyses of process water samples. Since chemical additives were not detected in the process waters within and around the tailings basin, no health risk is expected from the organic process chemicals added during taconite ore processing.

4.6 Uncertainties of the Health Risk Assessment

Uncertainties are associated with the assumptions or methods used in developing the health risk assessment. Determining the uncertainties is an important aspect of a health risk assessment since it can have a significant effect on the outcome. See Appendix G for a summary of the uncertainties considered.

The most important uncertainties in this assessment lie in the fate and transport of the ECCs through the aquifer. The fate and transport of the ECCs are determined by the characteristics of the rocks and water flow through the aquifer as well as the geochemistry of the water in the tailings, aquifer, and pit. In addition, the physical and chemical characteristics of water in the receiving pit (i.e., Missabe Mountain Pit) are also important. Significant uncertainties are associated with the lack of information regarding the geology and hydrology of the site. Apart

Table 11. Estimated concentrations of ECCs and Drinking Water Standards for ECCs (These values do not include the effects of oxidation and biologic processes that are expected to occur in the pit)

ECC	Drinking Water Standard * (μg/L)	Projected Maximum Concentrations of ECC in Groundwater leaving the Minorca Pit without dilution (μg/L)	Projected Maximum Concentrations of ECC in the Missabe Mountain Pit with a 5-fold dilution (20% contribution) (μg/L)	Projected Maximum Concentrations of ECC in the Missabe Mountain Pit with a 2.5-fold dilution (40% contribution) (μg/L)
Arsenic	2	8	Less than 1	Less than 1
Fluoride	4,000	4,500	900	1,800
Manganese	1,300	See below	See below	See below
Projected concentration based on modeling and monitoring wells - worst case scenario		6,000	1,200	2,400
Projected concentration based on tailings basin data.		100	20	40
Molybdenum	30	50	10	20
Organic Process Chemicals	See Table 10	Not detected	None	None

* The drinking water standard for fluoride is a MCL developed by the U.S. EPA. The standards for molybdenum and manganese are health based values developed by MDH from information taken from the U.S. EPA's IRIS database (see Appendix B, Table 3).

from MDNR research, minimal information is available on the specific hydrologic characteristics of the rock separating the Minorca Pit and Missabe Mountain Pit. Uncertainty is also associated with the geochemical data and modeling. The quality of the geochemical data describing process water is acceptable to the MDH, even though the number of analyses was limited.

Although temporal trends were not specifically examined, samples were taken over a 1.5-year period. Given the available data, it is not possible to project variations in levels of different ECCs over a longer period of time. This may cause an error in estimation of the concentrations of ECCs leaving the Minorca Pit. Due to assumptions made, reliance on available data, and time constraints, uncertainty may also exist in the hydrogeochemical models created.

With the natural waters, samples were taken at each of the different pits in the study area. Yet, the number of full analyses is limited to 1-2 samples per location. The samples collected from natural waters were not filtered, and therefore, the elevated levels of some constituents may be attributed to dissolution of solid material in the water by acid added for sample preservation.

The limnologic data also contains significant uncertainties. The health risk assessment assumes that the water within the Missabe Mountain Pit lake will mix during the year. The assumption is based on the characteristics of lake water to mix or turn over in spring and fall with thermal layers forming during the summer and winter months. The layers prevent mixing and oxygenation of water, with anoxic conditions possibly forming at the bottom of the water body. Four oxygen concentration profiles taken at depths of 98 and 144 feet in the Missabe Mountain Pit were available. Quantitative information over a longer time period was not available. Also, the total depth of the water in the Missabe Mountain Pit is estimated at 245 feet. Profiles taken in the pit did not extend deeper than 144 feet. Changes in dissolved oxygen and other characteristics of the water at depths greater than 144 feet were not mapped.

Although the quality of the hydrologic data is of most concern, data quality for the human health characterization is also important. Uncertainties associated with toxicological data sets also exist and the scientific evidence needed for determining risk is often inconclusive. Available toxicological data are frequently developed in non-human species making it difficult to compare these data to humans. Intraspecies variation also plays a role in the uncertainty of reactions to toxic materials. Likewise, demographic characteristics such as age, nutritional status, and disease state can cause variations.

In addition to biological uncertainty, uncertainties exist in the data sets themselves. Data sets may be incomplete, may have errors in measurement or recording data, or may be interpreted erroneously. All of these factors can contribute to the uncertainties in the statistical strength of the analysis.

The above-mentioned uncertainties govern the use of a conservative approach to ensure that consumption levels are protective. Assumptions must err, then, in the direction of more conservative values. A consequence of this approach is often a number that is overprotective for the population.

5.0 Conclusions and Recommendations

Purpose: *Present conclusions of the health risk assessment and recommendations for the proposed project, if implemented.*

Based on the outcome of this health risk assessment, the MDH concludes that implementation of the proposed project would pose negligible risk to the population of the city of Virginia. However, certain steps should be taken to maintain the quality of the water both during and after tailings disposal. The proposed steps are as follows:

- Install monitoring wells and/or monitoring sites between the Minorca Pit and Missabe Mountain Pit to determine changes in water quality over time. When water begins to flow from the Minorca Pit, the ability to detect migration of potential contaminants from the Minorca Pit to the Missabe Mountain Pit is imperative.

- Continue quarterly monitoring of natural water sites, including the adjacent pits, and available process water sites for ECCs and changes in water geochemistry. The data collected to date established a baseline for natural waters in the study area. Periodic analysis of the waters will pinpoint any changes in water quality that may occur from the proposed action. Increasing the baseline database for the natural waters will allow for detection of the natural variation in the water quality. The MDH recommends the determination of levels of potential tracers, specifically chloride, bromide, fluoride, and isotopes (O^{18} and deuterium) over time. Projections indicate that stable isotope signatures will become more fractionated over time making it usable as a tracer.

- Conduct periodic limnologic profiles of the Missabe Mountain Pit for its entire depth (estimated at 245 meters) to ascertain the level of anoxia, if any, and the degree of mixing that occurs in the pit. The profile should include determining temperature, pH, Eh, dissolved oxygen, and other parameters as required.

- Monitor quality and levels of ECCs in the recycled water. Determine if there is a significant buildup in concentrations of ECCs in the recycled water that may subsequently lead to more enriched waters entering the Biwabik Iron Formation from the Minorca Pit.

- Prevent disposal of organic compounds or other material that may change the geochemistry within the tailings. The reclamation plan should not include swamp- or wetland-type vegetation unless it is proven such environments will not cause development of greater reducing conditions within and adjacent to the tailings. Research has shown the mobility of some of the ECCs will increase with decreasing pH and changes in water geochemistry. Arsenic, manganese, and iron may become more enriched in the migrating water if the waters in contact with the tailings become more reducing.

- Develop a **Source Water Protection Program** for the Missabe Mountain Pit. The pit receives water from multiple sources and protection of the city of Virginia's drinking water requires monitoring and control of these sources of water unrelated to the proposed activity. The city should establish a protection program for the Missabe Mountain Pit to protect it from the effects of multiple development in the area.

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Appendix A.

Units of Measure

Glossary of Terms

UNIT OF MEASURE ABBREVIATIONS

ft: feet

gpm: gallons per minute

µg/L: micrograms per liter of water.

mg/L: milligrams per liter of water.

mV: millivolts. Represents one-one thousandth of a volt.

mg/day: milligrams per day. Milligram is one-one thousandth of a gram.

mg/kg/day: milligrams per kilogram (body weight) per day.

gm/day: grams per day.

GLOSSARY OF TERMS

Absorption: The process of taking something in through pores or openings. Some materials may be absorbed through the skin.

Adsorption: The accumulation of elements or compounds dissolved in water on the surface of a solid material, specifically the surface of a particle of tailings or a fracture in the Biwabik Formation.

Desorption: The process of removing an element or compound from the surface of a solid material. Desorption of elements or compounds may occur if the chemistry of the water changes significantly.

Dilution factor: Water from the Minorca Pit is expected to mix with other waters in the Missabe Mountain Pit. With mixing, concentrations of ECCs in the Missabe Mountain Pit will be lower than those found in water from the Minorca Pit. The amount of dilution will depend on the amount of water entering the Missabe Mountain Pit from the Minorca Pit. With 40% of the water coming from the Minorca Pit, the ECCs will be decreased by a factor of 2.5 (Concentration of ECC divided by 2.5). With 20% coming from the Minorca Pit, the ECCs will be decreased by a factor of 5 (Concentration of ECC divided by 5).

Drift: A horizontal or nearly horizontal passageway in a mine.

ECC: Elements or compounds of concern. Elements or compounds in the water that are elevated by taconite processing or disposal to levels above present or future drinking water standards. Also, elements or compounds that are elevated above levels in natural waters that may be high enough to cause a potential health risk.

Eh: Oxidation-reduction (redox) potential of a system. The actual value of Eh (in millivolts) has little meaning, but expresses the tendency of a system to accept or donate electrons. Many metal and organic contaminants found in groundwater are sensitive to redox reactions. Depending on the contaminant, a decrease or increase in redox potential may increase or decrease chemical mobility in the water or may increase or decrease the toxicity of an element or chemical. The value of Eh, expressed in millivolts, is a general indicator of the intensity of oxidizing or reducing conditions within a system (MPCA, 1998b, p 74).

EIS: Environmental Impact Statement. Requirement of Minnesota Statute Section 116.0717 for tailings deposition into mined-out taconite pits. A detailed written statement that discusses the potential short-term and long-term environmental impact of a proposed action.

Health-Based Value: An exposure value that utilizes a reference dose (RfD) or cancer potency slope to calculate a concentration of a groundwater contaminant that can be safely consumed for a lifetime. A 70 kg person with a drinking water intake of 2 liters per day and a relative source contribution of the chemical from drinking water of 20% was assumed in the calculations (From MDH, 1997). The HBVs have not undergone a formal rule-making process and have a variable degree of uncertainty associated with them.

Health Risk Assessment. An assessment conducted to determine possible risk to the health of a human population if a proposed action is implemented.

Homeostatic: Relates to the processes through which a body's equilibrium is maintained.

HRL: Health Risk Limit. A HRL is the concentration of a groundwater contaminant, or a mixture of contaminants, that can be safely consumed daily for a lifetime. Health Risk Limits have gone through a formal rule-making process and uncertainty is estimated.**

Hydraulic Conductivity: A measure of how easily water will travel down-gradient through an aquifer.

Limnologic: Pertaining to the study of life in and the characteristic of fresh water environments, especially lakes and ponds.

Mesabi Iron Range: Also referred to as the Iron Range, the Mesabi Iron Range is a band of iron-bearing rock formation present in the northern part of Minnesota. The Iron Range extends from east of Hoyt Lakes in eastern St. Louis County to Grand Rapids in Itasca County.

Metasedimentary: A general term for rocks that were originally deposited as sediments that, through geologic time, formed sedimentary rocks. These rocks were then altered, over time, by pressure and heat.

Mobility: The ability of an element or compound to move from place to place. If an element or compound is mobile, it is a part of the water and capable of moving within the aquifer.

Natural Water: 'Natural water' is defined as water samples taken from the pits, water wells, and Sauntry Creek. Also included in the natural water category are samples from the MPCA's Ground Water Monitoring and Assessment Program (GWMAP) database (See Appendix A1).

NOAEL: No observed adverse effect level.

NPDES/SDS permit: National Pollution Discharge Elimination System and the Minnesota State Disposal System permits cover discharges into surface waters. The permits regulate the quality of water allowed to be released into surface waters and groundwater from a facility, as well as establish appropriate monitoring and operational requirements for the facility.

Ore Processing: Taconite ore is first crushed dry, then ground with water. Iron-bearing mineral is separated from the ground ore using magnetic separation. The remaining ore is re-ground and is again subjected to magnetic separation to remove the iron. Small amounts of organic process chemicals are added as collectors, frothers, defrothers and flocculents in a floatation process.

Oxidized: A substance combines with oxygen which makes it into an oxide. In the study area, the iron minerals in the taconite ore, in places, have been altered to an oxidized form (e.g. hematite). The oxidized iron-bearing material is called natural iron ore in the study area.

pH: The acidity of substances (hydrogen ion activity) is measured by the pH scale of zero to fourteen. Water with a pH of approximately 7 is considered neutral. If the water has a pH greater than 7, the water has a smaller concentration of hydrogen ions and is considered 'alkaline'. The higher the value of pH, the more alkaline the water. If the water has a pH less than 7, the water has a greater concentration of hydrogen ions and is considered 'acid'. The lower the value of pH, the more acid the water. Pure rain water is slightly acidic with a pH of approximately 5.6. pH is reported in Standard Units (SU). Standard Units are defined as the negative logarithm of the hydrogen ion concentration. A neutral solution has 10^{-7} moles of hydrogen per liter of solution. A basic solution would have a lower concentration of hydrogen. with a pH of 9 containing 10^{-9} moles of hydrogen per liter of solution. An acidic solution would have a higher concentration of hydrogen with a pH of 4 containing 10^{-4} moles of hydrogen per liter of solution.

Process Water: Defined as water samples that were in contact with taconite tailings. Process water includes water from the tailings processing plant, the tailings basin, monitoring wells below the basin, a seep at the north end of the basin, and the laboratory column experiments conducted by U of M.

Reducing conditions: Water bodies with reducing conditions usually have a lower pH and Eh. In a reducing environment, dissolved oxygen is not present in large amounts , sulfates are reduced, and hydrogen sulfide and other gases may be generated.

RfD: Reference dose is the amount of a chemical that is without harm when consumed on a daily basis for a lifetime. The units are in milligrams per kilogram body weight per day (mg/kg-day).

Shaft: A long narrow vertical (or near vertical) passage sunk into the earth during underground mining of ore.

Source Water Protection Program: The 1996 Amendments to the Safe Drinking Water Act (SDWA) focused on protection of the nations drinking water supply. Under the SDWA, the states are required to develop a comprehensive program to identify the areas that supply public tap water, inventory contaminants and assess water system susceptibility to contamination, and inform the public of the results. After the assessments are completed, the EPA encourages implementation of source water protection programs to protect local drinking water supplies. The program requires states to provide for opportunities for community involvement in the decision-making process.

Surrogate: A substitute. A substance that is used in place of another. For the human health risk assessment, the toxicologic information for a related compound is used when no information is available for the specific compound.

Taconite Tailings: Taconite tailings are the remaining waste products generated from processing iron taconite ore. During processing, iron is removed from the ground ore leaving rock particles of different sizes. The ground rock particles are made up of silicates, iron oxides, carbonates and traces of other minerals. The particle size of the tailings can range from very fine (similar to talc) to coarse. The coarse tailings have been used as road aggregate. There are no known uses for the fine tailings and these must be disposed of in an appropriate manner.

Tracer Tests: A tracer is a distinguishable constituent in the groundwater that can be measured at different points in the aquifer. Tracer tests are used to measure different hydrogeologic characteristics of an aquifer and to identify possible sources, velocity, and direction of movement of a contaminant.

Tritium: Tritium (^3H) is a radioactive isotope of hydrogen that is naturally present at low levels in the earth's atmosphere. Levels of tritium in the earth's atmosphere increased significantly following atmospheric atomic weapons testing from 1952 to the mid-1960's. During that time period, groundwater sources were being recharged by precipitation that contained elevated amounts of tritium. Through the years, scientists have kept track of the amount of tritium in precipitation in different parts of the world. By comparing results from groundwater samples to known tritium levels through time, scientist are able to approximate the age of the groundwater. The units for tritium are Tritium Units (TU). A tritium unit is the ratio of tritium atoms to hydrogen atoms ($^3H/^1H$) and represents one tritium atom per 10^{18} hydrogen atoms.

Uncertainty: A qualitative or quantitative estimate of how much an observed or calculated value or condition may vary from the true value or condition that exists or will occur. It includes what is not known or established on a certain subject. It also takes into account the potential for change and variability in areas such as water quality or groundwater flow over time.

Virginia Horn: During the history of the earth, thick layers of rock in the crust were folded by forces in the earth. One such fold is the Virginia Horn. The Virginia Horn is described as a Z-shaped fold which is evident when viewing the Biwabik Formation outcrop in the Virginia – Gilbert area.

Water Balance Study: In a water balance study, the input of water into a mine pit (including rain, groundwater, surface runoff, stream discharge, and pumping) are balanced with the water coming out of the pit (including evaporation, transpiration, pumping, other surface water discharge). The study focuses on changes in the pit's water balance as result of an activity.

Appendix B

Table 1: General listing of geologic and hydrologic data sources used in preparation of the health risk assessment

Table 2: General listing of water chemistry data sources used in preparation of the health risk assessment

Table 3: General listing of toxicologic data sources used in preparation of the health risk assessment

Table 1: General listing of geologic and hydrologic data sources used in preparation of the health risk assessment

Report/ Data Source	Prepared by/Date
Results of hydrologic and water balance research conducted by the DNR, Grand Rapids, MN. (Ongoing)	John Adams, 1998, personal communication. Ongoing DNR research.
Limnologic information on different pits in study area from 1992 and 1996.	Uof M and City of Virginia, 1998.
Geologic Map of the Mesabi Iron Range, Minnesota	David G. Meineke and others, 1993.
Water Resources of the St. Louis River Watershed, Northeastern Minnesota	G.F. Lindholm and others, U.S.G.S. Hydrologic Atlas HA-586, 1979.
Geology and Ground-Water Resources of the Grand Rapids Area, North -Central Minnesota.	Edward L. Oakes, U.S.G.S. Hydrologic Investigations Atlas HA-322, 1970
Hydrology, Water Quality, and Simulation of Ground-water Flow at a Taconite-tailings Basin near Keewatin, Minnesota.	Charles F. Myette, U.S. G. S. Water-Resources Investigations Report 88-4230, 1991.

Table 2: General listing of water chemistry data sources used in preparation of the health risk assessment.

Report / Data Source	Prepared by / Date
Minorca Mine Pit Tailings Disposal Surface and Ground Water Impacts. Phase I and Phase II Reports	Prepared for Inland Steel Mining Co. by HDR Engineering, Inc. January and May 1997.
Chemistry of Water Associated with Taconite Processing and Tailings Reactions in the Mesabi Iron Range District, NE Minnesota.	Dr. Michael Berndt (Uof M) and Kim Lapakko (DNR), 1997.
Computer Simulations of As, Mo, Mn, and F Mobility During In-Pit Disposal of Taconite Tailings in the Minorca Pit, Virginia, Minnesota	Dr. Michael Berndt (Uof M) , January, 1998.
Analysis of Water Isotopic Data from Virginia, Minnesota Area	Prepared for HDR Engineering, Inc. by Scott C. Alexander and E. Calvin Alexander, Jr. (Uof M), May, 1997.
Results of laboratory column experiments being conducted at DNR , Hibbing Office.	MDNR and UofM personnel. Ongoing
Groundwater quality data from the Ground Water Monitoring and Assessment Program (GWMAP) database.	Monitoring wells within grid from T57-59N, R7-26W. Received from MPCA, September, 1997.
Limnologic data for mine pits in the area, specifically the Missabe Mountain pit.	Received from HDR Engineering Inc. and the City of Virginia.
General water quality data.	MDH, City of Virginia, Inland Steel Mining Co.

Table 3: General listing of toxicologic data sources used in preparation of the health risk assessment

Report/ Data Source	Prepared by/Date
Integrated Risk Information System (IRIS)	U.S. Environmental Protection Agency. No specific date.
Materials Safety Data Sheets	From different sources on Internet, predominately University of Utah. No specific date.
Patty's Industrial Hygiene and Toxicology, Volume II, 4th Edition Parts B,D, E	Edited by G.D. Clayton and F.E. Clayton. John Wiley and Sons, Inc. 1994
Total Petroleum Hydrocarbon Criteria Working Group.	Vol. 4, Amherst Scientific Publishing, 1996.

Appendix C.

General discussion of available limnologic information on the Missabe Mountain Pit..

Figure 1. Limnologic profile of the Missabe Mountain Pit taken in May, 1992

Figure 2. Limnologic profile from the northern part of the Missabe Mountain Pit

Figure 3. Limnologic profile from the west central part of the Missabe Mountain Pit

Figure 4. Limnologic profile from the southern part of the Missabe Mountain Pit.

Table 1. Data for limnologic profiles of the Missabe Mountain Pit.

General discussion of available limnologic information on the Missabe Mountain Pit.

Known information available on the Missabe Mountain Pit was taken from three sources. Two of these sources are unpublished information received from City of Virginia and HDR Engineering, Inc.. The third source is a MPCA document.

In-situ profile data on the Missabe Mountain Pit lake during May of 1992 was provided by the City of Virginia. The profiles were completed by NRRI scientists. The data were collected at depths of from 0 - 44 meters using a submersible monitor. In addition, chemical analyses were run on samples from the top, middle, and bottom of the lake. The data, as described by Craig Tikkanen and Rich Axler of NRRI (Letter to Mike Wiskow of the City of Virginia dated September 23d, 1992), indicated a moderately oligotrophic[1] condition with low chlorophyll (2.0 µg/L), moderate clarity (3.8 meter secchi depth), low total phosphorus (<10 µg/L) and total organic carbon (described as less than Lake Superior) levels. Inorganic-N levels were higher (nitrate+ammonia about 500 µg/L), but it was noted in the letter that a higher level is not uncommon for a deep mine pit lake. Levels of temperature and dissolved oxygen with depth are presented in Table 1 (this appendix). Percent oxygen saturation was determined using a saturation monogram and the temperature and field oxygen readings collected at the site, and is included in Table 1 and graphically presented in Figure 1 (this appendix). Levels of selected elements from chemical analyses for 0 and 40 meter depths are shown below.

Depth (meter)	Chloride (mg/L)	Sulfate (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Hardness (mg/L as carbonate)	Alkalinity (mg/L as carbonate)
1	14.7	58.0	9.0	2.8	27.2	51.0	239.5	186.9
40	15.2	65.6	9.3	2.9	30.5	56.3	266.2	206.2

In-situ profile data was also collected on the Missabe Mountain Pit lake as part of a general reconnaissance on mine pits in the study area (HDR Engineering, Inc., 1997, Personal Communication). A total of three profiles were conducted in the Missabe Mountain Pit. The profiles were collected in late September, 1996 at a time expected to represent a period of maximum layering in the pit lakes (Alexander and Alexander, 1997). The data in the profiles included depth, temperature, and dissolved oxygen. Graphical representations of the data for the three sites are given in Tables 2-4 (this appendix).
Percent oxygen saturation was determined using a saturation monogram and the temperature and field oxygen readings collected at the three sites, and is included in the appendices.

General information on the Missabe Mountain Pit was available from the MPCA (Minnesota Pollution Control Agency, 1998, p. 45). The lake is given a Tropic State Index of 37 which

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[1] An oligotrophic lake is relatively nutrient-poor, is clear and deep and has a hypolimnion (A layer of cooler and heavier water near the bottom of the lake) that is high in dissolved oxygen.

classifies it as oligotrophic. Summer mean water quality for the Missabe Mountain Pit is presented in the following table. Analyses from the NRRI data are also included for comparison.

Parameter	Summer Mean Water Quality (MPCA, 1998, p45)	NRRI water quality data from May 1992
Chlorophyll - a µg/L (C.L.)	1 (2 measurements)	2 (single measurement)
Clarity. Secchi depth meters (S.M.)	3.3 (2 measurements)	3.8 (single measurement)
Total Phosphorus µg/L (TU)	8 (2 measurements)	7 (at 1 m depth, single measurement) 5 (at 40 m depth, single measurement)

Figure 1. Limnologic profile of the Missabe Mountain Pit taken in May, 1992. Generated from data provided by the City of Virginia, 1998.

