

FLUORIDE FATE AND TRANSPORT ANALYSIS INTALCO LANDFILL CLOSURE PROGRAM

Prepared for

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March 2006



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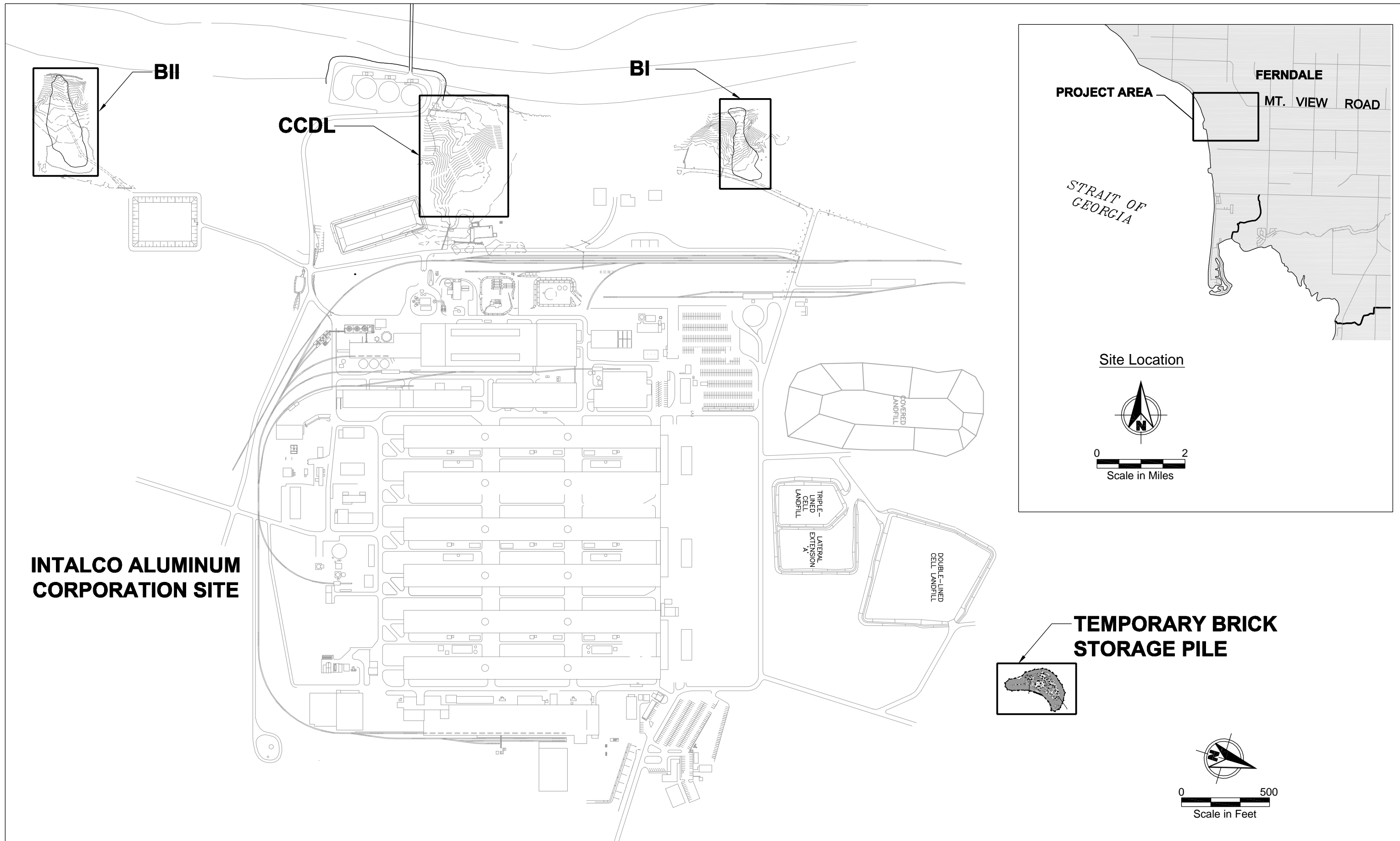
1 BACKGROUND

This report provides a technical evaluation of the fate and transport of fluoride in soils and groundwater associated with remediated landfills at the Intalco Aluminum Corporation (Intalco) primary aluminum reduction plant, located at 4050 Mountain View Road in Ferndale, Washington. This facility is located on an upland plain that overlooks the Strait of Georgia (Figure 1). Steep, 180-foot-high bluffs that flank the western portion of the property adjacent to the Strait contain the three historical landfills (the Beach I, Beach II, and Closed Construction Debris Landfills) under consideration. These landfills were created by filling, or partially filling, natural ravines that cut into the 180-foot bluff. All of the ravine landfills are located outside of the plant's active operations area. For the purpose of this study "Site" refers to the area within the footprint of the historical landfills.

Disposal at the historical landfills began as early as 1966 during plant construction. Beach II, was the latest landfill to be developed, beginning in 1971. Typical wastes deposited consist of bricks, various large and small metal objects, concrete, pieces of aluminum, rubber, hard and soft plastic, tires, wood, and wire. Landfilling of these materials resulted in elevated concentrations of fluoride in the native soils and ground water underlying the waste, and in surface water seeps emanating from the ravine slope. In addition to these historical areas, Intalco has maintained a temporary storage pile for anode furnace brick. This brick is similar in composition to the waste contained within Beach I; therefore, potential impacts to the underlying soil and groundwater in that area will also be addressed as part of this study.

The remainder of this section discusses the remedial approaches that were utilized at Beach I and Beach II, and the planned approach for the CCDL and the temporary brick storage pile, to prevent water quality impacts to the Strait of Georgia and groundwater at the Intalco property. The other sections of the report focus on the field investigations, site hydrology, and geochemical modeling that were performed to evaluate the ultimate fate and transport characteristics of fluoride at the Site. The results of these evaluations are used to develop recommended remedial goals for fluoride in groundwater (expressed as seep water) at the Site.

