



**PROGRESS REPORT  
Heavy Metal Removal  
from Hamilton Harbour Sediment  
Treatability Study for Pilot Demo**

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**Project # 4-6013**

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**HEAVY METAL REMOVAL FROM**  
**HAMILTON HARBOUR SEDIMENT**  
**TREATABILITY STUDY FOR PILOT DEMONSTRATION**  
**PROJECT # 4-6013**

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## 1.0 CONCLUSIONS AND RECOMMENDATIONS

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### 1.1 CONCLUSIONS

The Hamilton Harbour sediment after bioremediation of the organic contaminants was a very fine grained material. Particle size distribution was 0% oversize (>4 mesh), 10% gravel (4-10 mesh), 50% sand (10-270 mesh), and 40% silt and clay (<270 mesh). Of the 50% sand sized material, inorganic sand was 38% and organic vegetation made up 12% of the material. The metals which failed to meet the Ontario Draft Guidelines for urban industrial fill were cadmium, lead and zinc. Iron and manganese, which had no specific standards, were at greatly elevated levels and needed to be lowered.

Metals were found in all the particles size fractions and in both the organic vegetative matter and the inorganic sediment. A combination of attrition, particle size separation, flotation to remove organic vegetation, and magnetic treatment was found to generate four fractions: vegetation, magnetic material, treated sand, and fines. The treated sand met the Ontario Draft Guidelines on urban industrial fill for all metals. The iron was reduced in the sand by 75% and the manganese by 40%. The treated sand met the urban residential fill guideline for all metals except zinc (182 ppm achieved, 140 ppm is guideline). The other three fractions isolated were all well above the fill guidelines and will require disposal or recycle. The magnetic fraction should be recyclable in the steel mill. The vegetation may be recyclable and fines fractions will likely require controlled landfill disposal.

Physical treatment steps alone were found to meet the urban industrial fill guidelines for the sand. Density and higher field magnetic separation methods were also investigated, however, they were not found to give substantially improved results. Leaching was considered under acidic, neutral, and basic conditions. The high carbonate content of the sediment ruled out acidic leaching. Neutral leaching was shown to be completely ineffective. Ammonia leaching was moderately effective for removing zinc and copper. Zinc removal may be of some benefit, as ammonia leaching of the sand fraction could generate a product which met the residential fill guidelines instead of the industrial fill guidelines.

### 1.2 RECOMMENDATIONS

Pilot-scale demonstration of the process proven in this bench-scale Treatability Study is recommended. The proposed pilot-scale process would utilize the separation stages of particle size separation, vegetation flotation, and magnetic material removal, and include the following unit operations:

1. Feed system (feed hopper and conveyor)
2. Trommel (deagglomeration)

3. Oversize separation (screen)
4. Particle size separation (sand and fines separation)
5. Flotation (organic vegetation removal)
6. Wet Drum magnetic separation (magnetic fraction removal)
7. Sand dewatering
8. Fines dewatering
9. Misc. dewatering (magnetic and vegetation fraction)
10. Water handling, pumps, misc.

Additional unit operations could be tested if deemed necessary, i.e. higher field magnetic separation for additional magnetic material removal, and ammonia leaching of the sand fraction for additional zinc removal. Also, if deemed necessary to allow recycle of the magnetic fraction(s), zinc removal from the iron-rich magnetic material could be studied in the laboratory and implemented if proven effective. Reuse criteria for the magnetic, vegetation, and fines fractions should be studied to ensure their maximum level of recycle/reuse.

The goal of the pilot-scale demonstration remains the same as during the Treatability Study:

Generate as large a fraction as possible of material which meets the urban industrial fill guidelines and recycle as much other material as possible with a minimum amount of material requiring controlled landfill. Treatment costs should be kept at a minimum and allow maximum in-kind-services by stakeholders.

## 2.0 BACKGROUND

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### 2.1 SITE DESCRIPTION AND HISTORY

Information contained in this section was extracted from *Environmental Impact of Hamilton Harbour on the Nearshore Area of Western Lake Ontario*<sup>1</sup>.

Hamilton Harbour is situated at the western end of Lake Ontario in the Province of Ontario, Canada.