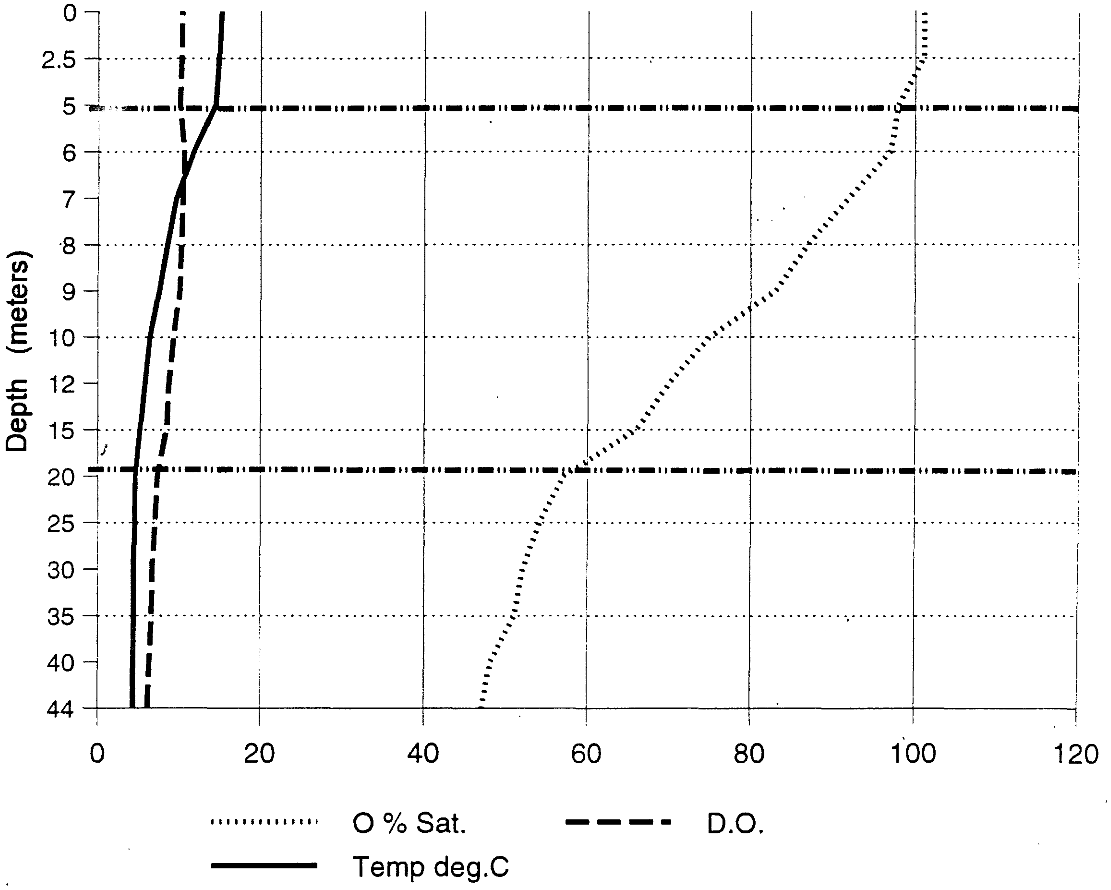


Figure 2. Limnologic profile from the northern part of the Missabe Mountain Pit. Profile taken in September of 1996. Generated from data collected by HDR Engineering, Inc., 1977

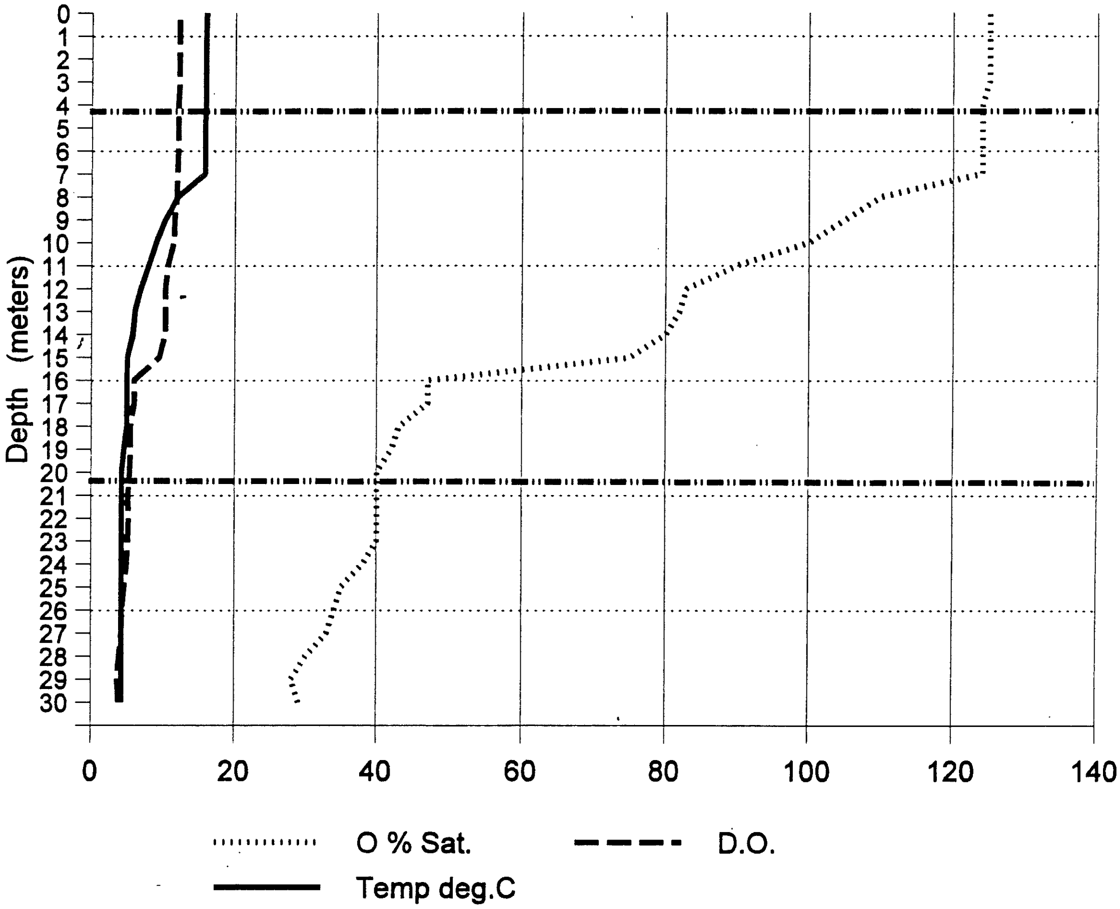


Figure 3. Limnologic profile from the west central part of the Missabe Mountain Pit. Profile taken in September of 1996. Generated from data collected by HDR Engineering, Inc., 1977

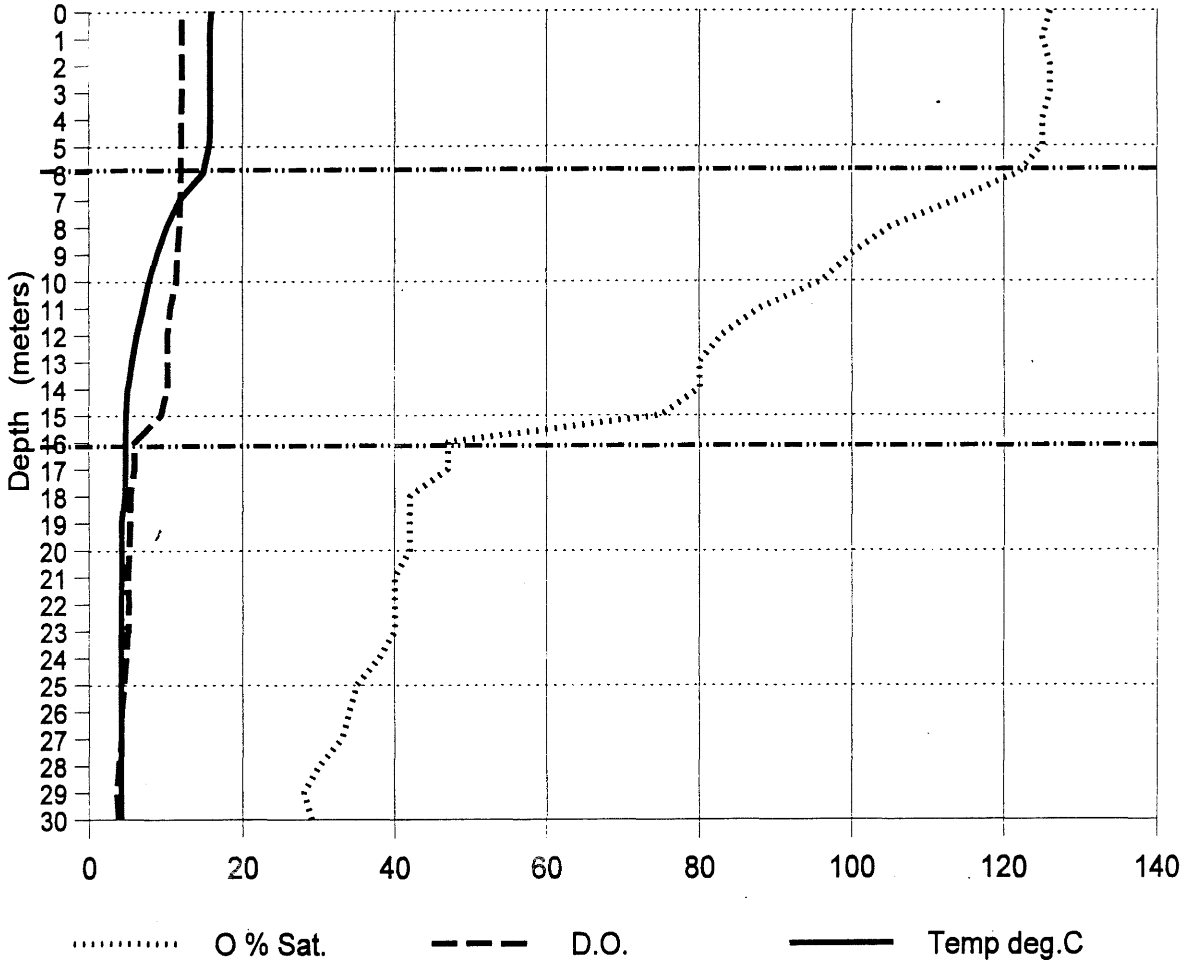


Figure 4. Limnologic profile from the southern part of the Missabe Mountain Pit. Profile taken in September of 1996. Generated from data collected by HDR Engineering, Inc., 1977.

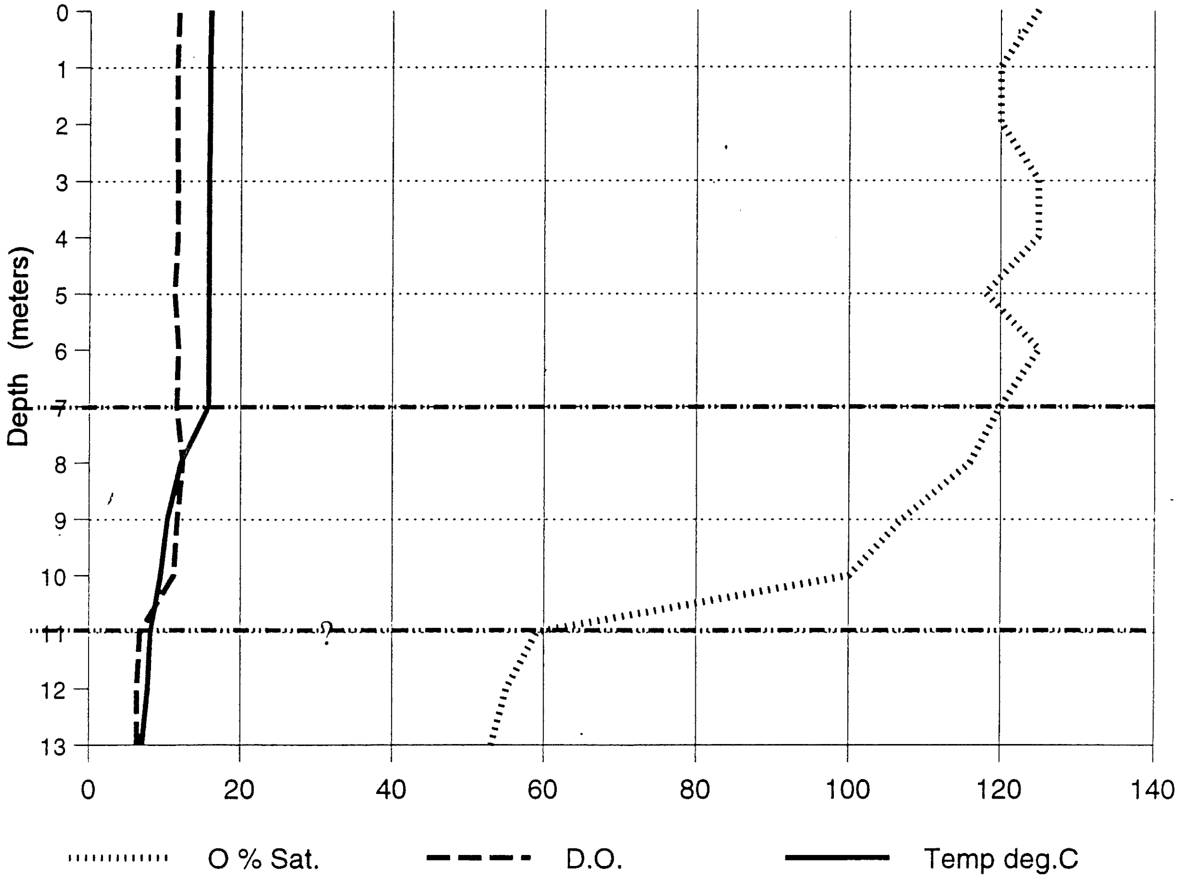


Table 1. Data for limnologic profiles of the Missabe Mountain Pit.

Mine Pit Name	Date	Depth m	Temp. C	D.O. ppm (field)	O Sat %
Missabi Mountain	A5-27-92				
		0	15.1	10.2	101
		2.5	14.8	10.2	100
		5	14.4	10	98
		6	11.7	10.5	97
		7	9.6	10.4	92
		8	8.5	10.2	87
		9	7.5	10	83
		10	6.4	9.3	75
		12	5.8	8.7	70
		15	5.2	8.4	66
		20	4.6	7.3	57
		25	4.5	7	54
		30	4.4	6.7	52
		35	4.4	6.6	51
		40	4.3	6.3	48
		44	4.3	6.1	47
		46 TD			

		Depth m	Temp. C	D.O. ppm (field)	O Sat %
Missabi Mountain	A9-26-96	0	15.9	12.1	125
A" North edge		1	15.8	12.1	125
		2	15.8	12.1	125
		3	15.8	12.1	125
		4	15.8	12	124
		5	15.7	12	124
		6	15.7	12	124
		7	15.7	12	124
		8	12	11.8	110
		9	10.2	11.5	105
		10	8.9	11.4	100
		11	7.9	10.6	90
		12	6.8	10.2	83
		13	6	10.2	82
		14	5.7	10.2	80
		15	5	9.4	75
		16	4.9	5.9	47
		17	4.9	5.9	47
		18	4.9	5.4	43
		19	4.5	5.4	42
		20	4.2	5.3	40
		21	4.2	5.1	40
		22	4.2	5.2	40

23	4.2	5.1	40
24	4.2	4.9	38
25	4.2	4.6	35
26	4.2	4.3	34
27	4.2	4.2	33
28	4.2	3.9	30
29	4.2	3.6	28
30	4.2	3.8	29

		Depth m	Temp. C	D.O. ppm (field)	O Sat %
Missabi Mountain	A9-26-96	0	15.9	12.1	126
Site B-Near PWS		1	15.8	12.1	126
		2	15.8	12.1	126
		3	15.8	12.1	126
		4	15.8	12	125
		5	15.7	12	125
		6	14.9	12	122
		7	11.8	11.9	114
		8	10.1	11.8	105
		9	8.8	11.5	100
		10	7.8	11.4	96
		11	7	10.6	88
		12	6.2	10.2	83
		13	5.6	10.2	80
		14	5.1	10.2	80
		15	4.9	9.4	75
		16	4.8	5.9	47
		17	4.8	5.9	47
		18	4.7	5.4	42
		19	4.3	5.4	42
		20	4.3	5.3	42
		21	4.3	5.1	40
		22	4.2	5.2	40
		23	4.2	5.1	40
		24	4.2	4.9	38
		25	4.2	4.6	35
		26	4.2	4.3	33
		27	4.2	4.2	33
		28	4.2	3.9	30
		29	4.2	3.6	28
		30	4.2	3.8	29

Missabi Mountain Site C- South end.	A9-26-96	Depth m	Temp. C	D.O. ppm (field)	O Sat %
		0	16	11.8	125
		1	15.9	11.6	120
		2	15.9	11.6	120
		3	15.8	11.7	125
		4	15.8	11.7	125
		5	15.8	11.3	118
		6	15.8	11.8	125
		7	15.8	11.6	120
		8	12.2	12.4	116
		9	10.4	11.7	107
		10	9.5	11.2	100
		11	8.2	6.8	59
		12	7.8	6.4	55
		13	7.1	6.4	53

Appendix D

Table 1: Analytical techniques used in the geologic and hydrologic assessments of the study area and summary of the results.

Table 2a. Analytical methods used in sample analysis of cations and anions, detection limits, and background information on sample handling and preservation for samples from Berndt and Lapakko (1997) and Berndt (1998)

Table 2b. Analytical methods used in sample analysis of other constituents and characteristics of the sampled water for samples from Berndt and Lapakko (1997) and Berndt (1998)

Table 3a.. Analytical methods used in sample analysis of cations and anions, detection limits, and background information on sample handling and preservation of samples from MPCA (1998)

Table 3b. Analytical methods used in sample analysis of other constituents and characteristics of the sampled water for samples from MPCA (1998)

Table 1: Analytical techniques used in geologic and hydrologic assessment of the study area.

Issue Addressed	Method Used	Description of Method	Results
Limited information on structural geology (fracturing, faulting, and folding of the Biwabik Formation) specific to the study area.	Lineament/fracture trace analysis of the study area using aerial photographs.	The study was conducted on Arcview using DOQ 1538 (Virginia area) and 1539 (McKinley area), and data from the Land Management Information Center or U.S. Geological Survey. The data was UTM15, NAD83, in meters, and in arc/info format.	Analysis of aerial photos revealed possible fracture traces between Minorca and Missabe Mountain Pits. Field checking of the land between the two pits did not indicate presence of any fractures. Traces also were found between the Minorca and Sauntry Pits. Smaller deep pits, presumed to be from mining oxidized natural iron ore, are present in a rough line between the two pits.
Limited information on structural geology (fracturing, faulting, and folding of the Biwabik Formation) specific to the study area.	Analysis of aeromagnetic point data and comparison of the data with known structural features and mine pits.	Used information from Hibbing Flight Area-Minnesota Aeromagnetic Data; National Geophysical Data Center-NOAA. The point data was on 400 m flight spacing. A positional error of ± 50 meters and north-south shift-error in offset is expected with the database.	The data confirmed an irregular pattern of oxidation of the Biwabik Iron Formation in the study area. Because of insufficient resolution of the method, large fracture zones or other features that could affect water flow could not be delineated.
Possible presence of abandoned underground mine workings in the study area that may act as a conduit for water migrating from Minorca Pit.	Review of available historic maps of the study area for abandoned mine workings.	Review of maps obtained from the City of Virginia dating from 1953-1973. The maps were scanned for location of shafts and associated mine workings.	Located three shafts and a mine drift possibly associated with one of the shafts. One shaft was in the Lincoln D Pit-no mine drifts associated with the shaft were present on the maps . One shaft was directly north of the abandoned Commodore Pit . The maps showed limited development of mine workings.. A third shaft was located southeast of the abandoned Norman pit-no mine drift development was recorded.

Issue Addressed	Method Used	Description of Method	Results
Verify the potential amount of groundwater inflow into the Minorca pit.	Determine area of recharge surrounding the Minorca Pit and approximate values for groundwater inflow based on annual precipitation for the study area. Compare results with the 355 gpm calculated by DNR.	Using Arcview, determined the potential recharge area for the Biwabik Iron Formation from land surfaces surrounding the Minorca Pit.	Calculations for total recharge were based on a precipitation of 1 ft/year. The estimated recharge area included the land to the north, east and west of the Minorca Pit. Calculations resulted in an estimate of 260 gpm. The calculated value is less than 355 gpm calculated by DNR, making DNR's value a conservative choice for the health risk assessment.
Determine limnologic characteristics of the Missabe Mountain Pit	Review of available information on the Missabe Mountain Pit including percent dissolved oxygen, temperature, and changes in water quality with depth.	Analyze profiles taken in the Missabe Mountain Pit and determine oxygen content at depth and changes in different water quality parameters with increasing depth. Review of available data with MPCA and NRRI limnologists.	There is no guarantee that mixing will occur. Under normal conditions, we can assume mixing two times per year, in spring and fall. The water will not mix well for a 120-day period between the mixing periods. The pit may develop a temperature and density gradient during that time and may have times of intermittent anoxia. Because of lack of data from 44 meter to 75 meter total depth and the limited available data, the pit needs to be monitored.

Table 2a. Analytical methods used in sample analysis of anions and cations, detection limits, and background information on sample handling and preservation for samples from Berndt and Lapakko (1997) and Berndt (1998).

Element	Method	Detection Limit	Preservation/Handling
Cations - Ag, As, Ba, Cd, Co, Cr, Cs, Ga, Ge, Mg, Mn, Mo, Ni, Pb, Rb, REE's, Sn, Sr, Th, Tl, U, V, W	Inductively coupled plasma mass spectrometry (ICP-MS)	<0.1 µg/L*	Filtered, 60ml, 200 µl HNO_3
Cations - Al, Be, Ca, Cu, Si, Zn	ICP-MS	0.1-1.0 µg/L*	Filtered, 60ml, 200 µl HNO_3
Cations - Li, K, Fe, Na, Se	ICP-MS	1.0 - 10.0 µg/L*	Filtered, 60ml, 200 µl HNO_3
Cation - Be (Be had to be re-analyzed due to possible discrepancies in the previously completed analyses.)	mass sector -ICP-MS fitted with a micro-concentric desolvating nebulizer. NIST-traceable multi-element standard for calibration.	Resolution of ~ 0.003 µg/L. Error of 0.015-0.030 µg/L	Filtered, 60ml, 200 µl HNO_3 Diluted by 5X
Cations - B	ICP-MS	10 - 50 µg/L*	Filtered, 60ml, 200 µl HNO_3
Anions - Br, Cl, F, NO_2-N, NO_3-N	Ion chromatography (IC)	1.0 - 10.0 µg/L*	Filtered, 4 °C
Anions - PO_4-P, SO_4	IC	10-50 µg/L*	Filtered, 4 °C

* Detection limits for analysis by ICP-MS and IC are determined by counting statistics and error analyses, respectively, and can vary slightly from day to day. Values listed in the table reflect the dilution of samples used during analysis (for major cations only). Table and information modified from Berndt and Lapakko (1997, p. 9) and Berndt and Lapakko (1998, personal communication).

Figure 2b. Analytical methods used in sample analysis of other constituents and characteristics of the sampled waters for samples from Berndt and LaPakko (1997) and Berndt (1998)*

Element	Method	Preservation/Handling
pH	On-site determination	Beckman model 11 meter with Ross model 8165 combination electrode.
Temperature	On-site determination	Beckman model 11 meter with Ross model 8165 combination electrode.
Eh	On-site determination	Values determined relative to the standard hydrogen electrode. For qualitative use only.
Alkalinity	Titration	Filtered, 4°C
Biological Oxygen Demand (BOD, 5 day)	STD meth 507	500 ml plastic, 4°C
Total Organic Carbon (TOC)	MDH No. 98	250 ml plastic, 0.5 ml H_2SO_4, 4°C
Chemical Oxygen Demand (COD)	Hach meth 8000	250 ml plastic, 0.5 ml H_2SO_4, 4°C
Phenol	EPA 420.1	1000 ml amber glass, 5 ml H_2SO_4, 4°C
Cyanide (CN)	EPA 335.2	500 ml plastic 2ml NaOH, 4°C
Oil and Grease	EPA 413.1	1000 ml amber glass, 5 ml 50% HCl, 4°C
Surfactants	MDH No. 35 (MBAS)	250 ml plastic bottle, 4°C
Amines	NTS	500 ml glass bottle, 1 ml glacial acetic, 4°C
Kjeldahl Nitrogen (TKN), NH_4	MDA	2 ml/L H_2SO_4,
Mercury (Hg)	AA, Cold Vapor	Filtered, 60 ml, 200 µl HNO_3
Volatile Organic Compounds (VOCs)	MDH No. 465	1:1 HCl in glass bottles supplied by MDH, 4°C
Base Neutral Acids (BNA's)	Gas chromatograph-mass Spectrometry , MDH No. 402	1000 ml glass bottles supplied by MDH, 4°C

* Table and information modified from Berndt and Lapakko (1997, p. 9) and Berndt and Lapakko (1998, personal communication).