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1.1 Summary of Landfill Remedial Actions

Two remedial investigation and feasibility studies (RI/FSs) were performed by MFG, Inc. (MFG), in 2002 to determine the most effective remediation methods applicable to the historical landfills at the Site (MFG 2002a and 2002b). As Beach I and Beach II border the Strait of Georgia shoreline, the RI/FS determined that both landfills should be excavated to prevent waste materials from migrating onto the beach during slope failures and to reduce impacts from surface water seeps into the receiving waters. The CCDL is setback approximately 250 feet from the shoreline at an elevation 60 feet higher than the beach, and surface water seeps emanating from the CDDL feed into a small, intermittent stream. Accordingly, the RI/FS determined that the landfill should be stabilized for slope protection and capped with a low-permeability, multi-component cover system. During the summer and early fall of 2005, Intalco commenced the remediation (excavation) work at Beach I and Beach II. Work at the CCDL will begin May 2006.

1.1.1 Beach I and Beach II

The excavations at Beach I and Beach II were completed in late fall of 2005. Approximately 42,000 tons of waste was removed from Beach I. The material consisted of fill, reinforced concrete floor slabs, and brick, among other constituents. Approximately 154,700 tons of waste, including 33,600 tons of Toxic Substances Control Act (TSCA) material, was excavated from Beach II. The material from Beach II was somewhat different from Beach I, in that it contained more general plant wastes and less brick material. At both landfills, material was removed until the native contact was observed. (There remains a small quantity of waste in Beach I that Alcoa will attempt to remove in the 2006 construction season.) The contact at Beach I was different than that observed during the excavation of Beach II. Most of the soil uncovered at Beach I was comprised of the Cherry Point formation, while at Beach II, a more pervious glacial marine drift was exposed.

As required by the Cleanup Action Plan (CAP), several confirmation samples were taken to characterize the post-remedy surfaces at Beach I and Beach II. Soil samples were analyzed for fluoride, polychlorinated biphenyls (PCBs), and polyaromatic hydrocarbons (PAHs). Most sample results for Beach I and Beach II did not detect PCBs or PAHs; the remainder were found to be below the Model Toxics Control Act (MTCA)

Method B Soil Cleanup Standards for Unrestricted Use. Fluoride concentrations ranged from 151 milligrams per kilogram (mg/kg) to 5810 mg/kg for Beach I and from 100 mg/kg to 370 mg/kg for Beach II.

Surface water seep samples were collected from Beach I at various locations within the ravine, as shown on Figure 2. The average fluoride concentration in the seep water (including data collected during the field investigation portion of this study, see Section 2) was calculated as 11.6 milligrams per liter (mg/L) from the data shown in Table 1. It was not possible to collect surface water seep samples at Beach II due to dry conditions and the porous nature of the exposed soils.

Table 1
Fluoride Concentrations in Seep Water at Beach I

Sample ID	Fluoride (mg/L)
ILCBI-Seep1	19.6
ILCBI-Seep2	4.1
ILCBI-Seep3	17.8
AIN-SEEP-A1	2.1
AIN-SEEPB-0201	12
AIN-SEEPB-0202	14

1.1.2 CCDL and the Temporary Brick Storage Pile

Surface water seeps at the CCDL were sampled and analyzed as part of the RI/FS (MFG 2002b). Fluoride concentrations ranged from 30.6 mg/L to 49.3 mg/L. After the remedial action is implemented at the CCDL, the low-permeability cover will limit infiltration and it is anticipated that seeps emanating from the landfill will be significantly reduced. The cover will also change the flow patterns in the small creek adjacent to the landfill; it will become dominated by surface runoff during precipitation events with a diminishing contribution from groundwater seeps after the remedial action is implemented.

Although fluoride associated with CCDL waste will be significantly reduced, elevated seep concentrations can be expected to persist post-remedy due to input from other Intalco sources. In particular, the CCDL is located in close proximity to the Intalco stormwater retention pond and transference ditches. Surface water that flows through these channels is permitted to contain fluoride concentrations up to 50 mg/L. The CCDL is also located near active Intalco operations (closer than Beach I and Beach II). Fluoride

from Intalco processes is suspended and subsequently deposited at various concentrations throughout the property (Intalco 2001). The contribution of fluoride from Intalco operations is a function of the magnitude of plant activity; therefore, it is difficult to quantify the long-term potential of this source.

As part of the CCDL remediation, brick from the temporary storage pile will be beneficially reused as structural fill beneath the low-permeability cover of the CCDL. This material is strong and angular, allowing it to serve as an excellent slope-stabilizing material. However, as previously stated, this material possesses fluoride concentrations greater than local background concentrations. Toxicity Characteristic Leaching Procedure (TCLP) tests indicate the potential for the brick to leach total fluoride concentrations between 16 mg/L and 92 mg/L. These results represent the most conservative leaching scenario (i.e., greatest potential) as the natural fluid that will cause leaching in the environment (rainwater) is less acidic than the fluid used in the test, which may cause more dissolution of fluoride from solid form into runoff. As part of the CCDL remediation, the brick will be placed beneath the low-permeability cover and above the groundwater table to isolate the brick from lateral flow. This will reduce the potential for additional fluoride to leach from the brick into the ravine adjacent to the landfill. The TCLP data further indicate that it is probable that fluoride concentrations in surficial soils currently underlying the brick storage area are elevated above background conditions. Following brick excavation from the storage area, soils will be evaluated for compliance with MTCA cleanup standards as described in Section 5.3.

1.2 Purpose and Scope of Fluoride Fate and Transport Analysis

The main goal of the remediation at the Site is to protect the Strait of Georgia (receiving waters). The overall goal of this study is to provide technical data to support the Washington State Department of Ecology (Ecology) in the designation of a Site-specific, point of compliance remedial goal that is appropriate to achieve the 1.5 mg/L surface water standard for the Strait of Georgia for the historical landfills. During confirmatory sampling at the site, Beach I fluoride concentrations measured in newly-exposed soil and surface water seeps were observed above typical background concentrations. It is believed that these elevated fluoride concentrations developed through years of surface water infiltration

through the waste into the porewater spaces of the upper portion of the underlying native soils.

Because MTCA does not clearly provide guidance for fluoride remediation, the fate and transport investigation summarized in this report was conducted to evaluate if fluoride associated with remediated landfill soils and water will provide a long-term potential impact to the quality of surface water in the Strait of Georgia.