The harbour is surrounded by the cities of Hamilton to the south and Burlington to the north. The steel industry sits on the south shore. The surrounding cities have used the harbour to dump effluent from their sewage treatment plants. The steel industry located on the south shore utilized the harbour waters as a source of cooling water, as well as a sink for cooling water effluent. Water quality in the harbour is severely impaired by high concentrations of organic and inorganic contaminants, eutrophication and oxygen depletion in the summer. Particulate iron, hematite and wustite, are in the harbour waters as a result of the iron and steel industry activities. There is concern that exchange of waters between the harbour and Lake Ontario is causing contamination in the lake.

The sediment to be treated in this Phase I investigation was dredged from Hamilton Harbour in 1992. The material has undergone biological treatment to remove polyaromatic hydrocarbons (PAHs) in a pilot demonstration of the Grace Dearborn DARAMEND™ process.

### 2.2 WASTE STREAM DESCRIPTION

#### 2.2.1 Waste Matrices

Samples were taken from the stockpiled DARAMEND™ treated sediment by Wastewater Technology Centre (WTC) personnel and supplied to COGNIS, Inc. Composites were taken in order to supply a representative sample of the material.

The waste matrix consisted of sediment with an organic amending agent added during biological treatment. Contaminants expected to be found in the sediment based on known activities in the harbour included, heavy metals and particulate iron containing species.

#### 2.2.2 Pollutants/Chemicals

The contaminant heavy metals of concern in this Treatability Study included

arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc. No specific cleanup criteria have yet been established for the Hamilton Harbour sediment. Therefore, Ontario landfill guidelines were used as targets for this study. These guidelines, outlined in Table 1, were supplied by Wastewater Technology Centre.

**Table 1.**  
**Fill Guidelines for Hamilton Harbour Sediment**

Metal	Ontario Fill Guidelines <sup>1</sup>			
	Inert	Urban Residential	Urban Industrial	Controlled
Arsenic	11	17	20	200
Cadmium	0.71	0.84	1.7	30
Chromium	58	62	120	7,500
Copper	41	65	130	1,500
Iron	-	-	-	-
Lead	45	98	200	2,000
Manganese	-	-	-	-
Nickel	38	38	76	1,500
Zinc	120	140	280	6,000

<sup>1</sup>Guideline not established for iron and manganese.

Sediment meeting the industrial fill criteria following cleanup could be disposed of without a permit in the Hamilton confined disposal facility or on industrial land. Sediment meeting the residential criteria could be used as fill anywhere.

Zinc, cadmium, and lead were known to exceed both the urban industrial and urban residential criteria at the onset of the study. Iron and manganese do not have landfill guidelines, but were considered very elevated.

## 2.3 TREATMENT TECHNOLOGY DESCRIPTION

The treatment technologies tested in this Phase I Treatability Study were soil washing and soil leaching. Soil washing is the separation of soil into its constituent particles of gravel, sand, silt and clay. Because of the much higher surface area



and surface binding properties of clay, most of the contaminants tend to adhere to the clay fraction. Soil washing, therefore, attempts to generate clean sand and gravel fractions by removing any fines adhering to the larger soil particles and if necessary transfer contaminants bound to the surface of the larger particles to the smaller soil particles. For sites contaminated with pieces of lead, steel, or other metallic debris, additional operations may be necessary to further clean the sand and gravel fractions. Ferrous metal fragments or certain minerals can be removed magnetically, and other much higher density materials can be removed with mining techniques such as jigging, spirals, or other gravity separation devices. The contaminated fines (silts and clays) fraction generated then requires further treatment or disposal.

Soil leaching is a process which attempts to remove adsorbed ionic contaminants from the finer soil particles. These adsorbed metallic components may consist of metal ions adsorbed onto ion exchangeable sites on clay surfaces, metal ions complexed to chelating binding sites in organic humic and fulvic acids, or metal ions surface or internally bound in ferric and manganese oxide particles. Additionally, small metallic fragments not removed by physical processing may require oxidative dissolution to remove them, particularly from a sand fraction. After the metals are dissolved, they require removal from the leachant solution by some means. Depending on each metal's properties, they may be removed from the leachant by reduction, precipitation, or ion exchange.

### **2.3.1 Treatment Process and Scale**

The soil washing treatment processes tested in this Treatability Study included particle size separation, density separation, magnetic separation, and flotation (lighter particle removal). The testing was all done on small, bench-scale apparatus. The selection of physical separation techniques was limited to techniques which could be readily scaled to pilot-scale and eventually field-scale. The purpose of this Treatability Study was to define the unit operations necessary for the pilot-scale demonstration.