Table 3a. Analytical methods used in sample analysis of cations and anions, detection limits, and background information on sample handling and preservation of samples from MPCA (1998)

Element	Method	Detection Limit	Preservation/Handling
Cations - Ag, Be, Ce, Co, Sb, Ti, Tl	Inductively coupled plasma - mass spectrometry (ICP-MS)	≤0.01 µg/L	250 ml Clear HDPE Level II cleaned bottle with white cap. Preserved with 5 ml nitric acid and refrigerate.
Cation - Bi, Cd, Cr, Pb, Sn, Zr	ICP-MS	≤0.05 µg/L	250 ml Clear HDPE Level II cleaned bottle with white cap. Preserved with 5 ml nitric acid and refrigerate.
Cations - Al, As, Hg	ICP-MS	≤0.10 µg/L	250 ml Clear HDPE Level II cleaned bottle with white cap. Preserved with 5 ml nitric acid and refrigerate.
Cations - Mn, Se, Sr,	ICP-MS	≤1 µg/L	250 ml Clear HDPE Level II cleaned bottle with white cap. Preserved with 5 ml nitric acid and refrigerate.
Cations - Ba, B, Cu, Fe, Li, Mo, Ni, V, Zn	ICP-MS	>1 - 20 µg/L	250 ml Clear HDPE Level II cleaned bottle with white cap. Preserved with 5 ml nitric acid and refrigerate.
Cations - Ca, Mg, K, Na, Si,	ICP-MS	118.5 µg/L for K All others - no samples were below the maximum reporting limit.	250 ml Clear HDPE Level II cleaned bottle with white cap. Preserved with 5 ml nitric acid and refrigerate.
Anions - Br, Cl, F, P PO_4-P, SO_4	Ion chromatography (IC)	0.20 µg/L for Br F censored at several detection levels. 14.9 µg/L for P 20 µg/L for total PO_4 200 µg/L for Cl 100 µg/L for SO_4	250 ml Clear HDPE Level II cleaned bottle with blue cap. Preserved with 5 ml sulfuric acid and refrigerate.
Anions - NO_3-N	Cadmium Reduction	500 µg/L for NO_3-N	250 ml Clear HDPE Level II cleaned bottle with blue cap. Preserved with 5 ml sulfuric acid and refrigerate.

Table 3b. Analytical methods used in sample analysis of other onstituents and characteristics of the sampled water for samples from MPCA (1998)

Element	Method	Preservation/Handling
pH	On-site determination	
Temperature	On-site determination	
Eh	On-site determination	
Alkalinity	Titration	
Total Organic Carbon (TOC)		20 ml glass vial. Preserve with 8 drops phosphoric acid and refrigerate.
Dissolved Oxygen (DO)	On-site determination	
Specific Conductivity (SC)		500 ml HDPE Level II cleaned bottle, no preservative, refrigerate
Total Suspended Solids (TSS)		500 ml HDPE Level II cleaned bottle, no preservative, refrigerate.
Total Dissolved Solids (TDS)		500 ml HDPE Level II cleaned bottle, no preservative, refrigerate
Volatile Organic Compounds (VOCs)	MDH No. 465	Three glass vials per sample. Preserve with two drops HCl and refrigerate

Note on samples from HDR Engineering Incorporated

Information on how samples were collected and methods of analyses are limited. What is known is that the samples were not filtered prior to acidification and analysis. It is felt that, upon analysis the presence of fine particles of tailings and acid sample resulted in elevated levels for some of the cations. The difference in value between filtered and unfiltered samples was most evident with beryllium. Therefore, a second set of samples was collected to determine actual levels of beryllium in the process waters.

Appendix E:

Table 1: Geochemical data used in selection of ECCs and in comparison of natural and process waters in the study area.

Display 1a. Summary information for arsenic levels from process waters in and near the tailings basin

Display 1b. Summary of information for arsenic levels from laboratory column experiments no.1 and no.2

Display 2a. Summary information for fluoride levels from the process waters in and near the tailings basin

Display 2b. Summary information for fluoride levels from laboratory column experiments no.1 and no.2

Display 3a. Summary information for manganese levels from process waters in and near the tailings basin

Display 3b. Summary information for manganese levels from laboratory column experiments no.1 and no.2

Display 4a. Summary information for molybdenum levels from the process waters in and near the tailings basin

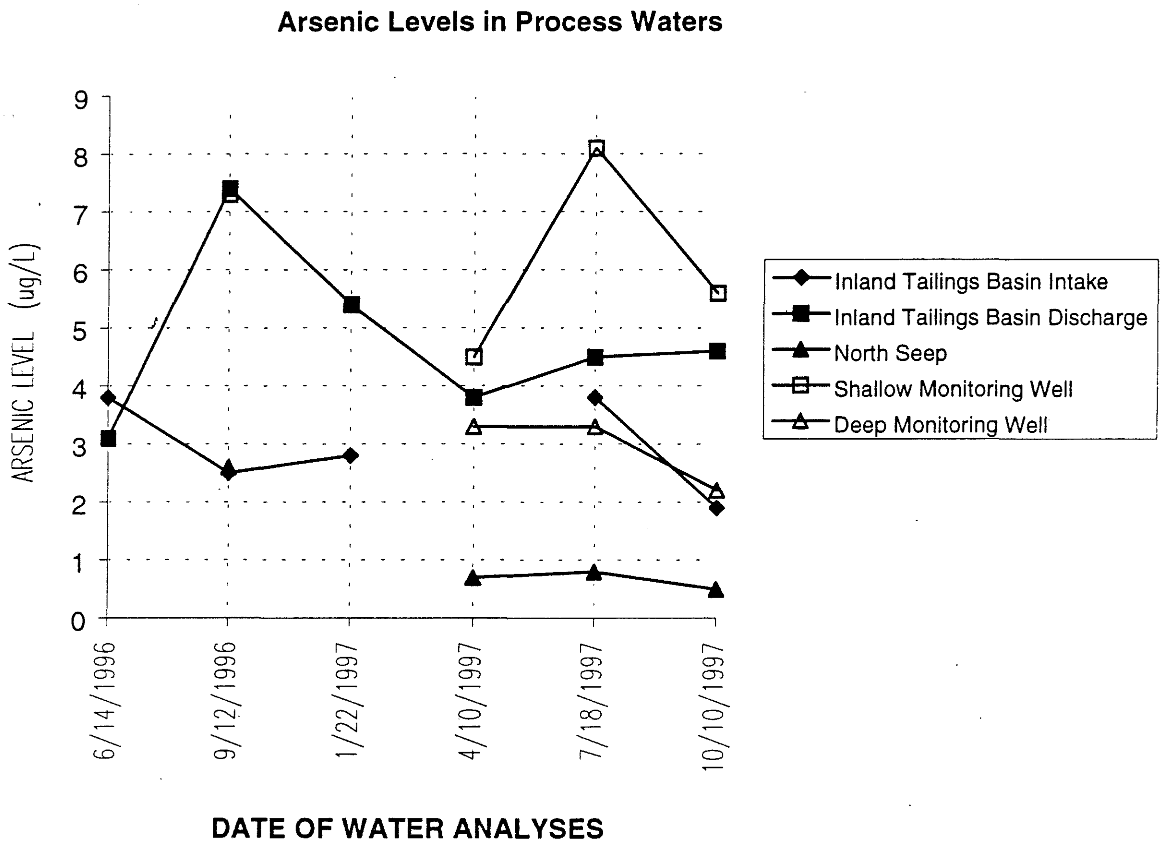
Display 4b. Summary information for molybdenum levels from laboratory column experiments no.1 and no.2

Table 1: Geochemical data used in selection of ECCs and in comparison of natural and process waters in the study area.

Type of Sample	Number of Samples	Source of Analyses	Time Coverage	Use of Analyses	Data Quality	Comments
Natural waters	9	HDR Engineering.	September 1996	Comparison	Moderate	Unfiltered samples.
Natural waters	26	Alexander & Alexander (1997)	September 1996	pH Temperature Conductivity Dissolved oxygen	Moderate-high.	Quality based on calibration of equipment.
Natural waters	31	MPCA GWMAP	One sample event - 1995-1996	Determine background levels where necessary	High	Taken from MPCA database.
Processing plant discharge	5	Berndt (1998) Berndt & Lapakko (1997)	Quarterly sampling 1996-1997	Comparison	High	Results represent 1.5 year time period.
Tailings basin discharge	6	Berndt (1998) Berndt & Lapakko (1997)	Quarterly sampling 1996-1997	Comparison	High	Results represent 1.5 year time period.
North seep and monitoring wells	11	Berndt (1998)	Quarterly sampling 1996-1997	Comparison	High	Results represent 1.5 year time period.
Test column 1	9	Berndt & Lapakko (1997)	Periodic sampling over 216 days	Comparison and geochemical trends	High.	pH values may be high. Qualitative use only.
Test column 2	9	Berndt & Lapakko (1997)	Periodic sampling over 216 days	Comparison and geochemical trends	High	pH values may be high. Qualitative use only
Groundwater/ rainwater column tests. (Ongoing)	Average of preliminary results of ongoing research.	Berndt (1998)	Periodic sampling over 9- 16 weeks.	Comparison and geochemical trends	High	Rainwater - 9 weeks Ground-water - 16 weeks. Qualitative use only

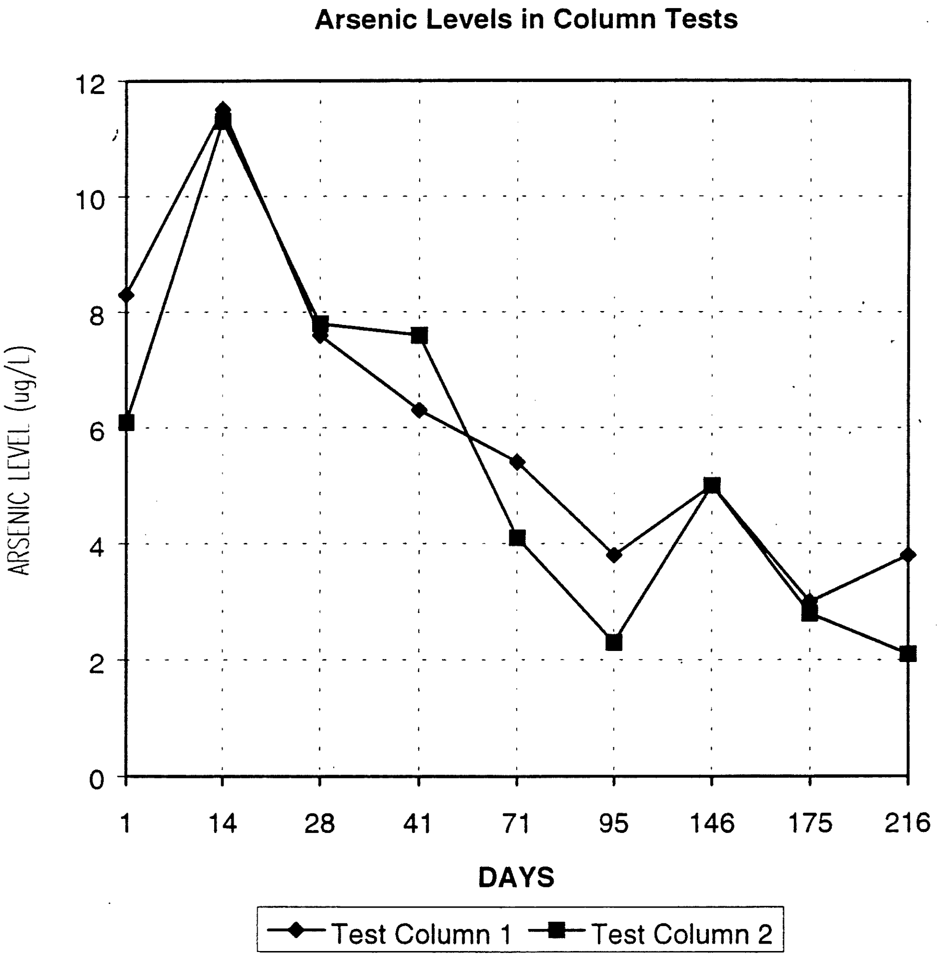
Display 1a. Summary information for arsenic levels (in µg/L) from the process waters in and near the tailings basin. Samples from Berndt (1998) and Berndt and Lapakko (1997)

Sampling Site	6/14/1996	9/12/1996	1/22/1997	4/10/1997	7/18/1997	10/10/1997
Inland Tailings Basin Intake	3.8	2.5	2.8		3.8	1.9
Inland Tailings Basin Discharge	3.1	7.4	5.4	3.8	4.5	4.6
North Seep				0.7	0.8	0.5
Shallow Monitoring Well		7.3		4.5	8.1	5.6
Deep Monitoring Well		2.6		3.3	3.3	2.2



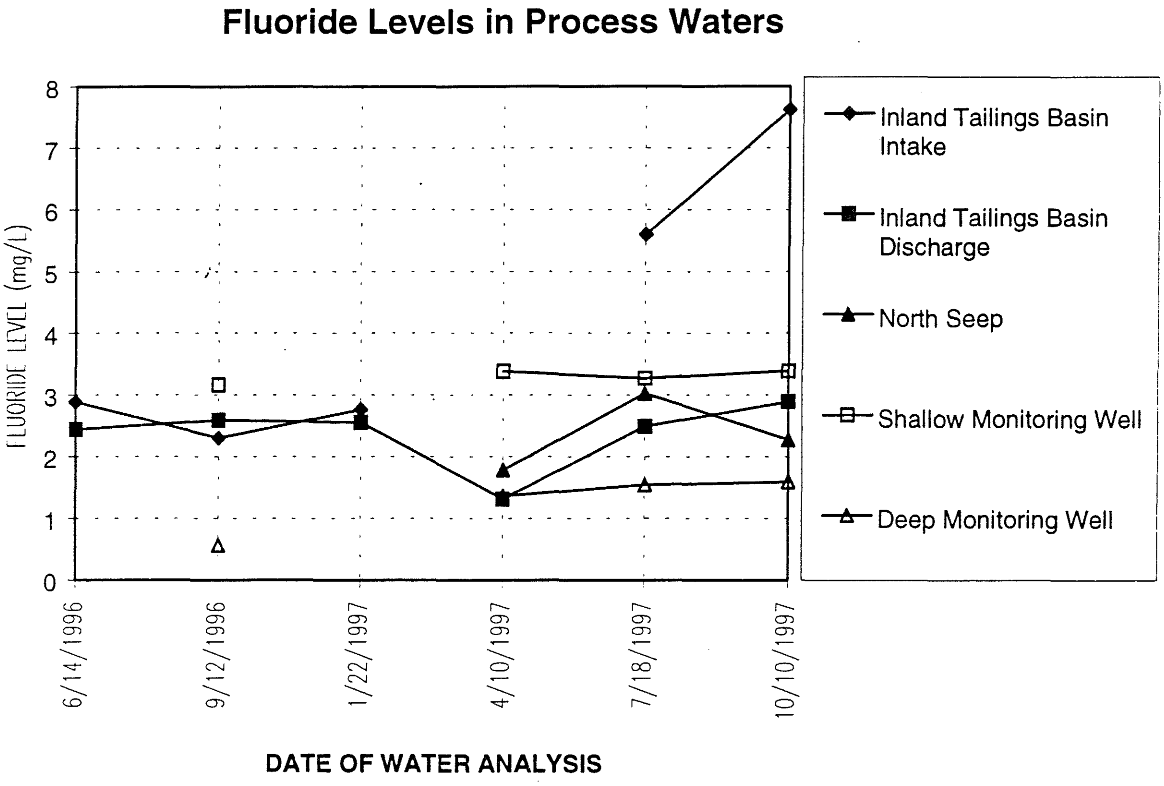
Display 1b. Summary information for arsenic levels (in µg/L) from laboratory column experiments No. 1 and No. 2. Sample data from Berndt and Lapakko (1997)

Days	Test Column 1	Test Column 2
1	8.3	6.1
14	11.5	11.3
28	7.6	7.8
41	6.3	7.6
71	5.4	4.1
95	3.8	2.3
146	5	5
175	3	2.8
216	3.8	2.1



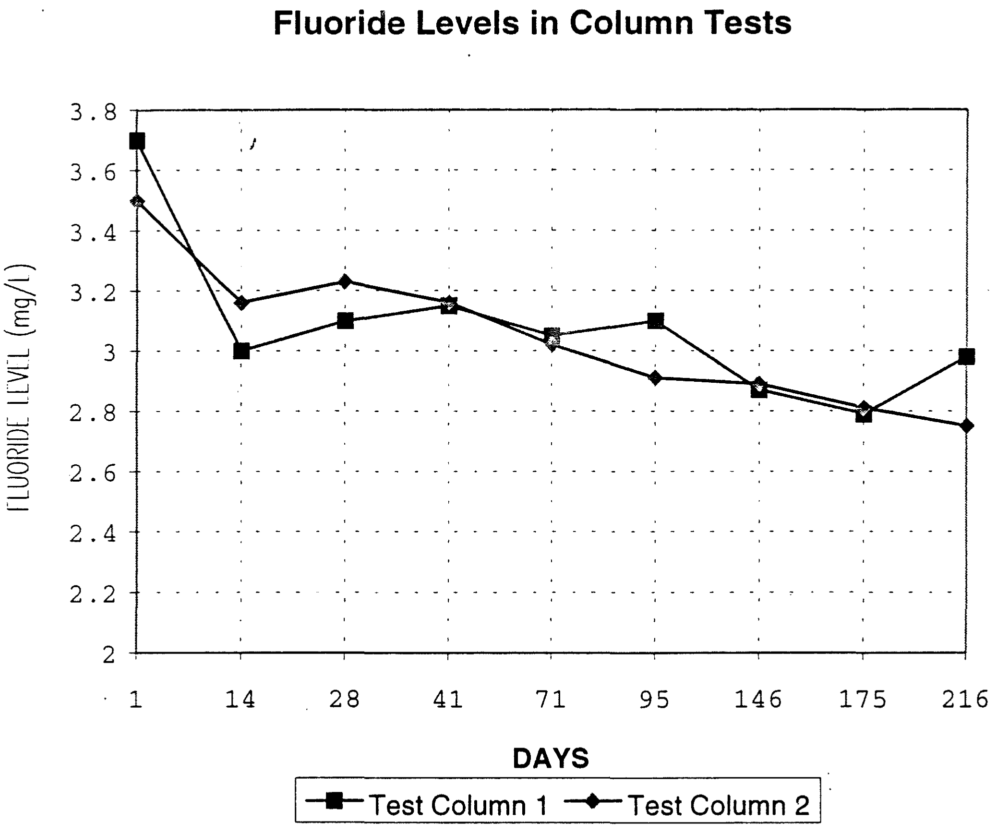
Display 2a. Summary in formation for fluoride levels (in mg/L) from the process waters in and near the tailings basin. Sample data from Berndt (1998) and Berndt and Lapakko (1997).

Sampling Site	6/14/1996	9/12/1996	1/22/1997	4/10/1997	7/18/1997	10/10/1997
Inland Tailings Basin Intake	2.88	2.3	2.76		5.6	7.62
Inland Tailings Basin Discharge	2.44	2.59	2.55	1.31	2.49	2.89
North Seep				1.78	3.02	2.27
Shallow Monitoring Well		3.16		3.38	3.27	3.39
Deep Monitoring Well		0.56		1.36	1.54	1.59



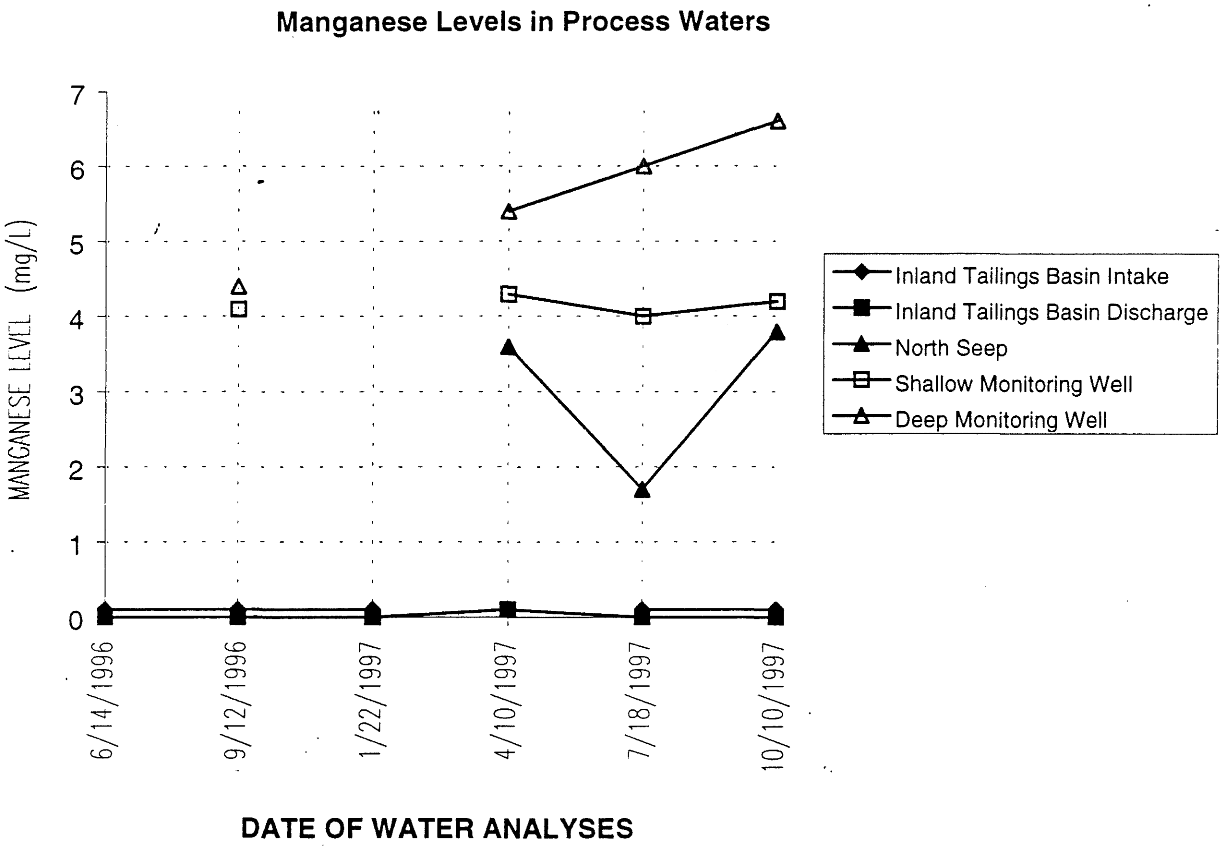
Display 2b. Summary information for fluoride levels (in mg/L) from laboratory column experiments No. 1 and No. 2. Sample data from Berndt and Lapakko (1997).