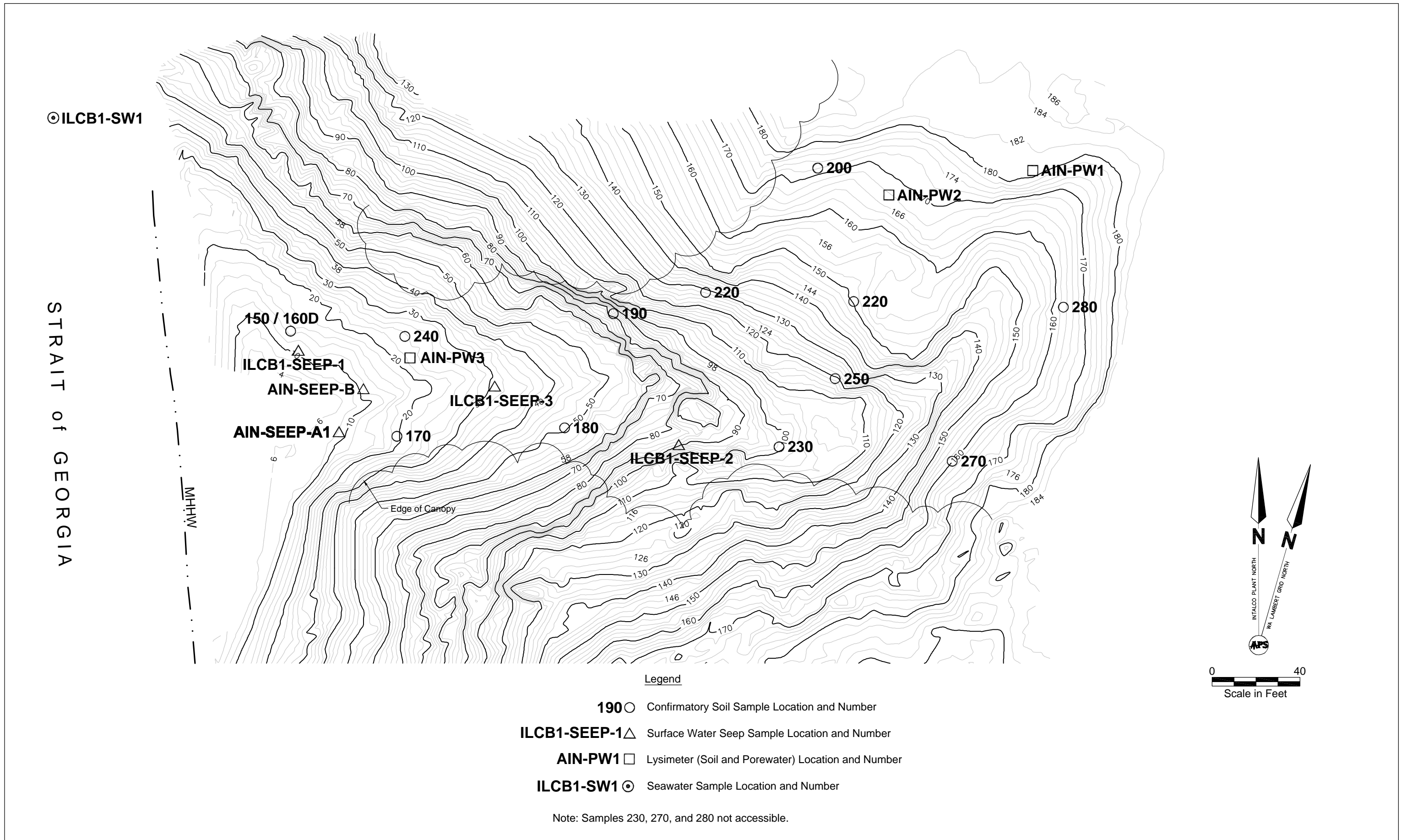


Figure 2
Seawater, Confirmatory, Seep, and Lysimeter Sampling Locations
Fluoride Fate and Transport Analysis
Intalco Landfill Closure Program

2 FIELD INVESTIGATIONS

Field investigations were conducted to provide further information regarding fluoride concentrations in soil, porewater, and surface seep water at Beach I, as well as the seawater adjacent to the Site. The results of these field investigations were used to support the geochemical modeling analyses described in Section 4.

2.1 Program Design

The goals of the field program were twofold: 1) determine the chemical characteristics of the various site media (soil, seep water, and seawater); and 2) determine the Site-specific relationship (partitioning coefficient, K_d) between fluoride concentrations in soil and porewater. To achieve the first goal, samples of seep water (ILCBI-Seep3) and seawater (ILCBI-SW1) were collected adjacent to the Site and analyzed for general chemistry, including the major cations and anions. X-ray diffraction testing was performed on a soil sample collected from the seep water location. The water samples serve as the baseline characterization of the geochemical equilibrium that exists in Beach I seep water and seawater. The soil mineralogy provides qualitative insight into the chemical reactions that occur between soil and porewater at the Site. To quantitatively determine the K_d for the Site, fluoride concentrations were determined for porewater using vacuum-lysimeters. The lysimeters provided a direct method of collecting porewater associated with the unsaturated soils on the excavated surface of Beach I. Porewater chemistry data were combined with soil chemistry data from the lysimeter boring materials to calculate a Site-specific K_d .

Three lysimeters were installed at the locations shown on Figure 2. The lysimeters were installed to obtain porewater samples at a depth of 12 inches below the existing ground surface. During installation of the lysimeters, soil samples were collected in 6-inch intervals and subsequently testing for total fluoride concentrations. Porewater samples were collected during two separate sampling events. The first event occurred approximately 24 hours after installation and did not include a purging cycle. The second event occurred 2 weeks following the first event, and consisted of 4 days of sampling. On the first day any porewater collected in the lysimeters during the 2-week period was purged and the vacuum was reapplied. On day two, the porewater was again purged. Samples for fluoride analysis were collected on days three and four. On the days that porewater samples were collected

for analysis, seep water was also collected from the base of the ravine at the locations shown on Figure 2.

2.2 Field Program Results

One seawater, three soil, nine porewater, and four surface water seep samples were collected and analyzed at Beach I as part of this study. The results of those analyses are compiled in Tables 1 through 4 of this report.