The leaching portion of the testing evaluated leaching of the sediment to remove the various metals of interest. Leaching was conducted on the sand and fines fractions following removal of a substantial amount of vegetation and magnetic material. Leaching conditions tested included neutral, basic and acidic leachants.

### **2.3.2 Operating Features**

Soil washing relies on physical differences in particles to allow separation of contaminated and noncontaminated fractions, e.g. size, magnetism, density. Soil leaching relies on selectively dissolving and removing metallic contaminants from the matrix, separating the leachant solution from the soil matrix, and recovering the dissolved metals from the leachant.

### 3.0 TREATABILITY STUDY APPROACH

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The Treatability Study described here evaluated the treatment of metal contaminated sediment from Hamilton Harbour by soil washing and soil leaching methods. The main goal was to determine whether, on the bench-scale, the metal contamination levels in the sediment could be lowered to acceptable landfill requirements (reference section 2.2.2). The bench-scale processes utilized in the study were soil washing (particle size separation, density separation, flotation, magnetic separation) and leaching. All processes tested were applicable to pilot-scale demonstration.

#### 3.1 TEST OBJECTIVES AND RATIONALE

The specific objectives of this study included: (1) investigate the distribution of contaminants among the sediment fractions, (2) determine the effect of physical treatment on the sediment, (3) determine the effect of leaching treatment on the sediment.

The rationale for this approach was as follows:

(1) Understanding the distribution and nature of the contaminants guides the selection of physical and leaching processes. The distribution of the contaminants is usually related to the origin of the contaminants and any previous remediation done at the site.

(2) Physical separations are done whenever possible because of the generally low cost and effectiveness in removing certain types of particles which are often contaminant reservoirs. Physical removal of these particles is also important because such contaminant particles are generally not amenable to chemical leaching.

(3) Leaching is effective when the metal contaminants are adsorbed onto particle surfaces where the metals can be chemically displaced, but the particles are not physically separable.

Throughout the Treatability Study the project goal was kept in focus. Treatment techniques were chosen based on effectiveness and lowest cost. Isolable fractions were generated when there was a strong possibility of recycling or reusing these materials. The primary goal was to attain the industrial fill guideline by using the lowest cost technology, rather than trying to attain the residential fill guideline with a significantly more expensive technology.

## 4.0 EXPERIMENTAL RESULTS AND DISCUSSION

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### 4.1 SAMPLING

The samples used in this study were selected and supplied by Wastewater Technology Centre personnel. Composite samples were created from stockpiled sediment previously treated to remove organic contamination. Two different composites were received during the course of this study. Originally a 5 gallon sample was received and this was used for a majority of the work in this Report. In order to have magnetic separation conducted with larger, scaleable equipment, a second 5 gallon sample was requested. These samples, despite the fact that they were taken at different times, were found to be similar in composition and metal content and were therefore regarded as the same throughout this study (reference data in sections 4.2.2 and 4.6.1).

Upon receipt of each treatability sample, the buckets were poured out into a large polypropylene tray and homogenized by hand. During homogenization clay balls were broken up and the sediment was thoroughly mixed to assure that representative samples would be obtained in subsequent sub-sampling.

### 4.2 PRELIMINARY ANALYSIS

#### 4.2.1 Physical Description

The first sediment sample was dry upon receipt and contained considerable vegetative material and a few obvious clay balls. As expected, the sediment sample contained virtually no oversized ( $> 1/4"$ ) material, only some small rock and an occasional large piece of vegetation.

#### 4.2.2 Metal Concentration in Whole Sediment

Preliminary metal concentration measurements were made on the homogenized whole sediment sample utilizing X-Ray Fluorescence (XRF). Three measurements were made on a single sample, the readings averaged and the results are shown in the first data column of Table 2.

Triplicate samples of the whole sediment were also analyzed by digestion (EPA Method 3050A) followed by analysis of the digest solution by Inductively Coupled Plasma Spectroscopy (ICP) (EPA Method 6010A). The results are shown in Table 2.

Note: XRF is a good tool for obtaining rapid analyses of samples during processing. The results from XRF analyses however are to be considered as estimates only, as XRF tends to deviate from the results obtained from samples analyzed by an EPA approved acid digestion followed by

spectroscopy. Table 2 contains data from XRF and digest/ICP and illustrates how these two measurement methods compare for the Hamilton Harbour sediment matrix. Throughout this Treatability Study both methods were utilized. Reference Appendix A which contains comparative charts for zinc, lead, manganese and iron. Using these charts one can estimate a digest value based on an XRF result. Throughout this study when rapid processing information was desired, XRF was employed, when a more definite measurement of a sample was needed digest/ICP was utilized.