Days	Test Column 1	Test Column 2
1	3.7	3.5
14	3	3.16
28	3.1	3.23
41	3.15	3.16
71	3.05	3.02
95	3.1	2.91
146	2.87	2.89
175	2.79	2.81
216	2.98	2.75



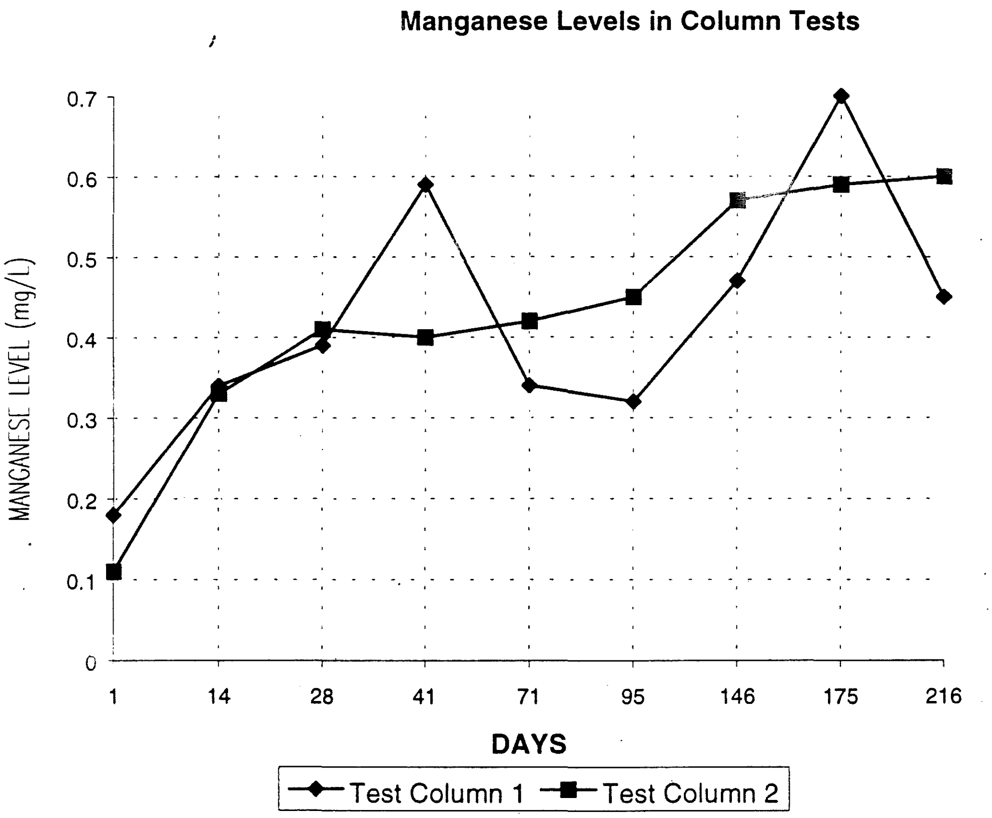
Display 3a. Summary information for manganese levels (in mg/L) from the process waters in and near the tailings basin. Sample data from Berndt (1998) and Berndt and Lapakko (1997).

Sampling Site	6/14/1996	9/12/1996	1/22/1997	4/10/1997	7/18/1997	10/10/1997
Inland Tailings Basin Intake	0.1	0.1	0.1		0.1	0.1
Inland Tailings Basin Discharge	0	0	0	0.1	0	0
North Seep				3.6	1.7	3.8
Shallow Monitoring Well		4.1		4.3	4	4.2
Deep Monitoring Well		4.4		5.4	6	6.6



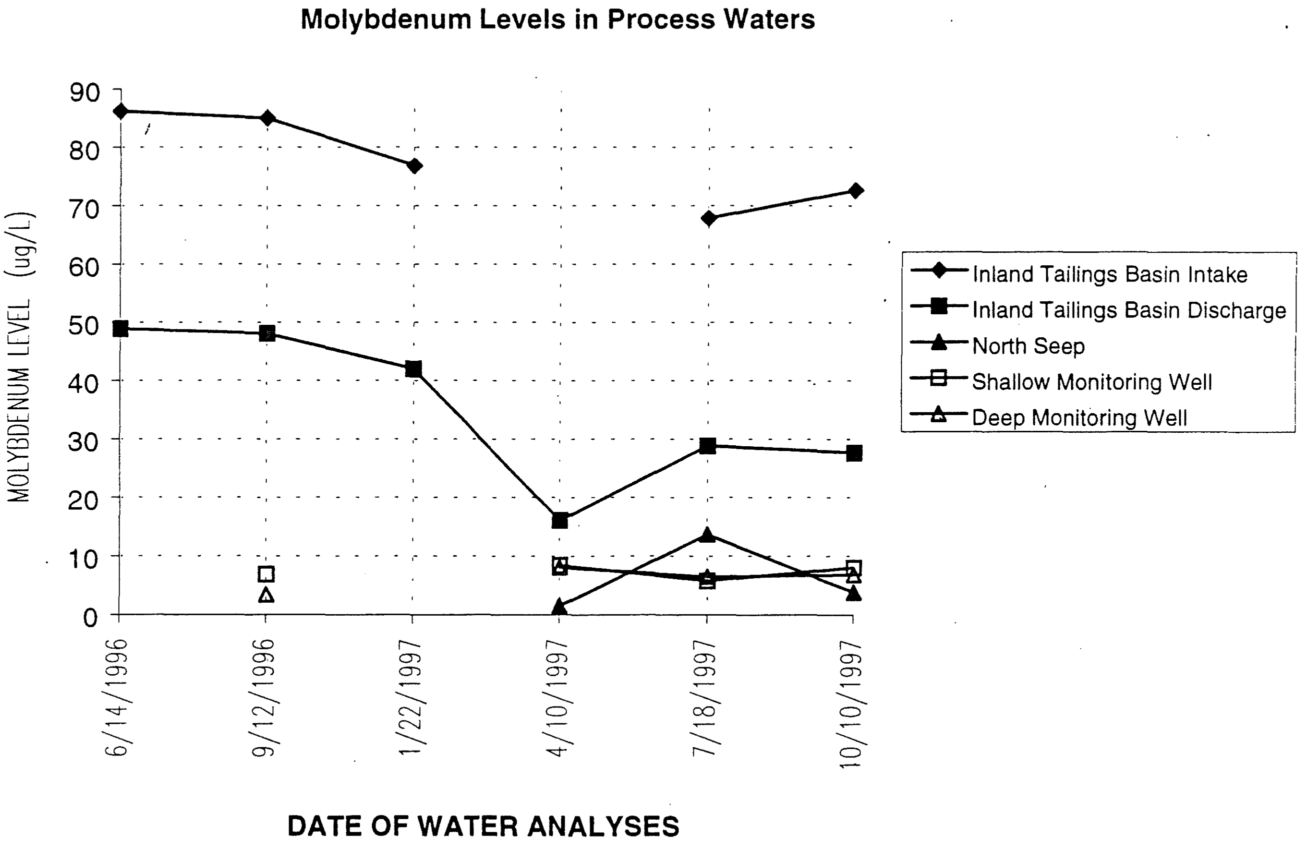
Display 3b. Summary information for manganese levels (in mg/L) from laboratory column experiments No. 1 and No. 2. Sample data from Berndt and Lapakko (1997).

Days	Test Column 1	Test Column 2
1	0.18	0.11
14	0.34	0.33
28	0.39	0.41
41	0.59	0.4
71	0.34	0.42
95	0.32	0.45
146	0.47	0.57
175	0.7	0.59
216	0.45	0.60



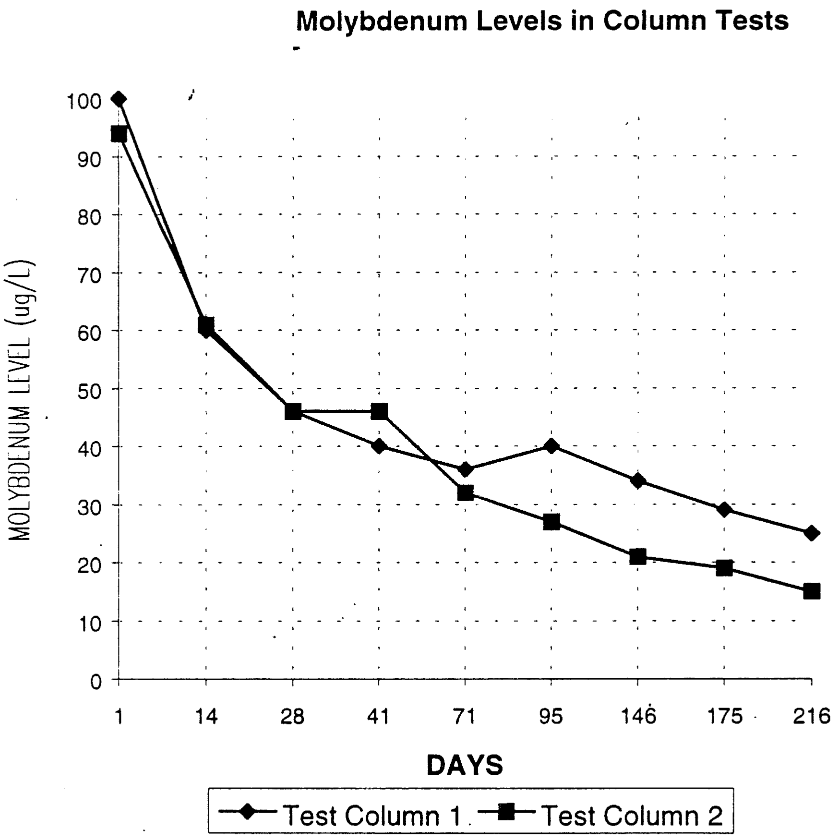
Display 4a. Summary information for molybdenum levels (in µg/L) form the process waters in and near the tailings basin (Sample data from Berndt (1998) and Berndt and LaPakko (1997))

Sampling Site	6/14/1996	9/12/1996	1/22/1997	4/10/1997	7/18/1997	10/10/1997
Inland Tailings Basin Intake	86.2	85	76.8		67.8	72.6
Inland Tailings Basin Discharge	48.9	48.1	42	16.1	28.9	27.7
North Seep				1.5	13.7	3.8
Shallow Monitoring Well		6.9		8.4	5.8	8
Deep Monitoring Well		3.4		8.1	6.5	6.8



Display 4b. Summay infromation for molybdenum levels (in μg/L) from laboratory column experiments No.1 and No.2 (Sample data from Berndt and Lapaako (1997))

Days	Test Column 1	Test Column 2
1	100	94
14	60	61
28	46	46
41	40	46
71	36	32
95	40	27
146	34	21
175	29	19
216	25	15



Appendix F

Letter from DNR on effects of organics in the tailings basin monitor wells.

DEPARTMENT: Natural Resources
Division of Minerals

STATE OF MINNESOTA

Office Memorandum

DATE: March 4, 1998
TO: Donna Boreck, MN Dept. of Health
FROM: Lyn Jakel
PHONE: 612/296-0908
SUBJECT: Inland's wells

Water samples were collected from two monitoring wells and a seep associated with the taconite tailings basin at Inland Steel. Water quality of the wells was substantially different from other water sources at Inland, including the seep. The water quality at the seep and wells evolved due to intimate contact with the tailings under conditions remote from atmospheric interaction. However, the base of each well was located within an organic substrate which may have impacted the quality of the well waters. The differences between the water quality of the wells and the seep was consistent with reduced conditions at the wells, presumably due to the oxidation of dissolved organic matter in the water.

Oxidation of dissolved organic matter lowers Eh and pH, creating a reducing environment, which was observed in the wells at Inland. The average measured Eh and pH of well waters were approximately 222 mV and 7.1, respectively, compared to average seep values of about 358 mV and 7.7, respectively. The concentrations of redox-sensitive elements (sulfate, iron, manganese, arsenic, and molybdenum) in the wells relative to the seep were consistent with the lower Eh and pH values. Hydrogen sulfide gas, which was detected in both wells, provided another indication that reducing conditions existed. Hydrogen sulfide is produced by the reduction of sulfate, which was observed at lower levels in the shallow well (17 ppm compared to 32 ppm in the seep). Iron concentrations in the wells were at least ten times those in the seep, which is consistent with reducing conditions and low pH in the wells (>66 ppb versus 6 ppb).

Manganese and arsenic concentrations in the well waters were consistent with a reducing environment. Manganese in the well waters was most likely controlled by the solubility of solid phase manganese carbonate, which dissolves at low pH. As a result, manganese in the well waters was approximately two and a half times higher than the seep (approximately 5 ppm versus 2 ppm). Arsenic levels in the well waters were elevated relative to the seep (averaging 4.5 ppb compared to 0.6 ppb). However, the concentrations observed in the wells were not clearly different from the range of arsenic concentrations normally found in the tailings basin. The difference between the wells and the seep may have been caused by coprecipitation of arsenic with iron at the seep.

Although molybdenum is generally considered redox sensitive elements, at the observed Eh and pH values, molybdenum concentrations were not substantially different (6.7 and 6.1 in the wells and seep, respectively). The concentrations of other elements that are not sensitive to redox and pH changes (e.g. fluoride and boron) remained relatively constant in both the wells and the seeps

In conclusion, the presence of organics appears to contribute to a reducing environment in the wells at Inland, and the water quality of these wells may not be representative of that expected solely due to intimate contact between tailings and pore waters (i.e. represented by the seep). While most parameters should be unaffected by the presence of dissolved organic matter, the concentrations of some redox sensitive elements are likely to change. The data show that manganese and arsenic levels in a reduced environment may be elevated two-fold on average, and iron by at least an order of magnitude. In contrast, sulfate concentrations in the reducing environment were roughly half those at the seep. However, only manganese levels were elevated above the current drinking water quality standard. This was not solely due to the reducing conditions, as evidenced by the high levels of manganese at the seep (2 ppm). Therefore, of the waters sampled at Inland, the wells provided the highest observed concentrations of manganese and iron.

Appendix G

Uncertainties in the health risk assessment

Table 1. Uncertainties in the health risk assessment

Assumption	Direction of Effect of Risk	Comments
ECCs		
Analyses of process waters from the tailings basin, monitoring wells, seep, and columns are used to predict the water quality expected to occur in the Minorca Pit and in the Biwabik Formation aquifer.	May under- or overestimate the risk.	Quality of the data is good. Methods of collection and analyses are appropriate. Sampling represents 1.5-year period. Number of samples were 3-6 samples per site for 5 sites. A total of nine samples were taken from each column. Values given for simulated rainwater and groundwater column experiments represent averages of samples taken for a 9 week- and 16 week-time period.
Analysis of natural water from the abandoned pits and water wells in the study area are representative of the natural water quality of the area.	May underestimate the risk.	Quality of the data is questionable because the water samples were not filtered prior to acidification and analysis.
Hydrology of study area		
A direct hydrologic connection exists between the Minorca Pit and the Missabe Mountain Pit.	Overestimates the risk.	A direct hydrologic connection has not been proven. Water may migrate to other pits.
Flow in the groundwater aquifer is fracture controlled. As such, the aquifer between the two pits is not considered to act as a permeable media.	May overestimate the risk.	Analysis does not take into account those areas that may actually act as a permeable media.
Dilution or dispersion of the ECC will not occur in groundwater in the Biwabik Formation.	May overestimate the risk.	Dilution may occur in groundwater being recharged from other surface sources. As the study site is near the top of the watershed, contribution of other groundwater sources to north and east may not be significant.
The discharge from the Minorca Pit will make up a maximum of 40% of the total groundwater recharging the Missabe Mountain Pit.	Overestimates the risk.	Using the maximum of 40% does not reflect the results of reclamation and diversion of surface runoff.
With the tailings pile revegetated as grassland, the maximum discharge to the Missabe Mountain Pit is assumed to be 20% of total.	May over- or underestimate the risk.	Overestimation of the contribution factor may occur if successful forest vegetation is established on the tailings pile. The risk may be underestimated if grasses are not successfully established on the tailings pile.

Assumption	Direction of Effect of Risk	Comments
Mixing will occur in the Missabe Mountain pit allowing for dilution of incoming water from the Minorca Pit.	May underestimate the risk.	The pits are narrow and deep. Complete annual mixing is not guaranteed. Even with mixing, short periods of anoxia may occur between periods of mixing.. Anoxia may occur in deeper portions of the Missabe Mountain Pit.
Geochemistry/ Geochemical modeling.		
The laboratory column experiments represent what will be expected with tailings /water interaction	May over- or underestimate the risk.	Depending on time of exposure of water to tailings , values for ECCs may be higher or lower than what is predicted.
The seep represents water quality after migration through the fine tailings.	May over- or underestimate the risk.	The seep represents water that would saturate the tailings and migrate from the tailings into the Biwabik Formation.
Geochemical modeling is representative of what is expected in the future.	May over- or underestimate the risk.	Parameters utilized in geochemical modeling closely matched the geochemistry of natural waters and tailings basin effluent. Results matched with results from column experiments and water analyses from the study area.
Based on the mineralogy of the tailings, the pH of the process waters will not decrease below 6.5 and Eh will remain at or above 100 millivolts. Significantly reducing conditions are not expected to develop.	May over- or underestimate the risk	Assumption is based on geochemical modeling. Known water sources in the study area are above a pH of 6.5 and Eh of 100m. It is assumed that large amounts of organic material or materials capable of generating an acidic/reducing environment will not be added to the tailings.
Exposure assessment.		
The only significant exposure is through ingestion of drinking water	May underestimate the risk	The health risk assessment covers only groundwater migrating into the drinking water supply of the City of Virginia and ingestion of the water. Other routes of exposure, such as dermal contact and inhalation were not considered as potential exposure routes because of the characteristics of the ECCs.

APPENDIX D

DRAFT

Summary of Potential Impacts of Taconite Tailings Disposal in the Minorca Pit on Water Quality in the Missabe Mountain Pit

Draft Report to Rebecca Wooden

Kim Lapakko
Emmelyn Jakel

September 2, 1999

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EXECUTIVE SUMMARY

At current production levels, Ispat Inland Mining Company's (Inland) taconite operation near Virginia, Minnesota will exceed the capacity of their tailings basin in approximately four years. As an alternative to expanding the existing tailings basin, Inland has proposed disposing of both fine and coarse tailings in the Minorca Pit. The Minnesota Pollution Control Agency may issue permits for in-pit disposal of taconite tailings if it can be shown "that the deposition of tailings will not pose an unreasonable risk of pollution or degradation of ground water" (Laws of Minnesota, 1996, Chapter 407, Section 56). There is a specific concern for the potential impact that tailings disposal in the Minorca Pit may have on the drinking water supply for the city of Virginia, because of the close proximity of the Minorca Pit and the complex geology and hydrology of the area.

The Minnesota Department of Natural Resources (MN DNR) and the University of Minnesota (U of MN) have been studying the potential water quality implications of disposal of taconite tailings in existing mine pits across the Mesabi Iron Range (Berndt and Lapakko, 1997a, b; Berndt 1998; Berndt et al, 1998, 1999). Results from this study on tailings pore water chemistry were used by the Minnesota Department of Health (MDH) to conduct a health risk assessment for Inland's proposal (MDH, 1998). Their assessment focused on potential risks to human health, and did not consider secondary drinking water quality standards. The present assessment focuses on impacts of output from the Minorca Pit clear water pool and tailings pore water on water quality in the Missabe Mountain Pit with respect to primary and secondary drinking water quality standards. It also identifies chemical reactions that may reduce the levels of potential contaminants in local ground waters.

As the responsible governmental unit for the proposal, the MN DNR is currently preparing a supplemental environmental impact statement (SEIS) for Inland's proposal. This document summarizes aspects of the MN DNR/U of MN study that are directly related to the SEIS. Although several taconite operations across the Mesabi Iron Range participated in this study, the information presented in this document will focus primarily on operational measurements and controlled experiments using tailings and process waters from Inland. Data from other operations were used, in conjunction with those from Inland, to describe environmentally relevant chemical reactions associated with taconite tailings and the water which they contact.

This document summarizes findings relevant to the impact of tailings disposal in the Minorca Pit on concentrations of manganese, fluoride, molybdenum, and arsenic in the Missabe Mountain Pit. More detailed information on this assessment (Lapakko and Jakel, 1999) as well as the MN DNR/U of MN range-wide study (Berndt and Lapakko, 1997a,b; Berndt, 1998; Berndt et al., 1998, 1999) are available through the MN DNR, Division of Lands and Minerals, Saint Paul, MN (651-296-4807 or 1-800-766-6000 in Minnesota).

Projected levels of manganese, fluoride, molybdenum, and arsenic ~~which~~ that could evolve in the Missabe Mountain Pit as a result of taconite tailings disposal in the Minorca Pit, are discussed individually with regard to:

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1) short and long-term levels expected in flow leaving the Minorca Pit (source terms),
2) transport through the Biwabik aquifer (transport term),
3) dilution of inputs to the Missabe Mountain Pit, and
4) chemical reactions within the Missabe Mountain Pit.

For each of the above terms, a range of expected concentrations was determined. In order to provide the most conservative estimates, the upper end of this range, or "worst case scenario," is reported. For certain elements, evaluation of these geochemical processes provided a means to refine the source and transport terms, as well as chemical reactions within the Missabe Mountain Pit. These refined terms were judged to represent conditions that are more likely to occur than the worst case scenario.

The projected source terms are largely based on chemical analyses of process waters discharged from Ispat Inland Mining Company's (Inland) taconite processing plant near Virginia, MN. Data from laboratory and field experiments conducted on Inland's process waters and tailings were also considered. Geochemical modeling was used to describe environmentally relevant chemical reactions associated with taconite tailings and the water which they contact.

Manganese concentrations at the Virginia water supply intake are expected to meet the health-based water quality standard determined for this project (1.3 mg/L; MDH, 1998) as well as primary (0.1 mg/L) and secondary (0.05 mg/L) drinking water quality standards. This conclusion was reached using the following assumptions:

1) the maximum anticipated source term, 7 mg/L,
2) no removal in the Biwabik aquifer,
3) dilution to a concentration not exceeding 1.7 mg/L, and
4) removal due to chemical reactions (i.e. oxidation) within the Missabe Mountain Pit.

Removal by chemical reactions is supported by empirical data from Inland's tailings basin, field and laboratory experiments designed to assess this site, abandoned open pits, and geochemical equilibrium calculations which indicate that manganese levels are unlikely to exceed 0.01 mg/L in the Missabe Mountain Pit. Thus, manganese concentrations in the Missabe Mountain Pit will decrease below drinking water quality standards as a result of manganese oxidation.

Projected fluoride concentrations in the Missabe Mountain Pit are expected to meet both the primary (4 mg/L) and secondary (2 mg/L) drinking water quality standards. This conclusion was reached using the following assumptions:

1) the maximum anticipated source term of 6 mg/L,
2) no removal in the Biwabik aquifer,
3) dilution to a concentration not exceeding 1.6 mg/L, and
4) no removal due to chemical reactions within the Missabe Mountain Pit.

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Empirical data used to evaluate fluoride source terms were collected from surface and tailings pore waters around Inland's tailings basin, as well as field and laboratory experiments using process water and tailings from Inland. The worst case scenario assumes no chemical reactions will influence fluoride concentrations along the flow path. Fluoride concentrations in the Missabe Mountain Pit will decrease below drinking water quality standards as a result of dilution.

Maximum anticipated molybdenum levels in the Missabe Mountain Pit will meet the drinking water quality standard of 30 ug/L. This conclusion was reached using the following assumptions:

1) short-term source term of 130 ug/L, decreasing to 45 ug/L approximately eight years after tailings deposition begins,
2) no removal in the Biwabik aquifer,
3) dilution to a concentration not exceeding 25 ug/L, and
4) no removal due to chemical reactions within the Missabe Mountain Pit.

The worst case scenario for molybdenum assumed a source term of 130 ug/L during the period when the Minorca Pit clear water pool dominates ground water outflow chemistry. Elevated molybdenum concentrations in discharges from Inland's plant and an estimation of the amount of dilution available within the Minorca Pit clear water pool were used to calculate this short-term, operational source term. A subsequent source term of 45 ug/L represented long-term, tailings pore water dominated outflow chemistry. This value was based on measurements of tailings pore water chemistry at Inland's tailings basin and field and laboratory experiments designed to evaluate this site. Since taconite processing results in molybdenum release, long-term source of molybdenum will be eliminated when operations cease.

Even at maximum ground water input from the Minorca Pit, arsenic levels in Missabe Mountain Pit will be considerably lower than the current primary drinking water standard of 50 ug/L. This conclusion was reached using the following assumptions:

1) the maximum anticipated source term of 7 ug/L,
2) no removal in the Biwabik aquifer,
3) dilution to a concentration not exceeding 2.1 ug/L, and
4) no removal due to chemical reactions within the Missabe Mountain Pit.