Table 2
Fluoride Concentrations in Soil at Beach I

Sample ID	Sample Depth Interval (inches)	Fluoride (mg/kg)
AIN-PW1	0 to 6	871
AIN-PW1	6 to 12	565
AIN-PW1	12 to 18	204
AIN-PW2	0 to 6	269
AIN-PW2	6 to 12	187
AIN-PW2	12 to 18	179
AIN-PW3	0 to 6	424
AIN-PW3	6 to 12	365
AIN-PW3	12 to 18	354

Table 3
Fluoride Concentrations in Porewater at Beach I

Sample ID	Fluoride (mg/L)
AIN-PW1-0119	32.5
AIN-PW1-0201	37.9
AIN-PW1-0202	44.2
AIN-PW2-0119	3.5
AIN-PW2-0201	3.3
AIN-PW2-0202	13
AIN-PW3-0119	6.9
AIN-PW3-0201	44.8
AIN-PW3-0202	46.5

Soil samples were collected in 6-inch intervals during lysimeter installation to determine if fluoride concentrations decrease with depth at Beach I. A general trend of decreasing fluoride over increasing depth was observed at each lysimeter location. This observed

decrease in fluoride concentration supports the hypothesis that only the upper surface of the exposed native soils are impacted at Beach I.

Porewater samples were collected at a depth of 12 inches below the ground surface. This data was used, along with the soil concentrations, to calculate a Site-specific K_d . K_d values are used in models, along with other parameters, to determine the relationship between soil and groundwater (porewater) concentrations for a given site. In the Ecology three-phase model used by the MTCA program, the site-specific K_d value is critical in determining an acceptable soil concentration that will achieve a given cleanup goal. This approach is pertinent to this study, as collection of field data (seep water and porewater) is not possible at Beach II to verify that remedial goals have been achieved with respect to surface water. This approach is discussed in detail in Appendix A.

Also pertinent to the three-phase model is the site-specific dilution that occurs as water percolates through a soil stratum and combines with lateral, off-site groundwater prior to manifesting as a surface water seep. The dilution factor is the ratio of the porewater concentration to that of the measured seep. To determine a Site-specific dilution factor at Beach I, four seep water samples were collected in addition to the two samples that were previously collected as part of the confirmatory sampling program. The seep water samples presented in Table 1 also contain the results from two tests performed prior to this study, ILCBI-Seep1 and ILCBI-Seep2.

Data required as input parameters by the PHREEQC model (Parkhurst 1995) are presented in Table 4 and include the general seawater and seep water chemistry. The analytical results indicate that an abundance of phosphate is available in both the seawater and seep water to react with fluoride to facilitate the precipitation of fluorapatite. The presence of these ions as they affect the geochemical equilibrium of the receiving waters is discussed in detail in Section 4.

Table 4
PHREEQC Input Parameters

Parameter	Seawater	Seep Water
Temperature (degrees C)	25	25
pH	8.22	7.7
Pe	8.45	4.0
Density (gm/cm3)	1.023	1.0
Calcium (mg/L)	412	32.6
Magnesium (mg/L)	1290	22.7
Sodium (mg/L)	10,770	84.5
Potassium (mg/L)	400	10.7
Silica (mg/L)	4.28	55.4
Chloride (mg/L)	19,350	0.1
Sulfate as S (mg/L)	2,710	2.38
Alkalinity (mg/L)	142	173
Phosphate as P (mg/L)	0.08	0.05
Fluoride (mg/L)	1.3	100 - 400 ¹

Note:

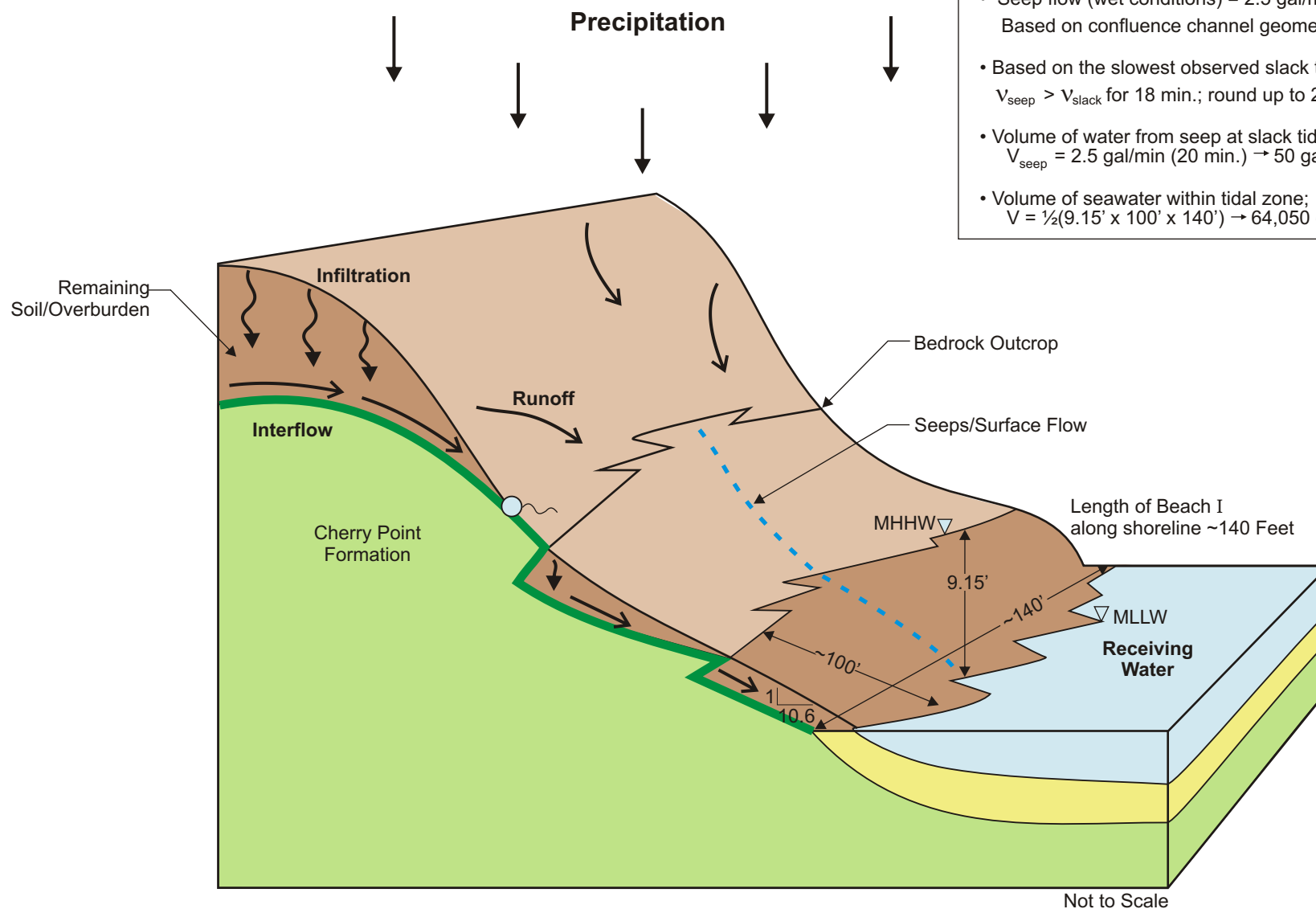
- 1 Actual measured fluoride concentrations in seep water at Beach I average 11.6 mg/L. The 100 mg/L to 400 mg/L range was used as input to determine the upper range of fluoride impacts.



3 BEACH I HYDROLOGY AND CONCEPTUAL MODEL

Most saturated groundwater flow at the Site occurs at the geologic interface between the Esperance Sand and the Cherry Point Formation; however, the variable lithology in the glacial till produces interflow associated with intermittent perched groundwater systems that form during and after precipitation events. Near-surface Beach I hydrology is therefore driven by rain events. Surface runoff and interflow seeps that form at outcrop boundaries of the Cherry Point Formation material and glacial till combine at the toe of the Beach I slope. Within Beach I, several outcrop and seep zones exist to the extent that the ravine walls appear to be weeping during wet weather conditions. At the base of the ravine, these zones converge into a single stream prior to discharge into the intertidal zone of the Strait of Georgia. As part of MFG's RI/FS (2002a), the Beach I seep water flow was observed to be 2.5 gallons per minute. This measurement was made during wet weather conditions and is expected to be less during dry months. Figure 3 depicts a graphical representation of the Beach I hydrology, including the tidal zone.

The tidal zone is an important component to Beach I hydrology when assessing fluoride impacts to the receiving waters, as this is the area where seep water discharges and combines with seawater. This interaction is most critical during slack tide, as seep water has the potential to enter the system at a velocity greater than the tidal water passing through the zone. As described in Section 4, geochemical modeling was used to assess the mineralogical reactions that could occur along the flow path at Beach I. The remainder of this section describes how physical input parameters to that modeling were derived.



- Average Slack Tide Velocity = (v_{seep}) 0.002 ft/sec
- Seep flow (wet conditions) = 2.5 gal/min
Based on confluence channel geometry; $v_{seep} = 0.0076$ ft/sec
- Based on the slowest observed slack tide;
 $v_{seep} > v_{slack}$ for 18 min.; round up to 20 min.
- Volume of water from seep at slack tide; } Will be less during
 $v_{seep} = 2.5$ gal/min (20 min.) → 50 gal. } dry months
- Volume of seawater within tidal zone;
 $V = \frac{1}{2}(9.15' \times 100' \times 140') \rightarrow 64,050$ cf or 479,127 gal.

3.1 Tidal Zone Designation and Current Flow

Data from the Cherry Point, Strait of Georgia, Washington, tidal benchmark station (National Oceanic and Atmospheric Administration 2006) indicate that the elevation difference between mean lower-low water and mean higher-high water datum is 9.15 feet. The slope of the shoreline adjacent to Beach I was surveyed at approximately 5.4 degrees, resulting in a horizontal tidal range of approximately 100 feet, as shown on Figure 3. The remainder of the tidal zone is defined by the lateral extent of the Beach I ravine toe. At its widest extent, the toe measures approximately 140 feet across. The volume of this tidal wedge at high tide conditions is the volume of seawater available for interaction during periods of seep water discharge. At Beach I, the tidal wedge volume equals 479,127 gallons.

Data from three tidal current meter stations (Boat Passage, British Columbia; Matia Island, Washington; and Toe Point, Patos Island, Washington; WWW Tide and Current Predictor 2006) were analyzed to characterize slack tide conditions at the Site. Data from each station for the months of January and June during the years 2004 through 2006 was queried in 2-minute intervals. The data were then compiled and sorted to determine the lowest observed current during each time period. The average value of the lowest observed slack tide velocities was calculated as 0.0021 feet per second.

3.2 Seep Water Contribution

As previously stated, interaction of seep water and seawater will occur during slack tide, particularly when the velocity of the seep is greater than the velocity of the tidal flow. Based on a generalized geometry of the confluence channel carrying the seep water to the point of discharge, the velocity of the seep at maximum flow (2.5 gallons per minute) can be calculated as 0.0076 feet per second. Review of the tidal current records indicates that the seep velocity potentially¹ exceeded tidal flow on June 19, 2004, at the Matia Island, Washington, station for 18 minutes. This is the extreme case, as tidal flow was not exceeded by seep velocity during most observed slack tides and, on average, periods of exceedance were generally less than 6 minutes. Taking a conservative approach, an exceedance time of 20 minutes was selected to calculate the seep water volume entering the Strait of Georgia during slack tide (volume = flow rate x duration). During maximum flow conditions,

¹ It is possible that the tidal flow was not exceeded, as seep flow during June is typically lower than the maximum measured flow.

approximately 50 gallons of seep water discharges during slack tide. The ratio of this volume to the tidal zone volume is approximately 0.0001:0.9999 (i.e., the volume of seep water that interacts with seawater is one-ten-thousandth of the total volume of water contained within the tidal zone).

4 FLUORIDE GEOCHEMISTRY

Fluoride is an ion of the element fluorine and is a component of most natural waters. The primary factors that control the concentration of fluoride in natural waters include mineral precipitation and dissolution reactions, and ion exchange with clay minerals. Common fluoride bearing minerals include fluorite (CaF_2) and a group of phosphate-bearing minerals called apatites. The general formula for apatite is $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, or Calcium (Fluoro, Chloro, Hydroxyl) Phosphate. Apatite is actually three different minerals, depending on whether fluorine, chlorine, or the hydroxyl group is predominant. These ions can freely substitute in the crystal lattice and all three are usually present in natural minerals, although some natural minerals have been close to 100 percent of one ion or another. The names of the three end-member minerals are fluorapatite, chlorapatite, and hydroxylapatite.