The US EPA is expected to lower the arsenic standard by the year 2001, although the new standard has not yet been announced. Arsenic levels in the Missabe Mountain Pit are anticipated to meet the future drinking water quality standard if it is reduced to the range of 5 - 10 ug/L. Therefore, no arsenic treatment issues at the Virginia Public Utility are expected to arise.

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6. Conclusions

LIST OF FIGURES AND TABLES

APPENDICES

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1. Introduction

At current production levels, Ispat Inland Mining Company's (Inland) taconite operation near Virginia, Minnesota will exceed the capacity of their tailings basin in approximately four years. As an alternative to expanding the existing tailings basin, Inland has proposed disposing of both fine and coarse tailings in the Minorca Pit. The Minnesota Pollution Control Agency (MPCA) may issue permits for in-pit disposal of taconite tailings if it can be shown "that the deposition of tailings will not pose an unreasonable risk of pollution or degradation of ground water" (Laws of Minnesota, 1996, Chapter 407, Section 56). There is a specific concern for the potential impact that tailings disposal in the Minorca Pit may have on the drinking water supply for the city of Virginia, because of the close proximity of the Minorca Pit and the complex geology and hydrology of the area.

The Minnesota Department of Natural Resources (MN DNR) and the University of Minnesota (U of MN) have been studying the potential water quality implications of disposal of taconite tailings in existing mine pits across the Mesabi Iron Range (Berndt and Lapakko, 1997a, b; Berndt 1998; Berndt et al, 1998, 1999). Results from this study on tailings pore water chemistry were used by the Minnesota Department of Health (MDH) to conduct a health risk assessment for Inland's proposal (MDH, 1998). Their assessment focused on potential risks to human health, and did not consider secondary drinking water quality standards. The present assessment focuses on impacts of output from the Minorca Pit clear water pool and tailings pore water on water quality in the Missabe Mountain Pit with respect to primary and secondary drinking water quality standards. It also identifies chemical reactions that may reduce the levels of potential contaminants in local ground waters.

As the responsible governmental unit for the proposal, the MN DNR is currently preparing a supplemental environmental impact statement (SEIS) for Inland's proposal to dispose of taconite tailings in the Minorca Pit rather than expand the existing tailings basin. This document summarizes aspects of the MN DNR/U of MN study that are directly related to the SEIS. Although several taconite operations across the Mesabi Iron Range participated in this study, the information presented in this document will focus primarily on operational measurements and controlled experiments using tailings and process waters from Inland. Data from other operations were used, in conjunction with those from Inland, to describe environmentally relevant chemical reactions associated with taconite tailings and the water which they contact.

This document summarizes findings relevant to the impact of tailings disposal in the Minorca Pit on concentrations of Mn, F, Mo, and As in the Missabe Mountain Pit. More detailed information on this assessment (Lapakko and Jakel, 1999) as well as the MN DNR/U of MN range-wide study (Berndt and Lapakko, 1997a,b; Berndt, 1998; Berndt et al., 1998, 1999) are available through the MN DNR, Division of Lands and Minerals, Saint Paul, MN (651-296-4807 or 1-800-766-6000 in Minnesota).

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2. Site Description

Inland's taconite processing operation is located approximately two miles northeast of Virginia, MN (Figure 1). The Minorca Pit lies approximately 0.5 miles south of Inland's taconite processing plant. At present, the water table in the Minorca Pit is at approximately 1400 feet mean seal level (m.s.l.), which may be as much as fifty feet lower than that of the adjacent ground water (Adams, 1998; MDH, 1998). Consequently, the pit acts as a hydrologic sink for surrounding ground water. Inland currently maintains the pit water level by pumping excess water to the Sauntry Creek at an average rate of 1419 gpm (Indeco, 1999).

The proposed action would involve pumping coarse and fine tailings slurried with process water from the processing plant to the Minorca Pit. Tailings settle to the pit floor creating a clear water pool. Some of the water from this pool will continue to be used to augment stream flow in the Sauntry Creek. Much of the water remaining in the clear pool will be pumped back to the plant for reuse.

After five years of tailings and process water deposition, the water level in the Minorca Pit is expected to reach the estimated water level, 1450 feet m.s.l. (Indeco, 1999). This will result in ground water outflow from the Minorca Pit into the Biwabik aquifer. The primary source of outflow is expected to be from the clear water pool until the tailings elevation reaches the lowest pit rim elevation (1470 feet m.s.l.). It is anticipated that once Inland begins to deposit tailings into the Minorca Pit, the tailings elevation will reach 1470 feet in approximately eight years (Indeco, 1999). Thus, the period during which Minorca Pit ground water outflow may be dominated by the clear water pool is estimated to be between years five and eight. After the tailings elevation reaches 1470 feet m.s.l., ground water outflow from the pit will be dominated by tailings pore water (i.e. all ground water output from the pit to surrounding ground water will be from tailings pore water). The pit is expected to reach its capacity ten years after disposal begins. At this time the surface will be prepared for vegetation.

The elevation at which ground water outflow from the Minorca Pit is anticipated is approximately 230 feet higher than the current water level in the Missabe Mountain Pit, which is used as the drinking water supply for the city of Virginia. Because of the complex geology in the area, the possibility of a hydrologic connection between these two pits cannot be ignored. In order to provide the most conservative estimate of the potential water quality impacts of disposal of tailings in the Minorca Pit, it was assumed that ground water outflow from the Minorca Pit will reach the Missabe Mountain Pit.

3. Approach

Out of more than 162 inorganic elements and organic compounds examined in waters associated with taconite tailings during the range-wide study (Berndt and Lapakko, 1997a), only five inorganic elements were identified as approaching or exceeding drinking water quality standards. Of these five, three (manganese, fluoride, and molybdenum) were found to approach or exceed drinking water quality standards at Inland's operation. A fourth element, arsenic, has been reported to the MPCA at levels as high as 18 ug/L as part of the National Pollution Discharge Elimination System (NPDES) program. Although this value did not approach the existing drinking water quality standard of 50 ug/L, arsenic was included in this assessment because the US EPA is considering lowering the drinking water quality standard in January 2001. These four elements will be referred to collectively as elements of concern, or ECs.

This document will describe EC concentration changes in the Missabe Mountain Pit which could result from taconite tailings disposal in the Minorca Pit. Each EC will be discussed individually with regard to expected levels in flow leaving the Minorca Pi (source terms), transport through the aquifer, and dilution and chemical reactions in the Missabe Mountain Pit (Figure 2).

3.1. Minorca Pit Source Terms

Currently, the Minorca Pit acts as a sink for ground water, precipitation and runoff from the surrounding area resulting in an average water level in the pit of approximately 1400 feet m.s.l. (MDH, 1998). If the Minorca Pit is filled with tailings, ground water outflow may take place once the water level reaches approximately 1450 feet m.s.l. (Adams, 1998). "Source term" refers to the range of expected EC concentrations waters leaving the Minorca Pit. This term includes waters exiting the Minorca Pit from the clear water pool as well as tailings pore waters. Source terms become important as soon as the water level in the pit reaches that of the surrounding ground water and the ground water gradient reverses. As described earlier, we anticipate that the clear water pool maintained in the Minorca Pit will influence outflow water chemistry between the fifth and eighth year after tailings deposition begins.

As the pit continues to fill with tailings and process water, conditions within the tailings mass will become less oxidizing. As the environment changes, chemical reactions between process water and tailings will change the composition of tailings pore waters within the Minorca Pit. Consequently, the quality of water observed in plant discharges is not always a good indication of tailings pore water source terms for the Minorca Pit. In order to determine appropriate source terms for each EC, it was necessary to examine the water chemistry resulting from tailings-water interactions in an environment isolated from the atmosphere. Source terms for each EC were determined by the concentration ranges for plant discharges, tailings pore waters collected from Inland's tailings basin, as well as field and laboratory experiments using tailings from Inland's operation.

3.2. Transport in the Biwabik Aquifer

As ground water flows out of the Minorca Pit, dissolved ECs may ultimately be transported to the Missabe Mountain Pit. The geology of the Biwabik Iron Formation is extremely complex with folded and fractured rocks, numerous fault zones, and abandoned mine pits. Each of these features affects the path of ground water flow within the Virginia Horn area.

Due to the complex hydrology, the flow time from the Minorca Pit to the Missabe Mountain Pit has not been quantified. A rigorous analysis of hydraulic conductivities in the area would be extremely difficult to develop due to the unknown frequency, dimensions, and location of fractures through which flow is transmitted. However, some generalizations about ground water flow may be useful.

Ground water flow depends on the hydraulic conductivity of the host rock. Flow through bedrock in the Biwabik Iron Formation has been estimated at 0.7 to 1.8 feet/day (HDR, 1997). At this rate, ground water leaving the Minorca Pit and flowing through intact bedrock will reach the Missabe Mountain Pit (4650 feet away) in 7 to 18 years. If a direct connection exists via fractures in the bedrock, flow times between the two pits may be reduced to months, or even weeks. These generalizations do not precisely quantify the length of time required for Minorca Pit waters to flow to the Missabe Mountain Pit, but rather roughly estimate the upper and lower bounds for the flow time.

To determine the highest possible impact of taconite tailings in the Minorca Pit on Missabe Mountain Pit water quality, it was assumed that the pits are hydrologically connected (i.e. water can flow between them). Furthermore, it was assumed that all of the ground water exiting the Minorca Pit reported to the Missabe Mountain Pit within a short time frame. This assumption has not been verified (MDH, 1998), and may affect the timing of impact on the Missabe Mountain pit. For example, if the flow time between pits is ten years, then the maximum concentrations in the Missabe Mountain Pit presented in this document are projected to occur ten years too soon.

Although ground water from the Minorca Pit may not react as it flows through the aquifer, it is more likely that Minorca Pit waters will react with the host rock and water in the Biwabik aquifer. Such reactions may affect EC levels. Based on the predicted chemistry of water leaving the Minorca Pit, measured water chemistry of the Biwabik aquifer, and minerals known to be present in the Biwabik Iron Formation, geochemical controls on EC levels during transport were determined. These calculations were used to predict the most likely EC levels in the Minorca Pit ground water as it enters the Missabe Mountain Pit.

3.3. Concentration Changes in the Missabe Mountain Pit

Present EC concentrations in Missabe Mountain Pit water are low, and meet drinking water quality standards. Flow from the Minorca Pit will contain elevated EC concentrations and its input to the Missabe Mountain Pit will tend to elevate aqueous concentrations in the pit. The extent to which concentrations are elevated will depend on the extent of dilution and EC removal by chemical reaction.

EC concentrations in Minorca Pit input will be diluted by other inputs to the Missabe Mountain Pit and the water initially present in the Missabe Mountain Pit. The other inputs to the Missabe Mountain Pit are precipitation and ground water from sources other than the Minorca Pit. These dilutional flows will persist over time. Based on the magnitudes of the impacted and dilutional flows and their quality, flow-weighted average input EC concentrations were calculated. These values were used by MDH for their Health Risk Assessment (MDH, 1998). The volume of water stored in the Missabe Mountain Pit will also provide dilution, although the duration of its impact is shorter. This volume and the associated water quality were considered in the calculation of predicted EC levels in this pit.

In addition to dilution, oxidizing conditions in the Missabe Mountain Pit may promote chemical reactions that further decrease EC levels. Therefore, geochemical controls on EC levels in the Missabe Mountain Pit were examined.

These hydrological and geochemical calculations provided a range of EC levels that can be expected in the Missabe Mountain Pit if taconite tailings are disposed of in the Minorca Pit. Since the Missabe Mountain Pit serves as the drinking water supply for the city of Virginia, the expected EC ranges were compared to existing primary and secondary drinking water quality standards. Any exceedence of these standards could result in water supply treatment issues for the city Public Utility.

4. Data Collection, Calculations and Analytical Methods

The methods used during this study have been described in detail elsewhere (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999; Jakel et al., 1998; Jakel and Lapakko, 1999 a, b,c). These methods are summarized here in order to illustrate the approach used in this document.

4.1. Minorca Pit Source Terms

4.1.1. Clear Water Pool Source Term

Operational field measurements of EC levels in waters closely associated with taconite tailings have been collected over a two and a half year period (Berndt and Lapakko, 1997a; Berndt et al., 1998, 1999). Ten water samples were collected at the point at which Inland discharges tailings and process water into the tailings basin. Since ECs are released during taconite processing, EC levels in process waters tend to increase over time. Therefore, concentrations of components which are not removed from solution by chemical precipitation or adsorption (e.g. F, Mo) tend to increase as water recycles through the plant (Berndt and Lapakko, 1997a). If such increases occur, the degree to which they occur depends on the amount of dilutional water (i.e. make-up water) introduced to the processing stream.

During the first two years of tailings deposition in the Minorca Pit, the amount of dilutional water available will be less than that introduced to the tailings basin during the MN DNR/U of MN study. Consequently, EC levels may increase during this time period. However, as the pit fills with tailings, the volume of water in the clear water pool, and therefore water available for recycling, decreases. In order to meet their process needs, Inland will have to supplement this flow with water from other sources. The make-up water required subsequent to year two of tailings deposition is predicted to exceed that during the MN DNR/U of MN study. As long as the source of the make-up water is dilute (e.g. the Enterprise or Sauntry Pits, which are already used as make-up water), EC levels in plant discharges will remain close to present levels. Therefore, plant discharge samples collected during the range-wide study represent the best available empirical estimate of the process water chemistry that will enter the Minorca Pit.

Since the Minorca Pit already contains water, it was necessary to calculate the change in water chemistry that results from mixing process water with that already present (i.e. the clear water pool) as well as ground water and precipitation inputs to the pit. Based on a preliminary tailings disposal plan (Indeco, 1999) and previous estimates of net precipitation and ground water flow (Normaco, 1997; Adams, 1998), two water balances were developed for the Minorca Pit clear water pool over the ten year tailings deposition plan. Changes in clear water pool chemistry were calculated assuming a well-mixed system and also a plug-flow system for both water balances. Thus four calculations provided a range of EC concentrations that can be expected in the clear water pool over the ten year operational time period. Since the clear water pool is anticipated to dominate ground water outflow from the Minorca Pit between deposition years five and eight, EC concentrations calculated for that time period represent the clear water pool source term.

4.1.2. Tailings Pore Water Source Term

Water samples collected from a seep and two wells in the north dike of the tailings basin at Inland represented the closest operational simulation of tailings-water interaction expected in the Minorca Pit (Berndt and Lapakko, 1997a; Berndt et al., 1998, 1999). An additional water sample was collected from a seep in the interior dike late in the study (Berndt et al., 1999). Six operational field measurements of tailings pore water chemistry were also collected from the Snively Pit at US Steel-Minntac (Jakel and Lapakko, 1999a). The Snively Pit represents the only existing case of in-pit taconite tailings disposal in Minnesota. This situation provided data which will be used to represent the potential long-term impacts of in-pit taconite tailings disposal on ground water quality.

Tailings pore water quality was also measured in controlled field experiments. In-pit disposal of Laurentian taconite tailings was simulated using polyethylene tanks (d = 4 ft., h = 10 ft.) at the MN DNR field experimental facility in Hibbing, MN (Berndt and Lapakko, 1997a; Jakel et al., 1998; Jakel and Lapakko, 1999b). Two tanks were filled with tailings and process waters from Inland's operation and left open to the atmosphere. Tailings pore water samples were collected from wells set approximately four feet into the tailings. Sixteen tailings pore water samples were collected over 116 weeks.

Laboratory experiments consisted of tailings from Laurentian ore and process waters collected directly from the tailings discharge pipe at Inland and transferred into two plastic columns (d = 2 in., h = 15 ft.) fit with a sampling port at the base (Berndt and Lapakko, 1997a). The columns were secured in a vertical position and covered with an opaque plastic sheet to eliminate light. These columns simulated conditions that would be expected in the Minorca Pit as it is filled with tailings. Nine water samples were collected periodically over a period of seven months.

Once tailings and process waters have been deposited in a pit, it is likely that process waters will eventually be replaced by precipitation and possibly ground water. In order to simulate these two events, process water in one column was replaced with deionized water to simulate rain water and the other was injected with ground water obtained from local wells drilled into the Biwabik aquifer (Berndt et al., 1998). The resultant water chemistry data from these experiments were used as input for geochemical modeling. These calculations provided additional insight into the reactions controlling EC levels in tailings pore waters.

4.2. Transport in the Biwabik Aquifer

Field measurements of water samples collected from eleven different wells in the Biwabik formation aquifer were analyzed during this study (Berndt et al., 1998). These measurements represented the best estimate of background EC levels in the Biwabik aquifer.

In order to gain additional insight into chemical controls on EC levels in the Biwabik aquifer, geochemical calculations were computed using the Geochemist's Workbench version 2.0 (Bethke, 1994). This model provided a useful tool for performing fluid speciation, mineral reaction, and surface adsorption calculations (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999).

4.3. Concentration Changes in the Missabe Mountain Pit

4.3.1. Dilution

Dilution by non-impacted inputs to the Missabe Mountain Pit (e.g. precipitation and local ground waters), as well as the volume of water stored in the pit will decrease elevated EC levels entering the Missabe Mountain Pit from the Minorca Pit. The Missabe Mountain Pit receives approximately 1.12 billion gallons of water per year from precipitation and ground water (Wiskow, 1998). Of the 1.12 billion gallons of water entering the Missabe Mountain Pit each year, a temporary maximum input from the Minorca Pit of 0.441 billion gallons per year (39%; Adams, 1998) is expected for years five to ten after tailings deposition in the Minorca Pit begins. The remaining 0.679 billion gallons per year represents non-impacted precipitation and ground water from local sources. For the post-reclamation scenario, flow from the Minorca Pit to the Missabe Mountain Pit will decrease to approximately 0.237 billion gallons per year (21%; Adams, 1998), or lower depending on the type of vegetation established on the tailings surface. These interpretations are considered to be the worst case scenarios.

Using the preliminary tailings deposition plan for the Minorca Pit (Indeco, 1999) along with the estimated contributions of ground water from the Minorca Pit (Adams, 1998, 1999) and a generalized water balance for the Missabe Mountain Pit (HDR, 1997; Wiskow, 1998), a multi hypothetical approach was developed for determining the extent to which Minorca Pit outflow will be diluted in the Missabe Mountain Pit. This multi hypothetical approach took into consideration numerous variables including:

1. multiple source term magnitudes,
2. a shift from a clear pool to a tailings pore water source term at deposition year eight,
3. changes in ground water flow rates from the Minorca Pit over time based on the two reclamation conditions,
4. two different lengths of time to represent the "temporary maximum" ground water outflow from the Minorca Pit, and
5. two different interpretations of the Minorca Pit contribution to the flow-weighted average concentration of Missabe Mountain Pit inputs.

This approach resulted in twelve separate calculations of EC concentrations changes in the Missabe Mountain Pit due to continuous dilution over a fifty year time period. In order to simplify the presentation, only the worst case scenarios are presented graphically. However, a summary of all twelve calculations can be found in Appendix 3.

In addition to the variables considered above, this approach was based on three important assumptions, each of which is intended to provide the most conservative analysis. First, it assumes that 100 % of Minorca Pit outflow reports immediately to the Missabe Mountain Pit. As discussed in section 3.2, this assumption can neither be proved nor disproved.

Second, tailings deposition into the Minorca Pit is assumed to begin in 2004. This is approximately when Inland anticipates running out of room in their existing tailings basin. 2004 is also a convenient year because it implies that ground water outflow from the Minorca Pit would begin in 2009, the year that the water levels in the Missabe Mountain and Rouchleau Pits are expected to breach the earthen berm between them. At this time, the volume of the Missabe Mountain Pit below the berm has been calculated to be 5.6 billion gallons (Wiskow, 1998). Thus, 5.6 billion gallons can be used as the starting, dilutional, volume of water in the Missabe Mountain Pit just before inflow from the Minorca Pit arrives. It is important to remember that the years selected here may not correspond to the final disposal plan, and therefore, must be treated as a hypothetical situation rather than fact.

Third, despite the fact that the water elevation in the Missabe Mountain and Rouchleau Pits will breach the berm separating them at some point during Inland's disposal plan, it was assumed that there would be no mixing of water between the two pits. Thus, an initial pit volume of 5.6 billion gallons was used rather than the total combined volume of 8 billion gallons. This is not entirely realistic, however, it reduces the amount of dilutional water available within the Missabe Mountain Pit. Consequently, it yields a conservative estimate of EC concentration changes due to inflow from the Minorca Pit.

4.3.2. Geochemical Reactions

Water quality data were collected from operational sites as well as field and laboratory experiments, which simulated the reaction environment in the Missabe Mountain Pit. Operational surface water measurements were collected from the plant discharge to the tailings basin and from the reclaim barge where clarified water is recycled back to the plant (Berndt and Lapakko, 1997a, b; Berndt et al., 1998, 1999). Tailings basin surface water and Missabe Mountain Pit water are similar in that they both receive dilutional water from precipitation and surface runoff. Furthermore, both waters are exposed to the atmosphere, and therefore, have similar chemical environments. Thus, geochemical controls on EC levels in the tailings basin will likely represent those in the Missabe Mountain Pit. As an additional measure of confidence in these assumptions, water samples from five depths in the Missabe Mountain Pit were collected in March, 1999 (Lapakko and Jakel, 1999).

Chemical controls in surface waters associated with taconite tailings were also examined in field and laboratory experiments. The field tank experiments were designed such that approximately 4.5 feet of surface water stood above the taconite tailings, exposed to the atmosphere (Berndt and Lapakko, 1997a; Jakel et al., 1998; Jakel and Lapakko, 1999b). This situation simulated conditions in the tailings basin, and provided information regarding the persistence of EC's in these waters.

In order to better define the persistence of manganese in the Missabe Mountain Pit, batch experiments were conducted using waters obtained from monitoring well #6 at Inland and the Missabe Mountain Pit (Jakel et al., 1999c). Five separate dilutions were mixed in 2.5 gal buckets with a small hole punched in the lids to allow air transfer and stored at approximately 46 °F. These experiments were intended to simulate a situation where water with elevated EC levels mixed with water in the Missabe Mountain Pit. That is, they examined reactions in mixtures of water exiting a tailings impoundment under reducing conditions and water from the Missabe Mountain Pit.

4.4. Chemical Analyses

Each water sample was analyzed for approximately 82 inorganic parameters including pH, alkalinity, temperature, and major and trace cations and anions. Temperature and pH (Beckman model 11 meter with Ross model 8165 combination electrode) were determined on site, while alkalinity titrations (APHA et al., 1995) were conducted at the MN DNR laboratory in Hibbing, MN. The levels of cations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer mode-SCIEX-Elan 5000) while anions were measured using ion chromatography (IC, Dionex Ion Chromatograph fitted with GP40 gradient pump, CD20 conductivity detector, and two AS4A anion exchange columns) at the U of MN.

5. EC Summaries

Source terms, transport terms, and expected levels in the Missabe Mountain Pit for each of the four EC's are presented in the following discussion. These values are also compared to primary and secondary drinking water quality standards (Table 1). Finally, potential treatment issues for the Virginia Public Utility are considered

5.1. Manganese

5.1.1. Manganese Source Term

Manganese is, released by dissolution of manganese-bearing minerals present in the tailings (Mattson, 1996). Based on the data collected during the range-wide study, a manganese source term range of 0.01 mg/L to 7 mg/L was selected for the Minorca Pit (Table 1). Manganese concentrations in oxygenated waters, which are representative of the **clear water pool** in the Minorca Pit, were at the lower end of this range. The oxygenated waters sampled include existing tailings basin surface waters, oxygenated waters in field tank and laboratory batch experiments, and water from abandoned open pits, including the Missabe Mountain Pit. These low levels are due to the unstable nature of dissolved manganese in oxygenated waters resulting in oxidation of manganese to MnO_2. Since water contained in the Minorca Pit clear water pool will be well oxygenated, manganese levels in the waters exiting the Minorca Pit through the clear water pool are expected to be approximately 0.01 mg/L.