The minerals fluorite and apatite are present in many natural systems and these minerals are known to control the concentration of fluoride in natural systems through equilibrium reaction. In its simplest form, this type of reaction is similar to that of dissolving salt (the mineral halite) in a glass of water—the salt will readily dissolve until the water reaches saturation with halite (NaCl), and at that point the concentration of dissolved Na^+ and Cl^- is said to be at equilibrium with the mineral halite. More halite can be added to the system, but the concentration of Na^+ and Cl^- in water will not change. If more dilute water is added to the saturated system, more halite will dissolve; conversely, if the water is allowed to evaporate, halite will precipitate out of solution. Natural mineral systems work in a similar manner and the concentrations of dissolved ions in these systems are controlled through predictable geochemical relationships. The remainder of this section evaluates those relationships for the fluoride system at the Site using the geochemical computer code PHREEQC (Parkhurst 1995).

4.1 PHREEQC Modeling

PHREEQC is a U.S. Geological Survey (USGS) computer program designed to model low-temperature geochemical reactions, such as the equilibrium reactions described above. Among other things, PHREEQC can calculate pH, redox potential, and the composition of solutions in equilibrium with multiple phases. The aqueous model definition, including elements, aqueous species, and mineral phases is exterior to the computer code and is completely user-definable. The model can be used to perform the following:

- Speciation and saturation-index calculations.

- Reaction-path and advective transport calculations involving mixing of solutions, mineral and gas equilibria, surface complexation reactions, and ion-exchange reactions.
- Inverse modeling, which finds set of mineral and gas mole transfers that account for compositional differences between waters, within specified compositional uncertainties.

4.2 Model Application to Site

Because of the need to understand the long-term fate and transport of fluoride in the Beach I seep water at the Site, PHREEQC was used to evaluate the saturation states of various fluoride-bearing minerals and the potential effect that those minerals may have on determining the ultimate dissolved concentrations of fluoride in Site water and in seawater of the adjacent Strait of Georgia.

Conceptually, the PHREEQC model was constructed to consider two distinct water sources at the Site. Those waters include seep water from Beach I and seawater adjacent to the Site from the Strait of Georgia. The calculation was performed step-wise so that fluoride solubility in each water source was considered independently and then again where the two combine at the seep point of discharge into the Strait of Georgia. Site-specific chemical data from each water source was used as input to the model. The input chemistry, summarized in Table 4, shows that high concentrations of fluoride (100 to 400 mg/L) are associated with the seep water in the model compared to the observed average concentrations of fluoride at the Site (25.8 mg/L in the lysimeters and 11.6 mg/L for the seep sampling). This concentration range of fluoride was used in the modeling to provide an environmentally conservative evaluation of potential fluoride impacts in the Strait of Georgia.

4.3 PHREEQC Modeling Results

The initial model results showed that both seawater and the site surface seep water are supersaturated with respect to the mineral fluorapatite, indicating that based on equilibrium thermodynamics, fluorapatite would tend to precipitate from solution. There is physical evidence of this type of precipitation in the hard pan mineralization observed in some the site soils at Beach I. The model also shows that the predicted concentration of fluoride in seawater in equilibrium with fluorapatite is 1.3 mg/L, which is equal to the observed

concentration of fluoride in seawater at the Site. This result indicates that the limiting factor to precipitation of fluoride that could be introduced into the Strait of Georgia from seeps associated with Beach I is controlled by the availability of the phosphate ion required for fluorapatite precipitation, based on the equilibrium reaction:



In simple terms, if there is an excess of fluoride from the seep water and there is sufficient calcium ion in seawater, then the concentration of phosphate, the other primary component of apatite formation, is the limiting factor. According to equilibrium calculations in PHREEQC, the concentration of phosphate in seawater in equilibrium with fluorapatite is 0.000008 mg/L, which is low compared to the 0.08 mg/L phosphate concentration observed in the Site seawater. These results and observations indicate that the Site seawater has an excess amount of phosphate ion that is available to combine with fluoride to form fluorapatite in the seep water discharge zone.

A sensitivity analysis was conducted using PHREEQC to develop an understanding of how much excess phosphate capacity is available to buffer fluoride entering the Strait of Georgia from the Beach I seep water. This set of calculations considered three scenarios, based on the hydrologic information presented in Section 3. Those scenarios included volume ratios of 0.9999:0.0001 (one-ten-thousandth), 0.999:0.001 (one-thousandth), and 0.99:0.01 (one-hundredth) parts seawater to site seep water. Based on the hydrologic discussion in Section 3, the one-ten-thousandth ratio of seawater to seep water is a realistic estimate of the zone of potential interaction and limiting factor into the total amount of phosphate availability for fluorapatite precipitation. However, the sensitivity analysis was developed to determine potential fluoride impacts to the Strait of Georgia under a more environmentally restrictive range of conditions. The results of the sensitivity analyses showed the following, using 100 mg/L fluoride in the seep water as the beginning for all calculations:

- The predicted fluoride concentration is 1.3 mg/L in seawater after seep interaction and fluorapatite precipitation at the one-ten-thousandth volume ratio.
- At the one-thousandth volume ratio, the predicted fluoride concentration is 1.42 mg/L in seawater.
- At the one-hundredth volume ratio, the predicted fluoride concentration is 2.30.

The model sensitivity analysis shows that if the amount of seep water in the intertidal zone exceeds the one-thousandth volume ratio, then the buffering capacity of the seawater is lost because excess phosphate is removed by precipitation of fluorapatite. Fluoride concentrations at this volume of seawater are predicted to be below the surface water standard of 1.5 mg/L. In order for an exceedance to occur, seep volumes at Beach I would need to increase 14 fold above typical wet weather conditions. Similarly, another set of calculations was run to find the maximum concentration of fluoride in seep water that could be adequately buffered at the one-ten-thousandth volume ratio of seawater to seep water. These calculations showed that phosphate is nearly fully consumed as seep fluoride concentrations approach 400 mg/L and the predicted concentration of fluoride in the seawater is predicted to exceed 1.36 mg/L.

These calculations show that based on conservative assumptions regarding the concentration of fluoride in Site seep water and the total volume of Site seep water compared to the zone of influence in the receiving water, the surface water standard of 1.5 mg/L fluoride should be maintained under current and foreseeable Site-wide conditions.

5 SUMMARY AND CONCLUSIONS

A fate and transport analysis was performed to determine the impact of elevated fluoride concentrations on the receiving waters of the Strait of Georgia. A field investigation was conducted as part of this study to determine Site-specific characteristics and relationships for use in geochemical modeling. The overall goal of the study was to provide technical data to support Ecology in the designation of a Site-specific, point of compliance remedial goal that is appropriate to achieve the 1.5 mg/L surface water standard.

5.1 Point of Compliance Remedial Goal Development

In accordance with the CAP, we recommend that the point of compliance location for surface water at Beach I be designated as the discharge points from the remediated ravine at the confluence of the intermittent surface seeps in the exposed banks directly below the remediated landfill areas. Furthermore, the point of compliance for surface water at the CCDL should be designated as the intermittent stream in the ravine adjacent to the landfill. Because it is not possible to sample surface water at Beach II, we recommend that compliance with the remedial goal be assessed using the confirmatory soil sampling data and Ecology's three-phase model with Site-specific data from this study. The rationale for this approach is further discussed in the following section. These recommendations are based on the following observations and modeling conclusions.

Seep waters were observed at flow rates of up to 2.5 gallons per minute during the wet season at Beach I. Flows at both Beach II and the CCDL were observed to be less than those at Beach I. These seeps emanate from the exposed surfaces between alluvial cover and formation materials within the excavated landfills and converge at the base of each ravine prior to entering the Strait of Georgia. The zone of potential impact from seeps is defined by the width of the landfill and the horizontal distance of the intertidal area.

The measured background concentration of fluoride in seawater at the Site was approximately 1.3 mg/L. Besides the common cations and anions that are present in seawater, Site-specific testing also indicated that approximately 0.08 mg/L of phosphate, as orthophosphate, was available. This observation is important because fluoride and phosphate ions are known to commonly form the mineral fluorapatite in natural environments. Based on the site-specific chemistry of the seep water and the receiving

water, the USGS model PHREEQC was used to evaluate if fluorapatite precipitation could buffer the concentration of fluoride in seawater at the zone of influence. The model showed that the concentration of fluoride in seawater at equilibrium with fluorapatite is approximately 1.3 mg/L, which is equal to the Site observed background concentration in seawater. The model also showed that there is an excess amount of phosphate available in the Site seawater that could be used to buffer fluoride associated with incoming seep water through fluorapatite precipitation.

Additional modeling was performed to determine a threshold fluoride load from the seeps that would coincide with consumption of excess phosphate in the seawater; thus, producing concentrations of fluoride above the observed equilibrium value of 1.3 mg/L as loading continued. Based on the seep flow conditions and local tidal currents, the model indicates that the seep fluoride concentrations would need to be approximately 400 mg/L before an imbalance in the equilibrium of fluoride and phosphate in receiving water is reached, which would increase seawater concentrations of fluoride to approximately 1.36 mg/L. Therefore, under worst-case seep flow conditions (i.e., wet weather conditions observed at 2.5 gallons per minute) fluoride concentrations below 400 mg/L will not cause an increase in receiving water concentrations above the surface water standard of 1.5 mg/L. For the purpose of this project, and to add an additional margin of protection, we recommend the Site-specific, point of compliance remedial goal for fluoride at Beach I, Beach II, and the CCDL be set at 100 mg/L. Table 5 provides a summary of remedial goals and point of compliance locations for the Site.

Table 5
Site Surface Water Standard and Point of Compliance Remedial Goals

	Fluoride Value (mg/L)	Point of Compliance Location
Site-wide Surface Water Standard	1.5	Not Applicable
Beach I Point of Compliance Goal	100	Toe of the ravine at the confluence of the intermittent surface seeps
Beach II Point of Compliance Goal	100 ¹	Compliance based on assessment of confirmatory soil samples
CCDL Point of Compliance Goal	100	Intermittent stream in the ravine adjacent to the landfill

Note:

1 Direct measurement of seep water is not possible, as discussed in Section 5.2.

It is likely that lower values may be achieved at the Site for the Beach I and Beach II locations; however, it is difficult to predict the near-term and long-term concentrations at the CCDL. In the near-term, we anticipate average fluoride concentrations in surface water seeps to be on the order of 30 mg/L, with a potential for concentrations up to 90 mg/L. As perched layers within the CCDL are depleted because of the lack of infiltration through the low-permeability cover, surface water seeps will also significantly reduce. In the long-term, several sources (i.e., stormwater and aeolian deposition) that are impacted by Intalco operations will persist and potentially contribute to elevated fluoride concentrations in the stream adjacent to the CCDL. Therefore, because fluoride concentrations in excess of 100 mg/L are protective of receiving waters, this value was selected as the remedial goal to ensure an additional factor of safety for CCDL compliance.

5.2 Beach II Compliance

Surface water sampling at Beach II is not possible due to generally dry conditions and the porous nature of the overburden soils exposed by the remedial action. In order to assess compliance with the Site-specific, point of compliance remedial goal, we recommend that confirmatory soil sampling data be compared to criteria generated by Ecology's three-phase model, based on Site-specific data from this study.

As discussed in Section 2, soil and porewater samples were collected and analyzed to determine a Site-specific K_d value for fluoride. K_d values are used in models, along with other parameters, to determine the relationship between soil and groundwater (porewater) concentrations for a given site. In the Ecology three-phase model used by the MTCA program, the site-specific K_d value is critical in determining an acceptable soil concentration that will achieve a given cleanup goal. Table 6 summarizes the porewater data and the associated K_d values. The Site-specific K_d is the average of these numbers, and is equal to 26.5.

Also pertinent to the three-phase model is the site-specific dilution that occurs as water percolates through a soil stratum and combines with lateral, off-site groundwater prior to manifesting as a surface water seep. The dilution factor is the ratio of the porewater concentration to that of the measured seep. To determine the Site-specific dilution factor at

Beach I, the average fluoride porewater concentration was divided by the average seep water concentration ($DF = 25.84 / 11.6 = 2.23$).