Manganese levels in **tailings pore waters** during the range-wide study ranged from 0.05 mg/L to 7 mg/L. The 0.05 mg/L value was representative of manganese concentrations observed in waters associated with tailings from the Laurentian Pit (e.g. column and tank experiments). It is likely that the tailings that Inland has proposed to dispose of in the Minorca Pit will be compositionally similar to these tailings. However, the ore body composition may vary, and therefore, there is no guarantee that manganese concentrations will remain as low as 0.05 mg/L. The upper end of this range, 7 mg/L, was defined by the maximum manganese concentration observed in the wells on the north dike of Inland's tailings basin. This value may have been elevated by factors not anticipated to be influential in the Minorca Pit (e.g. incorporation of organic matter or other acid generating material with the tailings).

5.1.2. Manganese Transport in the Biwabik Aquifer

The most conservative estimate of manganese levels in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the manganese transport term will equal the source term from the Minorca Pit. That is, the manganese transport term will range from 0.01 mg/L to 7 mg/L.

Despite this conservative assumption, it is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified. However, it was accounted for in the calculation of dilution in the Missabe Mountain Pit as the net dilution of Minorca Pit flow by water entering the Missabe Mountain Pit (i.e. the flow-weighted average input concentration to the Missabe Mountain Pit).

If Minorca Pit ground waters do mix with ground water already present in the aquifer, geochemical processes can be expected to control manganese levels during transport. The relatively high levels of alkalinity found in the aquifer suggested that manganese levels may be controlled by the solubility of a manganese carbonate phase (e.g. rhodochrosite). Geochemical calculations based on the observed water chemistry in an environment isolated from the atmosphere indicated that manganese levels could not exceed 1 mg/L in the Biwabik aquifer if these levels are controlled by rhodochrosite solubility (Lapakko and Jakel, 1999).

5.1.3. Manganese in the Missabe Mountain Pit

In addition to water from the Minorca Pit, the Missabe Mountain Pit will receive input from precipitation and other ground water sources. It is estimated that Minorca Pit outflow will constitute a temporary maximum of 39 percent of this total input (Adams, 1998). At this temporary maximum, manganese levels in the Missabe Mountain Pit would be 1.7 mg/L based on dilution alone. This assumes that manganese levels in other input waters are similar to that of the Biwabik aquifer (It should be noted that manganese concentrations in precipitation will be lower than this level). This calculation further assumes that the water in the Rouchleau Pit does not provide dilution in the Missabe Mountain Pit. Thus, it is likely that manganese levels in the Missabe Mountain Pit will be less than 1.7 mg/L.

After the site has been reclaimed flow from the Minorca Pit to the Missabe Mountain Pit will decrease (Adams, 1998). This would increase dilution in the Missabe Mountain Pit, and manganese concentrations could potentially be reduced to less than 1.6 mg/L once forest vegetation becomes established.

In addition to dilution, manganese concentrations in the Missabe Mountain Pit will be reduced by oxidation and subsequent precipitation of manganese oxyhydroxide, which occurs commonly in oxygenated natural waters (Stumm and Morgan, 1981; Langmuir, 1997). Oxidation is the mechanism responsible for maintaining the low manganese concentrations in large abandoned open pits across the range reported by Pierce and Tomcko (1989) and in surface waters associated with taconite tailings (Berndt et al., 1999; Jakel et al., 1998; Jakel and Lapakko, 1999b). Operational measurements and field and laboratory experiments indicate that manganese levels are unlikely to exceed 0.01 mg/L in oxygenated waters associated with taconite tailings (Figure 3; Berndt et al., 1999; Jakel et al., 1998; Jakel and Lapakko, 1999b,c; Pierce and Tomcko, 1989).

The presence of oxygenated water in the Missabe Mountain Pit was reported in previous work (MDH, 1998) and verified by measurements in this study (Lapakko and Jakel, 1999). Under these conditions, thermodynamics predict equilibrium manganese concentrations of at least three orders of magnitude below those measured during this study. Oxidation of manganese and precipitation of manganese oxyhydroxide was verified as operative in a laboratory experiment conducted in the course of this study (Jakel and Lapakko, 1999c). The experiment was conducted using a mixture of water exiting a tailings impoundment under reducing conditions and water from the Missabe Mountain Pit. For mixtures with initial manganese concentrations less than 2 mg/L, manganese concentrations decreased to less than 0.01 mg/L within fourteen weeks. The retention time for water in the Missabe Mountain Pit is approximately twenty two times longer than the time required for this reaction to occur. Therefore, oxidation is expected to control manganese levels within the Missabe Mountain Pit below the secondary standard.

5.1.4. Comparison to Water Quality Standards

Manganese concentrations will meet the health-based water quality standard determined for this project (1.3 mg/L; MDH, 1998) as well as primary (0.1 mg/L) and secondary (0.05 mg/L) drinking water quality standards at the Virginia water supply intake (Figure 3). This conclusion was reached using the maximum manganese source concentration (7 mg/L), assuming no removal in the Biwabik aquifer, using the minimum projected dilution and chemical reactions within the Missabe Mountain Pit. Thus, manganese concentrations in the Missabe Mountain Pit will decrease to meet these standards largely as a result of chemical reaction.

Several factors which may further mitigate manganese concentrations at the Virginia water supply intake were ignored in the analysis presented above. First, the source concentration may be considerably lower than the 7 mg/L value used, as low as 0.05 mg/L based on field experiments. Furthermore, manganese levels in the Snively Pit tailings averaged 1.3 mg/L, indicating that long-term manganese concentrations will not increase over time. Second, it is not unlikely that manganese concentrations will decrease during flow through the Biwabik aquifer due to dilution and/or chemical reaction. Third, dilution will likely reduce manganese concentrations to lower levels in the Missabe Mountain Pit.

5.1.5. Treatment Issues for the Public Utility

The Virginia Public Utility currently relies on sedimentation basins and pressure sand filters to remove particulate matter from their water supply (Wiskow, 1998). However, they are testing a membrane filtration system on a pilot-scale for possible future use. They are also considering a gravity filtration system. These systems are expected to be able to remove manganese as long as the input concentration is below 0.05 mg/L, the secondary water quality standard. Manganese concentrations in the Missabe Mountain Pit presently meet water quality standards, and it is predicted that these standards will be met if tailings are disposed in the Minorca Pit. Consequently, no treatment issues are anticipated.

5.2. Fluoride

5.2.1. Fluoride Source Term

Fluoride is released from soluble fluoride phases produced as a result of the induration and scrubbing processes during taconite processing (Berndt and Lapakko, 1997a; Berndt et al., 1998, 1999; Jakel and Lapakko, 1999d). Based on the data collected during the range-wide study, a fluoride source term range of 1 to 6 mg/L was selected (Table 1). Analyses of plant discharges and calculation of dilution in the Minorca Pit clear water pool led to a **clear water pool source term** of 6 mg/L. Since fluoride is released during taconite processing, fluoride levels in plant discharges may increase if plant process waters are not supplemented with make-up water from dilute sources (e.g. Sauntry and Enterprise Pits). However, the preliminary tailings disposal plan (Indeco, 1999) indicates that substantial amounts of make-up water will be required after the first two years of tailings deposition in the Minorca Pit.

Fluoride levels in **pore waters** associated with Inland's tailings during the range-wide study ranged from 1 mg/L to 6 mg/L. Unlike the other three ECs, the range of fluoride concentrations in tailings pore waters appeared to be normally distributed. Therefore, it is appropriate to use an average concentration as a refined source term. Based on sixty two tailings pore water samples collected from field and laboratory experiments, as well as measurements taken at Inland's tailings basin, the average fluoride concentration in tailings pore waters was 3.2 mg/L with a standard deviation of 1.2. This value represents the most likely tailings pore water source term for fluoride in the Minorca Pit. The upper end of the range of observed fluoride concentrations (6 mg/L) was typical of tailings pore analyses from field tank experiments. This value will be considered the worst case scenario in this assessment.

5.2.2. Fluoride Transport in the Biwabik Aquifer

The most conservative estimate of fluoride levels in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the fluoride transport term will range from 1 mg/L to 6 mg/L. Despite this conservative assumption, it is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified. However, it was accounted for in the calculation of dilution in the Missabe Mountain Pit as the net dilution of Minorca Pit flow by water entering the Missabe Mountain Pit (i.e. the flow-weighted average input concentration to the Missabe Mountain Pit).

If Minorca Pit ground waters do mix with ground water already present in the aquifer, geochemical processes can be expected to control fluoride levels during transport. Fluoride levels would be expected to remain below the fluorite solubility limit. Using the solubility constant determined by Berndt et al. (1999) and calcium levels in the Biwabik aquifer (33 to 70 mg/L; Berndt et al., 1998), the fluoride concentrations in the aquifer could be in the range of 4.3 to 6.2 mg/L.

5.2.3. Fluoride in the Missabe Mountain Pit

Within the Missabe Mountain Pit fluoride concentrations will be diluted by surficial and local ground water inputs to the pit. At the temporary maximum input of 39 percent from the Minorca Pit, the maximum calculated fluoride concentration in the Missabe Mountain Pit will be 1.6 mg/L (Figure 4) assuming a fluoride concentration in other ground water inputs is similar to that of the Biwabik aquifer (i.e. approximately 0.28 mg/L; Berndt et al., 1998). It should be noted, however, that fluoride concentrations in precipitation will be lower than this level. This calculation further assumes that the water in the Rouchleau Pit does not provide dilution in the Missabe Mountain Pit. Thus, it is likely that fluoride levels in the Missabe Mountain Pit will be less than 1.6 mg/L. After the Minorca Pit has been reclaimed, dilution in the Missabe Mountain Pit will result in fluoride levels lower than 1.5 mg/L.

Once the water exiting the Minorca Pit is dominated by tailings pore water, fluoride concentrations in flow from the Minorca Pit will decrease. Based on the more refined source term for this period, 3 mg/L, yielding a maximum fluoride concentration of 0.9 mg/L in the Missabe Mountain Pit. Once final reclamation is in place flow from the Minorca Pit will decrease and, consequently, so will average concentrations for the water input to the Missabe Mountain Pit.

5.2.4. Comparison to Drinking Water Quality Standards

At maximum ground water input from the Minorca Pit, fluoride levels in the Missabe Mountain Pit are expected to be lower than both the primary and secondary drinking water standards of 4 and 2 mg/L, respectively. Using fluoride concentrations of 6 mg/L for the source term and 0.28 mg/L for other inputs to the Missabe Mountain Pit yields a maximum fluoride concentration of 1.6 mg/L (Figure 4).

5.2.5. Treatment Methods Used at the Virginia Public Utility

Currently, the Virginia Public Utility fluoridates the water supply for the city of Virginia (Wiskow, 1998). Fluoride levels in water entering the public utility are monitored an a monthly basis. If fluoride levels were to increase in the Missabe Mountain Pit due to disposal of taconite tailings in the Minorca Pit, additional fluoride in the water supply may not be necessary. If fluoride levels in the Missabe Mountain Pit were to increase rapidly, water entering the utility may require more frequent monitoring intervals.

5.3. Molybdenum

5.3.1. Molybdenum Source Term

The only potential mechanisms of molybdenum release that have been identified at present are the breakdown of lubricants containing MoS_2 and corrosion of grinding media used during taconite processing. Based on the data collected during the MN DNR/U of MN study, a molybdenum source term range of 1 to 130 ug/L was selected (Table 1). The upper end of this range was calculated based on dilution of process water discharged from the plant in the Minorca Pit clear water pool. This represents a short-term, **clear water pool source term** that is appropriate to use between the fifth and eighth years of operation at the Minorca Pit.

Molybdenum levels in **tailings pore waters** during the range-wide study ranged from 1 ug/L to 45 mg/L. The upper end of this range represented analyses of tailings pore waters from the field and laboratory experiments (i.e. process water columns). The lower end of this range was defined by tailings pore waters from wells and seeps around Inland's tailings basin. Since the molybdenum release is the result of operational processes, the source term is expected to decrease to extremely low levels (as seen in the Snively Pit) after site closure.

5.3.2. Molybdenum Transport

The most conservative estimate of molybdenum levels in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the manganese transport term will range from 1 ug/L to 130 ug/L. Despite this conservative assumption, it is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified. However, it was accounted for in the calculation of dilution in the Missabe Mountain Pit as the net dilution of Minorca Pit flow by water entering the Missabe Mountain Pit (i.e. the flow-weighted average input concentration to the Missabe Mountain Pit).

If Minorca Pit ground waters do mix with ground water already present in the aquifer, geochemical processes can be expected to control molybdenum concentrations during transport. Geochemical calculations indicated that molybdenum may be attenuated by iron oxides in the aquifer depending on the pH of water in the aquifer. Based on measurements from wells in the Biwabik formation, the pH of these waters ranges from 6.7 to 8.1. In this pH range, molybdenum levels in the aquifer are expected to decrease during transport through the aquifer, although the extent to which this will occur cannot be quantified. In general, molybdenum adsorption to iron oxides is most likely to occur during the period of maximum flow from the Minorca Pit (e.g. prior to reclamation of the site). This is also the time period in which dilution will have the least impact on molybdenum levels in the Missabe Mountain Pit.

5.3.3. Molybdenum in the Missabe Mountain Pit

Molybdenum concentrations from the Minorca Pit to the Missabe Mountain Pit will be diluted by inputs from other sources. At the temporary inflow maximum, the maximum molybdenum concentrations in the Missabe Mountain Pit may be as high as 25 ug/L (Figure 5), assuming molybdenum concentrations in inputs other than that from the Minorca Pit are similar to those of the Biwabik aquifer (e.g. approximately 0.24 ug/L; Berndt et al., 1998). It should be noted, however, that molybdenum concentrations in precipitation will be lower than this level. This calculation further assumes that the water in the Rouchleau Pit does not provide dilution in the Missabe Mountain Pit. Thus, it is likely that molybdenum levels in the Missabe Mountain Pit will be less than 25 ug/L.

The maximum molybdenum level in the Missabe Mountain Pit is reached during the time period when the clear water pool dominates outflow from the Minorca Pit (i.e. clear water pool source term = 130 ug/L). As the pit continues to fill with tailings, the source term will become dominated by tailings pore waters, reducing the source term to 45 ug/L. Consequently, molybdenum concentrations in the Missabe Mountain Pit will decrease to less than 22 ug/L. No chemical controls are expected to influence molybdenum levels in the Missabe Mountain Pit.

5.3.4. Comparison to Water Quality Standards

Even at maximum ground water input from the Minorca Pit, molybdenum levels in the Missabe Mountain Pit are expected to be lower than the primary drinking water standard of 30 ug/L (Figure 5). Consequently, no treatment issues at the Virginia Public Utility are expected to arise.

5.4. Arsenic

5.4.1. Arsenic Source Term

Arsenic is believed to be released by the oxidation of trace amounts of pyrite present in the tailings. Based on analyses of Inland's plant discharges and tailings pore waters an arsenic source term range of 0.1 to 7 ug/L was selected (Table 1). The lowest arsenic levels were found in the north seep at Inland. These values are actually lower than those measured in the Biwabik aquifer (Berndt et al., 1998) and the Missabe Mountain Pit (Lapakko and Jakel, 1999). The upper end of this range was defined by a calculated value for the **clear water pool** and a few high values observed in the wells at Inland and the "rain water" column experiments. Despite this wide range of values, the majority of **tailings pore waters** sampled during this study contained 2 - 4 ug/L arsenic.

5.4.2. Arsenic Transport

The most conservative estimate of arsenic levels in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the arsenic transport term will range from 0.1 ug/L to 7 ug/L.

Despite this conservative assumption, it is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified. However, it was accounted for in the calculation of dilution in the Missabe Mountain Pit as the net dilution of Minorca Pit flow by water entering the Missabe Mountain Pit (i.e. the flow-weighted average input concentration to the Missabe Mountain Pit).

If Minorca Pit ground waters do mix with ground water already present in the aquifer, geochemical processes can be expected to control arsenic levels during transport. Geochemical calculations indicated that arsenic will be attenuated by iron oxides in the aquifer 2 to 13 times longer than nonreactive elements chloride and bromide. Arsenic levels in the aquifer are expected to decrease during transport through the aquifer, although the extent to which this will occur cannot be quantified. In general, arsenic adsorption to iron oxides is most likely to occur during the period of maximum flow from the Minorca Pit (e.g. prior to reclamation of the site). This is also the time period in which dilution will have the least impact on arsenic levels in the Missabe Mountain Pit.

5.4.3. Arsenic in the Missabe Mountain Pit

Arsenic levels in the Missabe Mountain Pit are expected to be 2.2 ug/L at the temporary inflow maximum from the Minorca Pit (Figure 6), assuming concentrations in the dilutional water similar to those of the Biwabik aquifer (e.g. approximately 0.5 ug/L; Berndt et al., 1998). It should be noted, however, that arsenic concentrations in precipitation will be lower than this level. This calculation further assumes that the water in the Rouchleau Pit does not provide dilution in the Missabe Mountain Pit. Thus, it is likely that arsenic levels in the Missabe Mountain Pit will be less than 2.2 ug/L. After the site has been reclaimed, flow from the Minorca Pit to the Missabe Mountain Pit will decrease (Adams, 1998) and arsenic concentrations in the Missabe Mountain Pit will decrease to less than 2 ug/L.

Arsenic levels in the Missabe Mountain Pit may also be reduced by chemical and/or biological oxidation and subsequent precipitation of iron oxides. Geochemical calculations indicate that arsenic will tend to co-precipitate with iron oxides (Berndt, 1998), further reducing arsenic levels in the Missabe Mountain Pit.

5.4.4. Comparison to Water Quality Standards

Even at maximum ground water input from the Minorca Pit, arsenic levels in the Missabe Mountain Pit are expected to be considerably lower than the primary drinking water standard of 50 ug/L (Figure 6). However, the US EPA is expected to lower this standard by the year 2001. Arsenic levels in the Missabe Mountain Pit are anticipated to meet the future drinking water quality standard if it is reduced to the range of 5 - 10 ug/L. Therefore, no treatment issues at the Virginia Public Utility are expected to arise.

6. Conclusions

6.1. Worst Case Scenario

Outflow from the Minorca Pit will have EC levels which are elevated relative to those presently in the Missabe Mountain Pit and Biwabik aquifer. Minorca Pit flow which enters the Missabe Mountain Pit will elevate EC levels in the Missabe Mountain Pit above those presently observed. However, based on evaluation of the worst case scenario, dilution and geochemical controls are expected to maintain EC levels in the Missabe Mountain Pit below existing health-based and drinking water quality standards.

Manganese levels in Missabe Mountain Pit input waters are expected to meet the health-based standard set by the MDH (1998) and the secondary drinking water quality standard due to chemical reactions in the pit. Oxidizing conditions in the Missabe Mountain Pit are expected to promote manganese removal which will reduce manganese concentrations to levels presently found in the pit.

Fluoride and molybdenum levels are not expected to exceed the drinking water quality standards in the Missabe Mountain Pit. No geochemical controls are expected to reduce these levels during transport in the Biwabik aquifer. However, dilution of Minorca Pit inputs to the Missabe Mountain Pit is expected to be sufficient to reduce fluoride and molybdenum concentrations to levels lower than the drinking water quality standards but higher than those presently found in the Missabe Mountain Pit.

Dilution is also expected to maintain arsenic concentrations in the Missabe Mountain Pit to levels lower than the drinking water quality standards but higher than those presently found in the Missabe Mountain Pit. Arsenic concentrations in the Missabe Mountain Pit may be reduced further by co-precipitating with iron oxyhydroxides.

6.2. Mitigating Factors to the Worst Case Scenario

The above assessment was based on the worst case scenarios for each EC. However, several mitigating factors exist that would tend to decrease EC levels actually observed in the Missabe Mountain Pit:

1. Clear water pool source terms were determined assuming the maximum EC levels measured in plant discharges to the tailings basin during the MN DNR/U of MN study. However, discharge concentrations may decrease after several years of tailings deposition in the Minorca Pit because process waters needs will have to be met with make-up water from other sources (presumable the Sauntry or Enterprise Pits). This is a particularly important consideration in assessing fluoride and molybdenum concentrations in the clear water pool.

2. During the time period when the clear water pool dominates outflow from the Minorca Pit (years 5 - 8), our calculations assumed that the clear water pool represented 100% of the outflow. It is more likely that ground water outflow during that time period will be a mixture of water from the clear water pool and tailings pore waters. This will tend to decrease the magnitude of the molybdenum source term (130 ug/L in the clear water pool, 45 ug/L in tailings pore waters). However, it would tend to increase the manganese source term (<0.01 mg/L in the clear water pool, 7 mg/L in tailings pore waters).

3. The manganese tailings pore water source term (7 mg/L) was based on the maximum measured concentration in wells along the existing tailings basin. In the absence of acid generating materials (e.g. organic matter) in the tailings mass, manganese concentrations in tailings pore waters are likely to be less than 1 mg/L.

4. Minorca Pit ground waters were assumed to flow through the Biwabik aquifer to the Missabe Mountain Pit with no interaction with existing ground water or host rock. However, it is likely that manganese, molybdenum, and arsenic will be attenuated to some degree in the aquifer. Based on geochemical calculations, manganese levels in the aquifer are unlikely to exceed 1 mg/L. Molybdenum and arsenic attenuation could not be quantified, but will decrease due to adsorption to iron oxides present in the host rock.

5. A value of 39% was used to represent the Minorca Pit contribution to the flow-weighted average EC concentrations in the net inputs to the Missabe Mountain Pit. This value was decreased to 28% after additional interpretation (Adams, 1999), which would decrease the impact that outflow from the Minorca Pit would have on water quality in the Missabe Mountain Pit.

6. Dilution within the Missabe Mountain Pit did not include the volume of water in the Rouchleau Pit nor precipitation and ground water inputs to that pit. Depending on the

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timing of tailings disposal in the Minorca Pit, it is likely that the water level in these two pits will have risen above the berm currently separating them. Therefore, the volume of dilutional water available will be larger than that used to assess the worst case scenario.

7. The water balance used to calculate flow-weighted average EC concentrations did not distinguish between precipitation and ground water. Therefore, it was assumed that all inputs, other than flow from the Minorca Pit, had EC levels similar to those measured in the Biwabik aquifer. This assumption overestimates EC levels in the net inputs to the Missabe Mountain Pit, since precipitation does not contain ECs.

6.3. Recommendations

1. Water quality of plant discharges into the Minorca Pit should be monitored. If EC levels in these waters become elevated, Inland will need to make adjustments to maintain concentrations in the Minorca Pit at acceptable levels. This may be particularly important for molybdenum in the clear water pool. Whereas rigorous analysis of acceptable discharge levels has not been conducted, the values used in this study resulted in Missabe Mountain Pit concentrations which met drinking water quality standards. Therefore, they represent one option for acceptable plant discharge levels.

2. Tailings pore water quality in the Minorca Pit should be monitored in order to insure accuracy of the predicted source terms. Conditions in the Minorca Pit may not be fully represented by those encountered in Inland's tailings [illegible] or controlled experiments. Natural mineralogical variations in tailings composition or unforeseen changes in taconite processing methods could result in elevated levels of the four EC's or other elements in the Minorca Pit. Variables such as these could not be accounted for in this analysis.

3. Conditions in the Missabe Mountain Pit should be monitored to ensure that oxidizing conditions are maintained as the water level in this pit rises. If pit waters become reducing, manganese removal by natural processes may be compromised.

4. Monitoring of incoming water to the water treatment plant should continue and may require an increased sampling frequency. This will be particularly important for fluoride, since fluoridation adjustments will be necessary if fluoride levels in the Missabe Mountain Pit increase.

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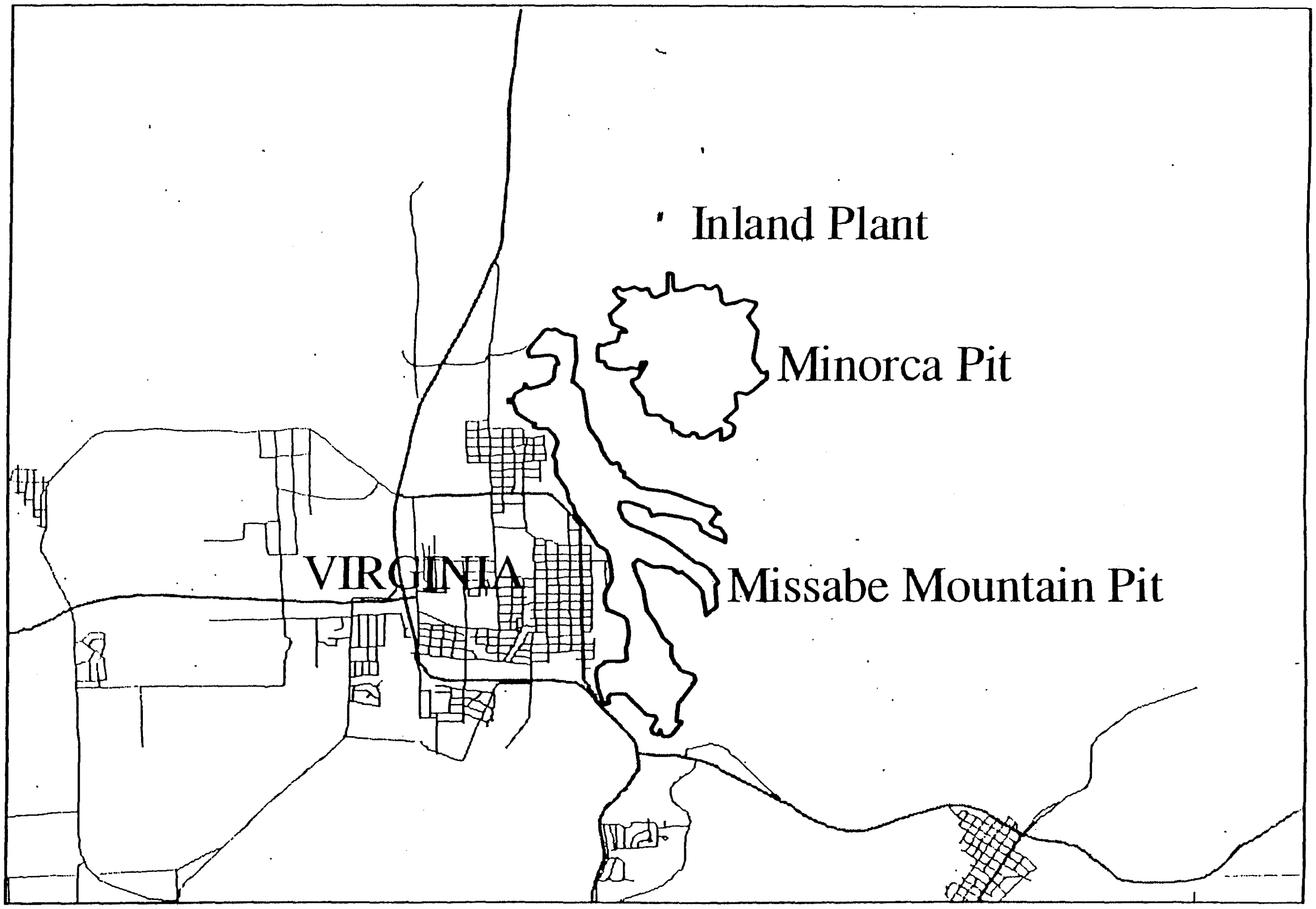

Figure 1. The Missabe Mountain Pit is located approximately one half mile south of the Minorca Pit. This map designates a complex of interconnected pits (including the Columbia, Commodore, Missabe Mountain, Shaw-Moose, and Rouchleau) as the Missabe Mountain Pit.

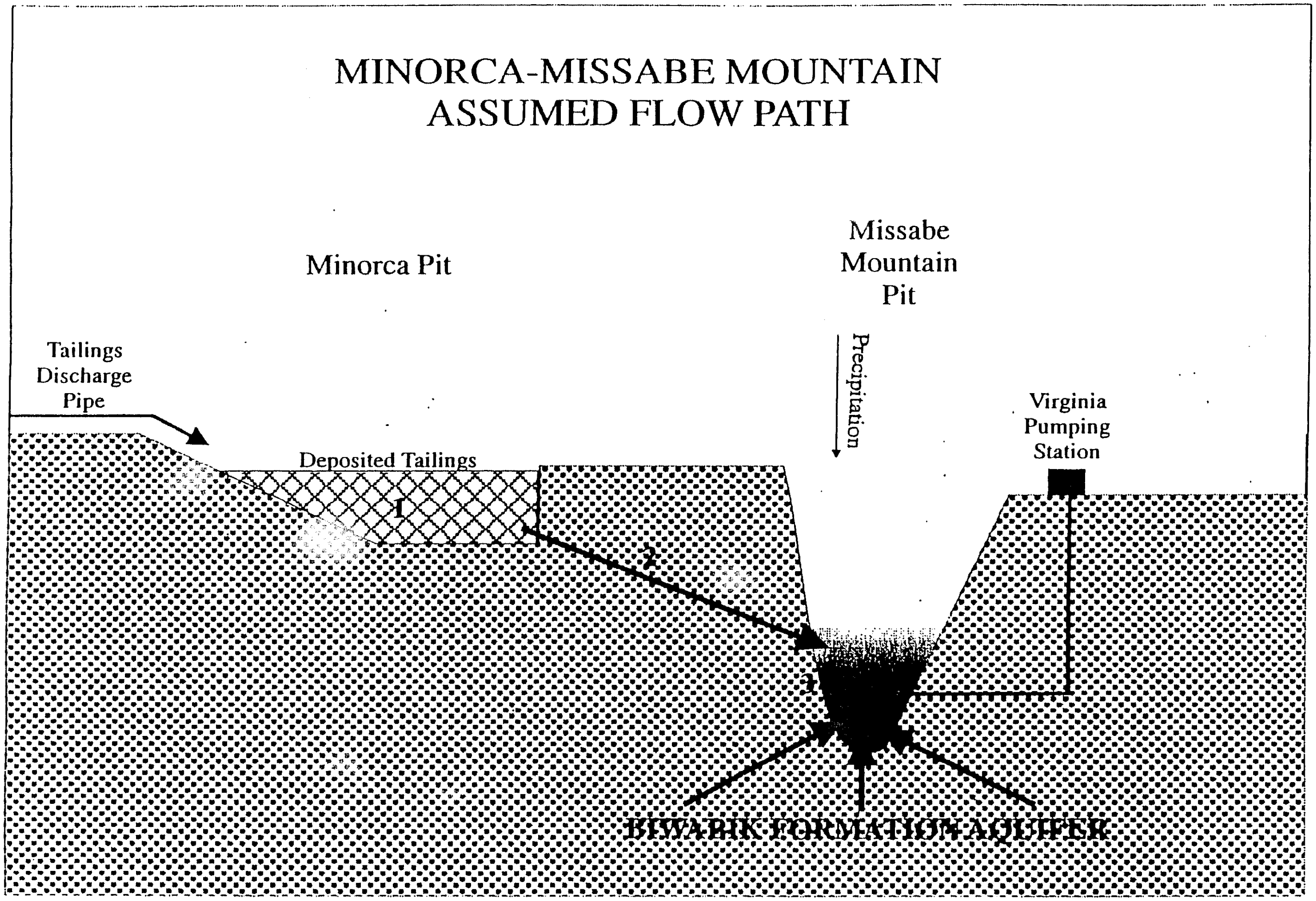

Figure 2. In order to evaluate potential impacts on water quality in the Missabe Mountain Pit, a direct connection with the Minorca Pit was assumed. EC concentrations were evaluated at four points along this flow path; 1) water exiting the Minorca Pit, 2) transport through the aquifer, 3) flow-weighted average concentrations of inputs to the Missabe Mountain Pit, and 4) dilution and chemical reactions within the Missabe Mountain Pit.

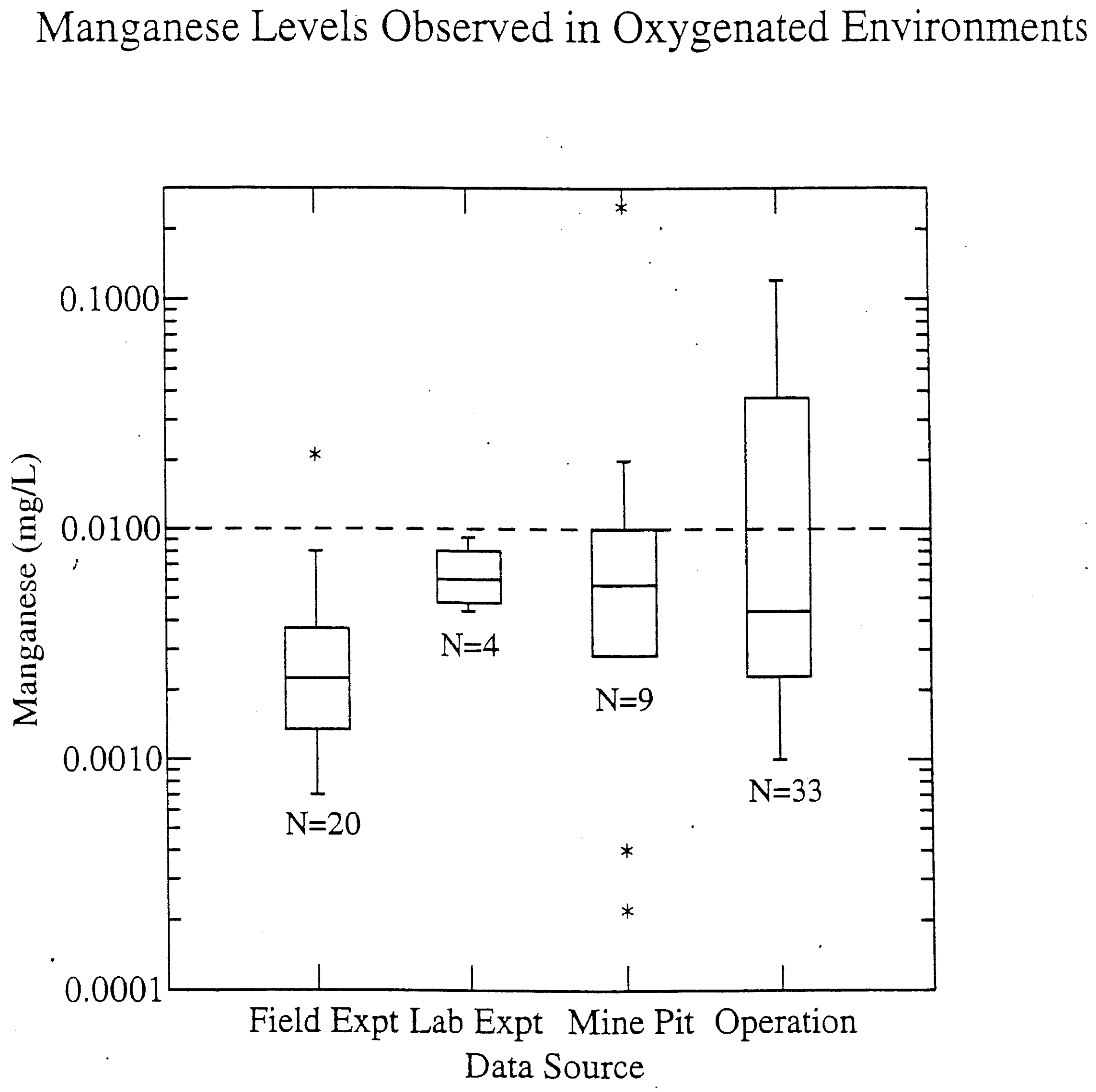

Figure 3. Manganese levels in the Missabe Mountain Pit are expected to be less than 0.01 mg/L (dashed line). Low levels of dissolved manganese are observed in surface waters associated with taconite tailings and in mine pits in northern Minnesota due to chemical oxidation of dissolved manganese, and subsequent precipitation of solid manganese oxide, MnO_2.. A few elevated manganese levels were observed in tailings basins during extended periods of ice cover (e.g. winter).

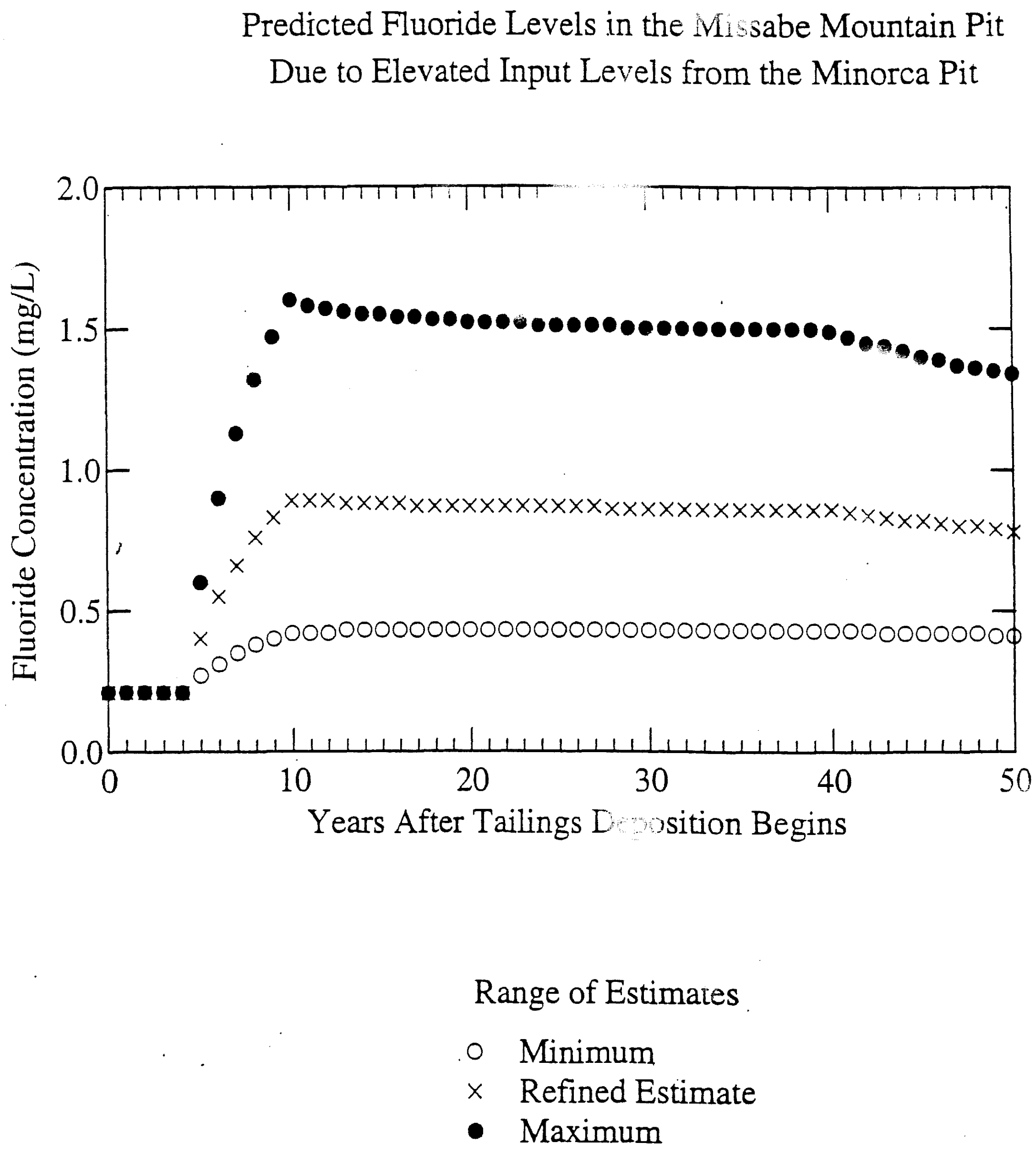

Figure 4. Although no geochemical controls are expected for fluoride in the Missabe Mountain Pit, dilution by the volume of water stored within the pit will be sufficient to reduce fluoride levels below the primary and secondary drinking water quality standards (4 mg/L and 2 mg/L, respectively).

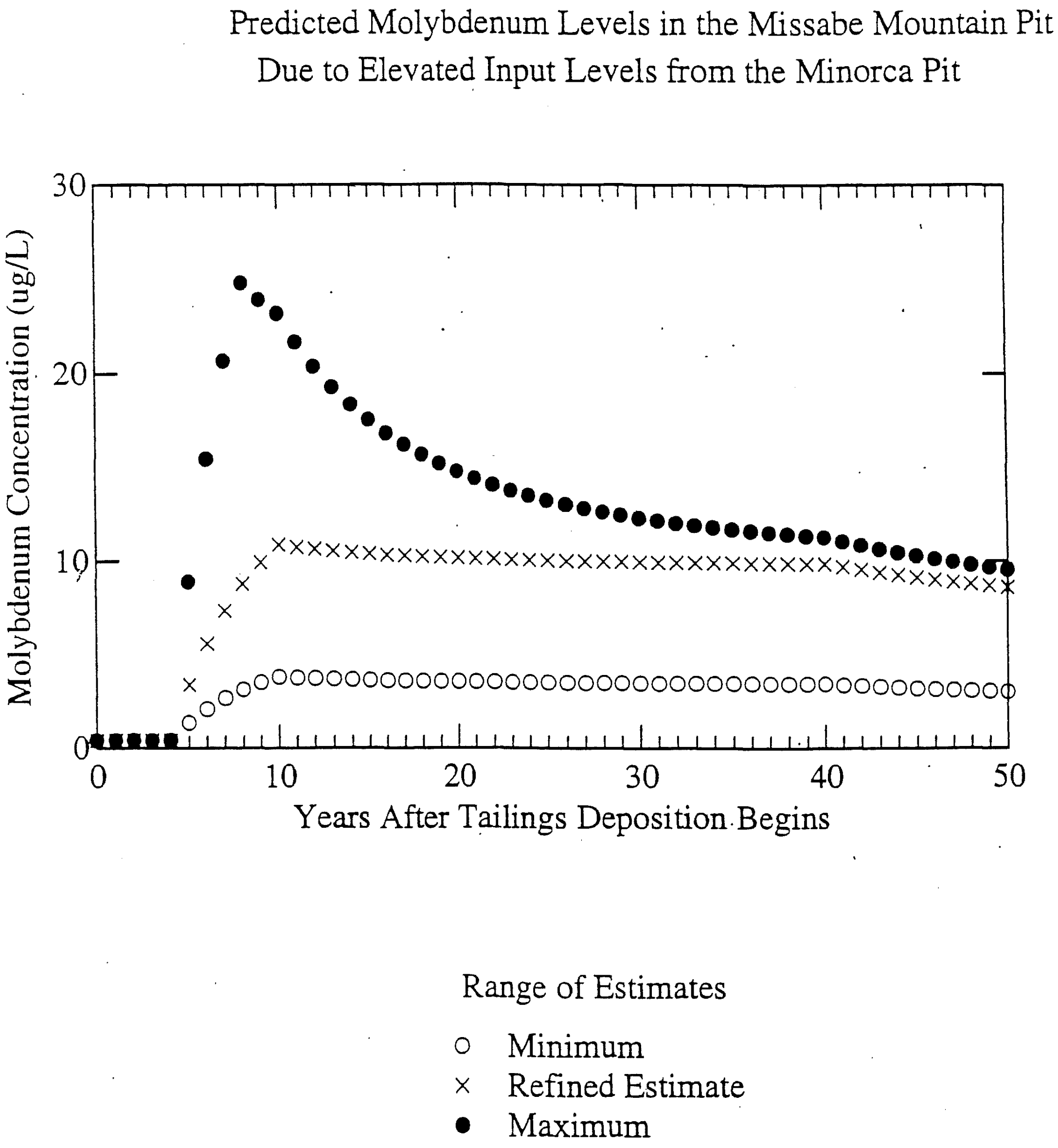
Predicted Molybdenum Levels in the Missabe Mountain Pit Due to Elevated Input Levels from the Minorca Pit

Figure 5. Although no geochemical controls are expected for molybdenum in the Missabe Mountain Pit, dilution by the volume of water stored within the pit will be sufficient to reduce fluoride levels below the drinking water quality standard (30 ug/L).

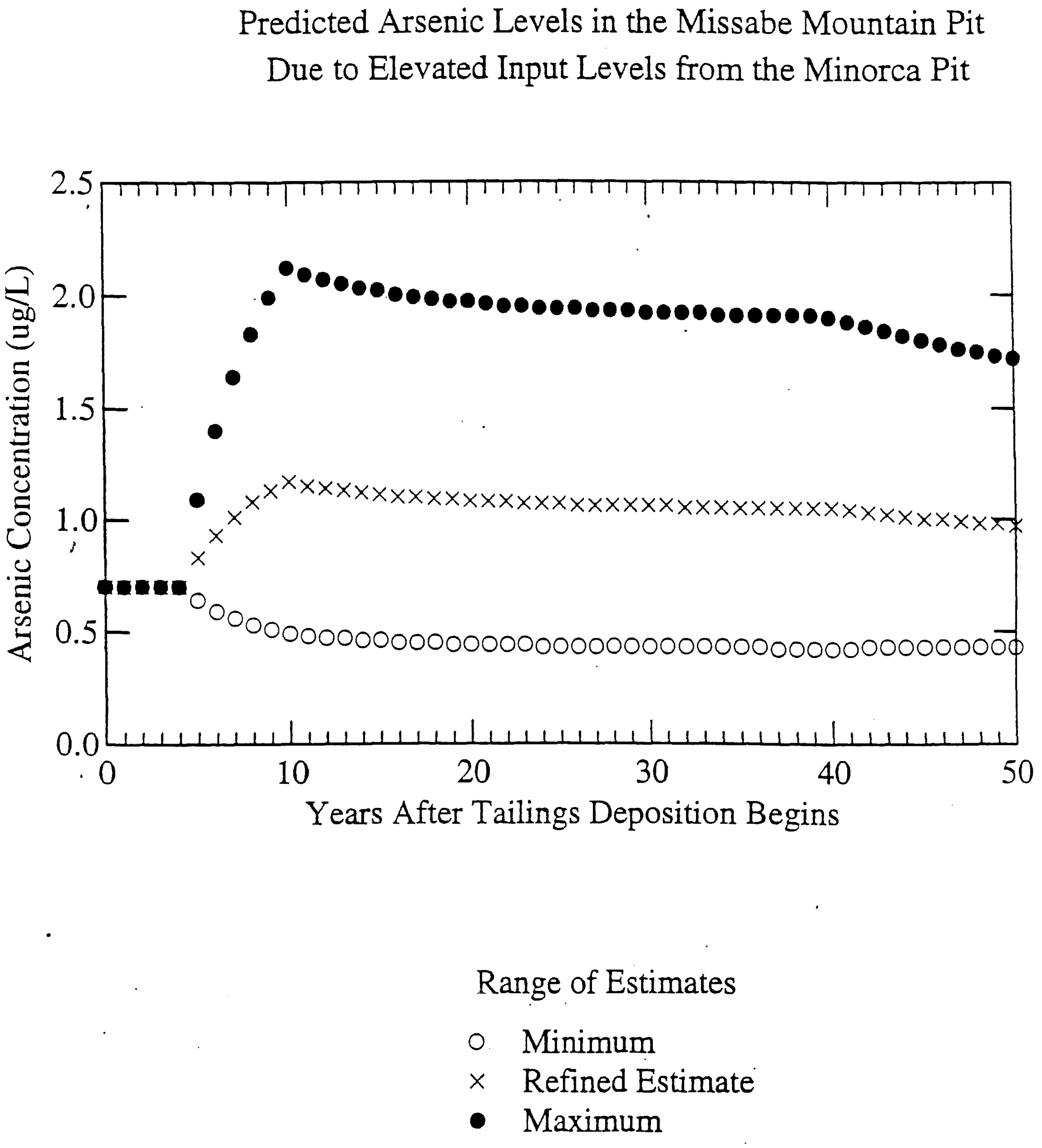

Figure 6. Even at maximum input from the Minorca Pit, arsenic levels in the Missabe Mountain Pit are expected to be well below the current drinking water quality standard of 50 ug/L.