Table 6
Summary of Fluoride Concentrations and Sample-specific K_d Values

Sample	Fluoride in Soil (mg/kg)	Fluoride in Porewater (mg/L)	Location-Specific K_d
AIN-PW1-0119	565	32.5	17.38
AIN-PW1-0201	565	37.9	14.91
AIN-PW1-0202	565	44.2	12.78
AIN-PW2-0119	187	3.5	53.43
AIN-PW2-0201	187	3.3	56.67
AIN-PW2-0202	187	13	14.38
AIN-PW3-0119	365	6.9	52.90
AIN-PW3-0201	365	44.8	8.15
AIN-PW3-0202	365	46.5	7.85

Using the Ecology three-phase model with the Site-specific K_d , dilution factor, and point of compliance remedial goal (100 mg/L), we generate a soil cleanup level for fluoride of 5,947 mg/kg (refer to Figure 4 for model output). The maximum observed fluoride soil concentration at Beach II was 370 mg/kg. This value is an order of magnitude less than the soil cleanup level generated by the model. Therefore, it is reasonable to assume that fluoride concentrations will be protective of the surface water standard (1.5 mg/L) without a direct point of compliance measurement.

3-Phase Model Assumptions									
Hazardous Substance	CAS No.	Gd H ₂ O C/U Level (mg/l) (1)	Soil Properties			Chemical Properties			Dilution Factor (6) (dimensionless)
			Bulk Density (g/cc) (2)	Soil Water (cc/cc) (2)	Soil Air (cc/cc) (2)	H' (cc/cc) (3)	Solubility (mg/l) (4)	Kd (cc/g) (5)	
Fluoride		100.000	1.5	0.3	0.13	0	40,000	26.5	2.23

3-Phase Model Results									
Hazardous Substance	CAS No.	Pore Water Concentration (mg/l) (7)	Water Mass (mg/kg) (8)	Vapor Concentration (mg/m ³) (9)	Vapor Mass (mg/kg) (10)	Soil Concentration (mg/kg) (11)	Soil Mass (mg/kg) (12)	Sum Mass (mg/kg) (13)	Beach II Soil C/U Level (mg/kg) (14)
Fluoride		222.80	44.56	0	0.00	5902.89	5,902.89	5947.45	5947

- (1) Based on Site-specific data, PHREEQC model analysis, and the BC Canada Marine Surface Water Standard
- (2) Default in Equation 747-1
- (3) Non volatile substance, therefore a Henry's constant of 0 is assigned.
- (4) Assumes fluoride occurs as sodium fluoride. This is the solubility at 25 C from HSDS data base.
- (5) Based on empirical data - average of 9 values
- (6) Based on empirical data = porewater concentration / surface seep concentration
- (7) Pore water concentration = ground water cleanup level X dilution factor
- (8) Water mass = [Pore water concentration X soil water fraction] / soil bulk density. This is the mass of contaminant in the water phase.
- (9) Vapor concentration = Pore water concentration X Henry's Constant X 1000.
- (10) Vapor mass = [Vapor concentration X soil air fraction] / soil bulk density. This is the mass of contaminant in the vapor phase.
- (11) Soil concentration = Pore water concentration X Kd
- (12) Soil mass = [Pore water concentration X Kd X soil bulk density] / soil bulk density. This is the mass of contaminant in the soil phase.
- (13) Sum mass = water mass + vapor mass + soil mass. This value equals the soil cleanup level.
- (14) Calculated using equation 747-1 with model defaults and values shown in this table.

5.3 Temporary Brick Storage Pile Underlying Soils

Remediation of the temporary brick storage area will occur with the CCDL remedial action. Brick will be beneficially reused and soils will be assessed for compliance under the MTCA program. The remedial goal for this portion of the site is based on the Safe Drinking Water Act Maximum Contaminant Level (MCL) for fluoride, which is equal to 4 mg/L.

Compliance with the MCL will be assessed using the Ecology three-phase model with the Site-specific K_d determined in this study and the standard MTCA dilution factor of 20 (Figure 5). These parameters yield a soil cleanup criterion for protection of groundwater equal to 2,136 mg/L. After removal of the brick, the underlying soils will be sampled and analyzed for fluoride, and compared to the MCL-derived soil cleanup criteria. If the concentrations exceed the cleanup level derived by the three-phase model on a surface-area-weighted-average concentration, then they will be excavated and incorporated into the CCDL remediation as bulk fill below the low-permeability cover system.

3-Phase Model Assumptions									
Hazardous Substance	CAS No.	Gd H ₂ O C/U Level (mg/l) (1)	Soil Properties			Chemical Properties			Dilution Factor (6) (dimensionless)
			Bulk Density (g/cc) (2)	Soil Water (cc/cc) (2)	Soil Air (cc/cc) (2)	H' (cc/cc) (3)	Solubility (mg/l) (4)	Kd (cc/g) (5)	
Fluoride		4.000	1.5	0.3	0.13	0	40,000	26.5	20.00

3-Phase Model Results									
Hazardous Substance	CAS No.	Pore Water Concentration (mg/l) (7)	Water Mass (mg/kg) (8)	Vapor Concentration (mg/m ³) (9)	Vapor Mass (mg/kg) (10)	Soil Concentration (mg/kg) (11)	Soil Mass (mg/kg) (12)	Sum Mass (mg/kg) (13)	Beach II Soil C/U Level (mg/kg) (14)
Fluoride		80.00	16.00	0	0.00	2119.56	2,119.56	2135.56	2136

- (1) Based on 1996 Safe Drinking Water Act Maximum Contaminant Level (MCL) for Fluoride
- (2) Default in Equation 747-1
- (3) Non volatile substance, therefore a Henry's constant of 0 is assigned.
- (4) Assumes fluoride occurs as sodium fluoride. This is the solubility at 25 C from HSDS data base.
- (5) Based on empirical data - average of 9 values
- (6) Based on empirical data = porewater concentration / surface seep concentration
- (7) Pore water concentration = ground water cleanup level X dilution factor
- (8) Water mass = [Pore water concentration X soil water fraction] / soil bulk density. This is the mass of contaminant in the water phase.
- (9) Vapor concentration = Pore water concentration X Henry's Constant X 1000.
- (10) Vapor mass = [Vapor concentration X soil air fraction] / soil bulk density. This is the mass of contaminant in the vapor phase.
- (11) Soil concentration = Pore water concentration X Kd
- (12) Soil mass = [Pore water concentration X Kd X soil bulk density] / soil bulk density. This is the mass of contaminant in the soil phase.
- (13) Sum mass = water mass + vapor mass + soil mass. This value equals the soil cleanup level.
- (14) Calculated using equation 747-1 with model defaults and values shown in this table.

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