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Table 1. Summary of the source terms, transport terms, expected levels in the Missabe Mountain Pit, and drinking water quality standards for the five EC's.

Terms	Conditions	Criteria	Mn (mg/L)	F (mg/L)	Mo	As
Minorca Pit Source Term[1,2]	Clear Water Pool	Deposition Year 5-8	<0.01	6	130	4.5
	Tailings Pore Water	Deposition Year 8+	0.05 - 7	1 - 6	1 - 45[3]	0.1 - 7
Biwabik Aquifer Transport Term	No Removal or		0.05 - 7	1 - 6	1 - 130	0.1 - 7
	Chemical Controls		1[4]	4-6[5]	na	3[6]
Missabe Mountain Pit	Dilution[7,8]	Temporary Maximum	0.02 - 1.7	0.3 - 1.6	1.4 - 25	0.5 - 2.1
		Reclamation w/ Grasses	0.1 - 1.7	0.4 - 1.6	3.4 - 25	0.4 - 2.1
		Reclamation w/ forest	0.2 - 1.6	0.4 - 1.5	3.0 - 11	0.4 - 1.9
	Chemical Controls		<0.01[9]	na	na	na
Drinking Water Quality Standards		Health-based value	1.3[10]	na	na	na
		Primary	0.1	4	30	50
		Secondary	0.05[11]	2[12]	na	<10[13]

[1] A monitoring well should be installed in the Minorca Pit tailings in order to monitor fluctuations in the levels of the five EC's over time.

[2] Source terms for F and Mo will likely decrease over time, particularly after successful reclamation of the Minorca Pit.

[3] Mo source terms appeared to be dependent on the levels found in plant discharges, which may vary over time.

[4] Assumes chemical control by rhodochrosite solubility in the aquifer, calculation in Figure A2.1.

[5] Assumes chemical control by fluorite solubility (Berndt et al., 1999) in the aquifer based on measured calcium concentrations.

[6] This value was based on visual inspection of the distribution of arsenic levels in tailings pore waters during this study. It is intended to illustrate arsenic removal due to adsorption to iron oxides in the formation.

[7] These values were calculated assuming a dilution water composition based on that observed in the Biwabik aquifer wells (Berndt et al., 1998).

[8] Dilution factors of 6% - 21% depend upon implementation of successful reclamation at the Minorca Pit upon closure.

[9] This value assumes oxidizing conditions in the Missabe Mountain Pit will promote precipitation of manganese oxides. Based on measurements in the tailings basin and manganese oxidation experiments.

[10] This is a site-specific, health-based standard developed by the Minnesota Department of Health (1998).

[11] This is an aesthetic standard that the Virginia Public Utility must meet for the city water supply.

[12] The secondary fluoride standard is not an enforceable standard.

[13] The US EPA is considering lowering the primary arsenic standard to less than 10 ug/L in the future.

"na" = not applicable

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APPENDIX 1

SOURCE TERM DETERMINATIONS

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Table A1.1. Estimation of EC concentrations in the Minorca Pit clear water pool.

ELEMENT OF CONCERN	DISCHARGE CONC.	ASSUMED SYSTEM	SOURCE OF HYDROLOGIC DATA	CONCENTRATION AT YEAR 10
Mn (mg/L)	0.1	well-mixed	Indeco, 1999	0.08
			Adams, 1998	0.07
		plug flow	Indeco, 1999	0.08
			Adams, 1998	0.07
F (mg/L)	7.6	well-mixed	Indeco, 1999	6.2
			Adams, 1998	5.6
		plug flow	Indeco, 1999	6.2
			Adams, 1998	5.6
Mo (ug/L)	160	well-mixed	Indeco, 1999	130
			Adams, 1998	119
		plug flow	Indeco, 1999	130
			Adams, 1998	119
As (ug/L)	5.5	well-mixed	Indeco, 1999	4.5
			Adams, 1998	4.1
		plug flow	Indeco, 1999	4.5
			Adams, 1998	4.1

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Table A1.2. Summary of manganese source terms based on operational, field, and laboratory water chemistry measurements.

Clear Water Pool:

Data Source	N	Average Mn (mg/L)	Range (mg/L)
Tailings basin	11	0.01	0.001 - 0.076
Tank experiments	20	0.004	0.001 - 0.021
Mn oxidation experiments	4	0.002	0.004 - 0.009
Pierce and Tomcko, 1989	8	na	<0.01 - 22.5
Recommended Clear Pool Source Term			<0.01

Tailings Pore Water:

Data Source	N	Average Mn (mg/L)	Range (mg/L)
Tailings discharge pipe	10	0.06	0.05 - 0.09
North seep at Inland	7	3.2	1.7 - 4.1
North wells at Inland	15	4.6	1.2 - 7.2
Snively Pit (USX)	6	1.3	1.0 - 1.9
Tank experiments	32	0.08	0.05 - 0.12
Process water columns	6	0.6[1]	0.45 - 0.70
Rain water columns	6	0.3	0.26 - 0.34
Ground water columns	5	0.2[2]	0.16 - 0.21
Recommended Pore Water Source Term			0.05 - 7

na = not applicable

[1] Mn levels appeared to be increasing at the end of the experiment, therefore the average from the last three data points of both columns was used here.

[2] Represents an average of the last five samples (weeks 12 to 30), when Mn levels stabilized.

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Table A1.3. Summary of fluoride source terms based on operational, field, and laboratory water chemistry measurements.

Data Source	N	Average F (mg/L)	Range (mg/L)
Tailings discharge pipe	10	4.6	2.3 - 7.6[1]
North seep at Inland	8	2.3	1.2 - 3.0
North wells at Inland	15	2.5	0.6 - 3.6
Snively Pit (USX)	6	0.2	0.16 - 0.31
Tank experiments	22	4.7[2]	3.6 - 5.9
Process water columns	6	3.0[3]	2.8 - 3.0
Rain water columns	6	3.2	1.7 - 4.1
Ground water columns	3	2.2[4]	2.1 - 2.3
Recommended Source Term			1 - 6[1]

na = not applicable

[1] Clear water pool contribution expected to be no more than 6 mg/L.

[2] Fluoride levels stabilized after the first sixteen weeks of the experiment.

[3] Fluoride levels appeared to be decreasing at the end of the experiment, therefore, the average of the last three samples from both columns was used here.

[4] Fluoride levels appeared to be increasing at the end of the experiment, therefore, the average of the last three samples (weeks 20, 25, and 30) was used here.

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Table A1:4. Summary of molybdenum source terms based on operational, field, and laboratory water chemistry measurements.

Data Source	N	Average Mo (ug/L)	Range (ug/L)
Tailings discharge pipe	10	110	68 - 157[1]
North seep at Inland	8	7.1	1.5 - 13.7
North wells at Inland	15	6.4	3.0 - 8.4
Snively Pit (USX)	6	0.6	0.1 - 1.5
Tank experiments	32	24	13 - 45
Process water columns	6	24[2]	15 - 34
Rain water column	6	11[3]	7.1 - 19
Ground water column	3	9.4[4]	8.7 - 9.9
Recommended Source Term			1 - 130[1]

na = not applicable

[1] Clear water pool contribution expected to be no more than 130 ug/L.

[2] Mo levels decreased throughout the experiment, therefore, the average of the last three samples from the two columns were used here.

[3] Mo concentrations appeared to be increasing at the end of the experiment, however, all six values were used.

[4] Mo concentrations appeared to be increasing at the end of the experiment, therefore, an average of the last three samples (weeks 20, 25, and 30) was used here.

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Table A1.5. Summary of arsenic source terms based on operational, field, and laboratory water chemistry measurements.

Data Source	N	Average As (ug/L)	Range (ug/L)
Tailings discharge pipe	10	3.6	1.9 - 5.5
North seep at Inland	8	1.1	0.2 - 2.1
North wells at Inland	15	4.1	1.5 - 8.1
Snively Pit (USX)	6	1.2	0.1 - 4.8
Tank experiments	32	2.4	0.6 - 4.2
Process water columns	10	3.7[1]	2.1 - 5.4
Rain water columns	6	4.9	2.6 - 7.2
Ground water columns	8	2.5	1.2 - 3.7
Recommended Source Term	na		0.1 - 7

na = not applicable

[1] Arsenic concentrations stabilized after six to ten weeks.

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APPENDIX 2

TRANSPORT IN THE BIWABIK AQUIFER

Figure A2.1. Rhodochrosite solubility control on manganese levels in the Biwabik aquifer.
Figure A2.2. Fluorite solubility control on fluoride levels in the Biwabik aquifer.
Figure A2.3. Adsorption model depicting behavior of fluoride, molybdenum, and arsenic in the presence of iron oxide minerals.

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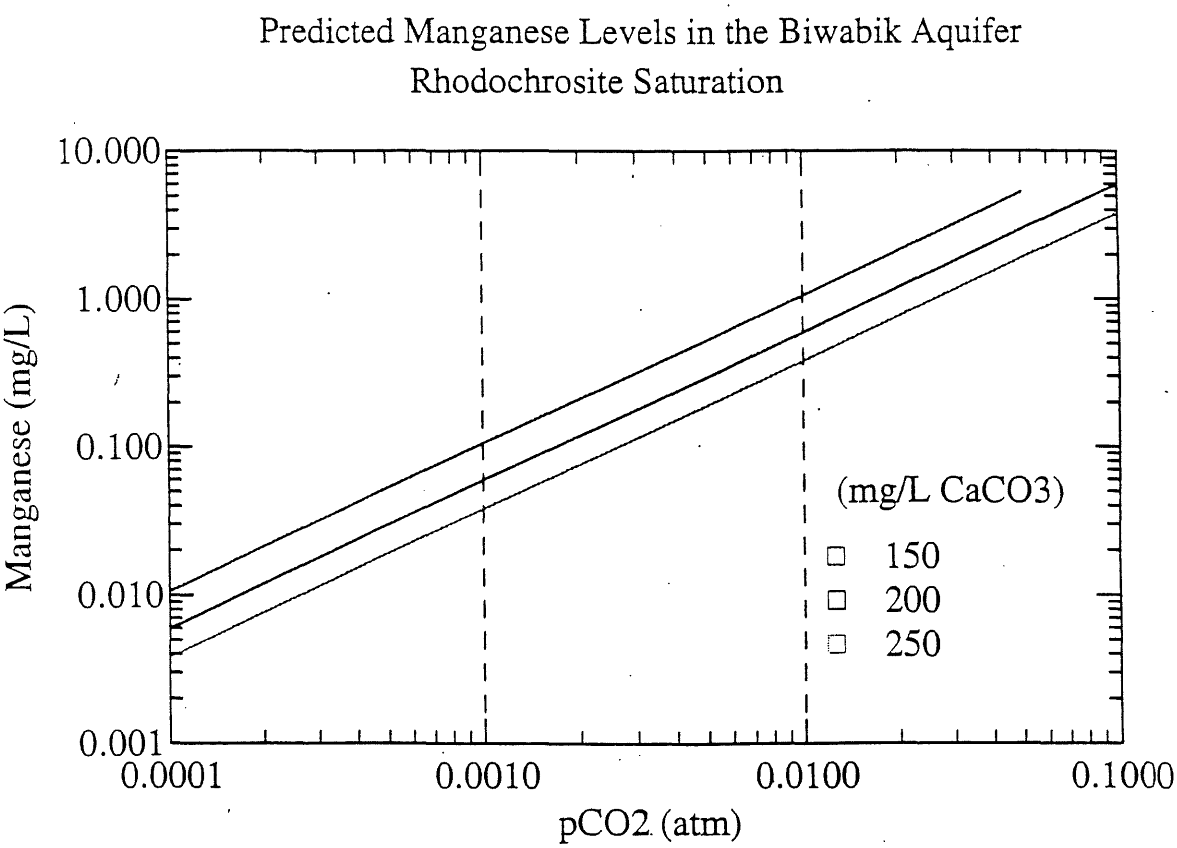

Figure A2.1. Manganese levels in Biwabik Formation aquifer waters are believed to be controlled by the solubility of the mineral rhodochrosite ($MnCO_3$). Within the range of pCO_2 (dashed vertical lines) and alkalinity (color lines) found in the Biwabik aquifer, manganese levels should not exceed 1 mg/L.

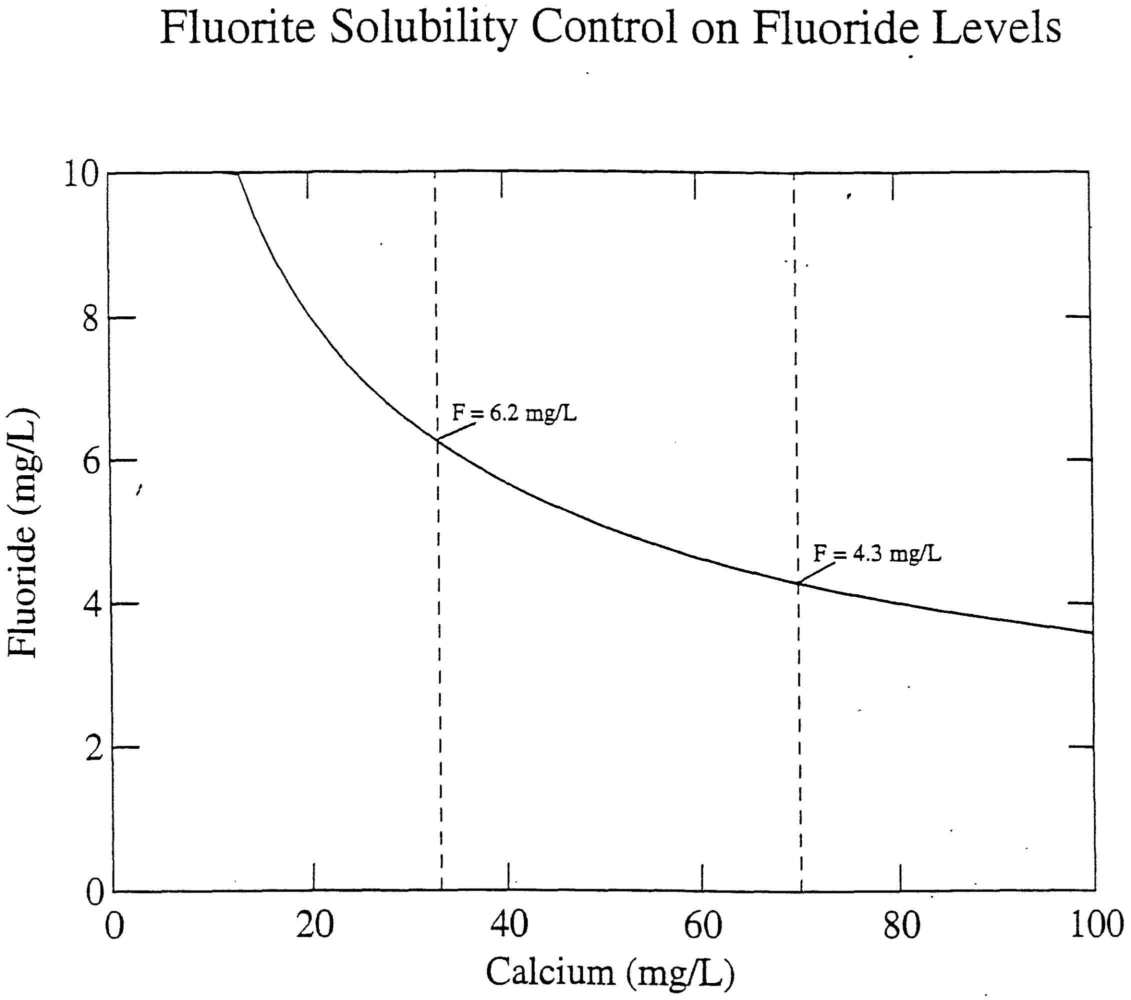

Figure A2.2. Maximum fluoride levels in the Biwabik Formation aquifer are likely to be controlled by the solubility of the mineral fluorite (CaF_2; Berndt et al., 1999). Within the range of observed calcium concentrations in the Biwabik aquifer (vertical dashed lines), fluoride levels are expected to range from 4.3 to 6.2 mg/L.

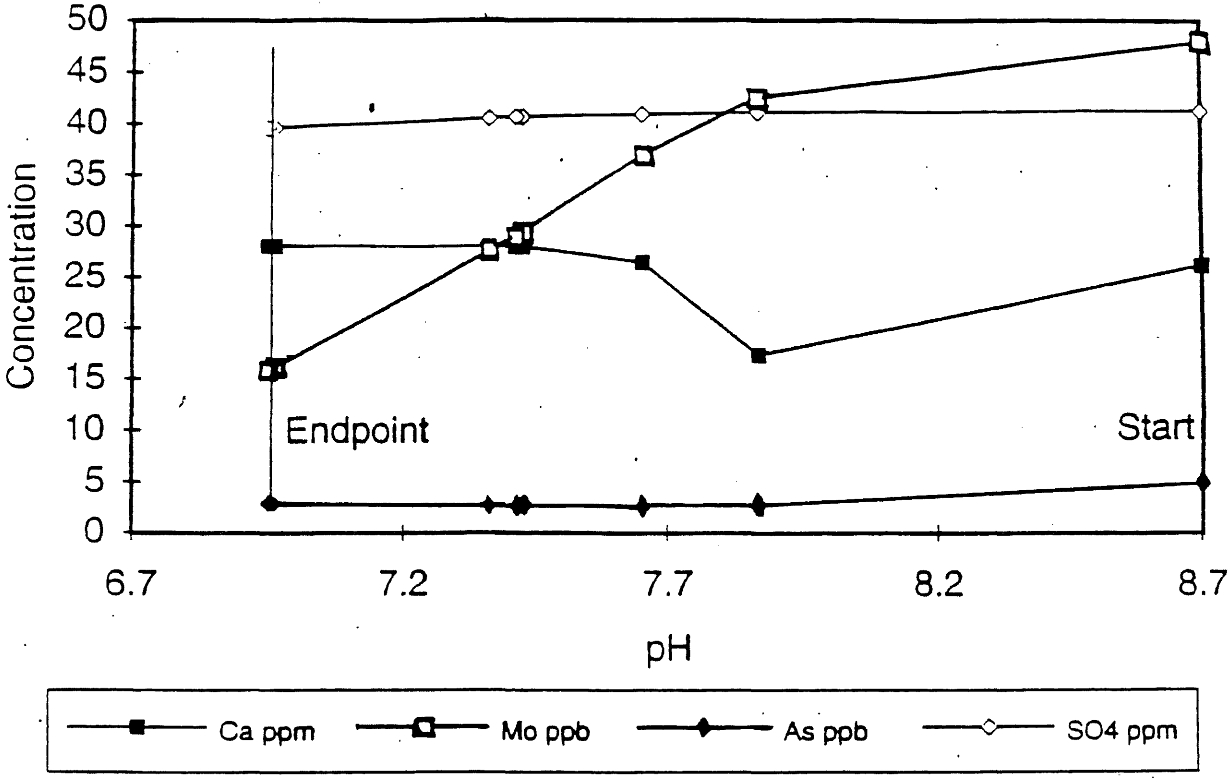

Figure A2.3. Geochemical adsorption model depicting behavior of adsorbing species in average tailings basin water reacting with minnesotaite, siderite, cristobalite, rhodochrosite, and 60 m^2 of hematite per liter of solution (Berndt, 1998). The reduction in pH leads to adsorption of arsenic and molybdenum.

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APPENDIX 3

PREDICTION OF EC LEVELS IN THE MISSABE MOUNTAIN PIT

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Table A3.1. Summary of approaches used to estimate maximum impact on manganese levels in the Missabe Mountain Pit. Concentrations in mg/L.

Operations within the Minorca Pit			Missabe Mt Pit Concentration Estimates (mg/L)			
Depositional Time Period (Years)	Period of Max. Outflow from Minorca (deposition year)	Reclamation Conditions	Minorca Source Term	Minorca Contribution to Missabe Net Input	Max. Net Input Conc.	Max. Estimated Conc. in Missabe During This Time Period
NO OUTFLOW FROM MINORCA PIT						
0-4	5-10	none	7	0%	0.003 (background)	0.0
0-4	5-10	none	7	0%	0.0	0.0
0-4	5-10	none	1	0%	0.0	0.0
0-4	5-10	none	1	0%	0.0	0.0
0-4	5-10	none	0.05	0%	0.0	0.0
0-4	5-10	none	0.05	0%	0.0	0.0
0-4	8-10	none	7	0%	0.0	0.0
0-4	8-10	none	7	0%	0.0	0.0
0-4	8-10	none	1	0%	0.0	0.0
0-4	8-10	none	1	0%	0.0	0.0
0-4	8-10	none	0.05	0%	0.0	0.0
0-4	8-10	none	0.05	0%	0.0	0.0
MINORCA OUTFLOW DOMINATED BY CLEAR WATER POOL						
5-8	5-10	none	7	39%	2.8	1.4
5-8	5-10	none	7	28%	2.5	1.2
5-8	5-10	none	1	39%	0.5	0.2
5-8	5-10	none	1	28%	0.4	0.2
5-8	5-10	none	0.05	39%	0.1	0.1
5-8	5-10	none	0.05	28%	0.1	0.1
5-8	8-10	none	7	39%	2.8	0.8
5-8	8-10	none	7	28%	2.5	0.7
5-8	8-10	none	1	39%	0.5	0.2
5-8	8-10	none	1	28%	0.4	0.2
5-8	8-10	none	0.05	39%	0.1	0.1
5-8	8-10	none	0.05	28%	0.1	0.1
MINORCA OUTFLOW DOMINATED BY TAILINGS PORE WATER						
8-10	5-10	none	7	39%	2.8	1.7
8-10	5-10	none	7	28%	2.5	1.4
8-10	5-10	none	1	39%	0.5	0.3
8-10	5-10	none	1	28%	0.4	0.3
8-10	5-10	none	0.05	39%	0.1	0.1
8-10	5-10	none	0.05	28%	0.1	0.1
11-40	5-10	grassy vegetation	7	21%	1.6	1.7
11-40	5-10	grassy vegetation	7	18%	1.4	1.4
11-40	5-10	grassy vegetation	1	21%	0.3	0.3
11-40	5-10	grassy vegetation	1	18%	0.3	0.3
11-40	5-10	grassy vegetation	0.05	21%	0.2	0.1
11-40	5-10	grassy vegetation	0.05	18%	0.2	0.1
41-50+	5-10	forest vegetation	7	13%	1.1	1.6
41-50+	5-10	forest vegetation	7	12%	1.0	1.4
41-50+	5-10	forest vegetation	1	13%	0.3	0.3
41-50+	5-10	forest vegetation	1	12%	0.3	0.3
41-50+	5-10	forest vegetation	0.05	13%	0.2	0.2
41-50+	5-10	forest vegetation	0.05	12%	0.2	0.2
8-10	8-10	none	7	39%	2.8	1.3
8-10	8-10	none	7	28%	2.5	1.1
8-10	8-10	none	1	39%	0.5	0.2
8-10	8-10	none	1	28%	0.4	0.2
8-10	8-10	none	0.05	39%	0.1	0.1
8-10	8-10	none	0.05	28%	0.1	0.1
11-40	8-10	grassy vegetation	7	21%	1.6	1.6
11-40	8-10	grassy vegetation	7	18%	1.4	1.3
11-40	8-10	grassy vegetation	1	21%	0.3	0.3
11-40	8-10	grassy vegetation	1	18%	0.3	0.3
11-40	8-10	grassy vegetation	0.05	21%	0.2	0.1
11-40	8-10	grassy vegetation	0.05	18%	0.2	0.1
41-50+	8-10	forest vegetation	7	13%	1.1	1.6
41-50+	8-10	forest vegetation	7	12%	1.0	1.3
41-50+	8-10	forest vegetation	1	13%	0.3	0.3
41-50+	8-10	forest vegetation	1	12%	0.3	0.3
41-50+	8-10	forest vegetation	0.05	13%	0.2	0.2
41-50+	8-10	forest vegetation	0.05	12%	0.2	0.2

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