**Table 2.**  
**Metal Analysis Data for Whole Sediment: Bucket #1**

Metal	Metal Concentration (ppm)					
	XRF	DIGEST/ICP				Previously Reported Values <sup>2</sup>
		#1	#2	#3	Average	
As	BDL <sup>1</sup>	<19	<19	<19	<19	5.7
Cd	BDL	2.5	2.3	2.5	2.4	4.9
Cr	70	40.4	38.1	42.2	40.2	49
Cu	BDL	41	40	43	41	43
Fe	78,740	44,800	43,800	46,300	44,967	3.8%
Pb	240	198	197	188	194	300
Mn	2,270	1,410	1,310	1,340	1,353	1,635
Ni	BDL <sup>1</sup>	<11.4	<11.4	<11.4	<11.4	27
Zn	2,060	1,160	1,110	1,170	1,147	1,790

<sup>1</sup>Below Detectable Level.

<sup>2</sup>Pre-Treatability Study data supplied by Wastewater Technology Centre.

Discussion. The initial metal levels found in the sediment samples provided to COGNIS are consistent with previous data on the sediment supplied by WTC. Therefore, the samples are representative of the site after bioremediation of the organic contaminants. The metals of most concern and the highest concentrations were iron, lead, manganese, and zinc. Triplicate digest samples of the sediment showed a very consistent distribution ( $\pm 5\%$  or less) of the contaminant metals. This is consistent with the metals existing as very small evenly distributed particles or being adsorbed onto many types of particles. The presence of large, readily

isolated metal fragments or a specific type of debris are not consistent with the data distribution observed.

#### 4.2.3 Vegetation Content

Cations are known to bind tightly to the surfaces of vegetative matter. For this reason organic matter from a metal contaminated soil is often found to contain higher metal concentrations than other soil components. Separation of vegetation can often lower the metal concentration(s) in the remaining soil.

A gross dry screening of the sediment was conducted to estimate the size of the vegetation present and to determine whether it could be separated from other components of the sediment with simple screening. US sieve sizes 18, 20 and 25 mesh were utilized for this purpose. Approximately 500 grams of whole sediment was screened and the resulting fractions recovered, weighed and observed for contents. The results are shown in Table 3.

**Table 3.**  
**Preliminary Vegetation Sizing**

Fraction	% Weight	Description
> 18 mesh	38	Mostly Vegetation, Some Small Rock
18 - 20 mesh	8	Vegetation and Sand
20 - 25 mesh	6	Vegetation and Sand
<25 mesh	48	Sand and Fines with Smaller Sized Vegetation

Vegetative matter was found throughout all the fractions. The larger fractions contained a majority of vegetation with some small rock and sand. The smallest fraction (<25 mesh) also contained considerable fine vegetation. These results suggest that a substantial fraction of the vegetation could be removed with screening. The presence of vegetation in all fractions indicates that it could not be completely removed from the sediment with screening.

A sample of whole sediment was sent to Environmental Technical Services (ETS) in Petaluma, CA for a series of soil tests including a detailed analysis of the organic matter (OM). In the OM test the soil is separated into fractions via wet sieving and hydrometer and then each fraction is measured for its percent organic matter. Organic matter is measured by wet oxidative

digestion. The results are shown in Table 4.

Note: The sediment had an elevated level of organic matter relative to standard soil and therefore the laboratory had some difficulty with the analyses. The standard wet oxidation was not effective enough for the amount of vegetation present and the organic mass had to be separated using water flotation with drying, and/or air stream separation. The OM data for the different fractions may be slightly underestimated.

**Table 4.**  
**Results From Organic Matter Evaluations**

Sieve Size	Fraction	Weight % of Sediment Retained	OM as % of Sediment Fraction	OM as % of Total
> 4 mesh	Gravel	1.1	0	0
4 - 10 mesh		8.5	0	0
10 - 18 mesh	Sand	14.2	29.8	4.2
18 - 35 mesh		12.5	39	4.9
35 - 270 mesh		23.5	13	3.1
< 270 mesh	Silt/Clay	40.2	24.2	9.7
TOTAL		100	-	21.9

The total OM content in the whole sediment, which was primarily vegetation, is reported above as roughly 20% by weight. Some of the sediment fractions were found to have a much higher OM content approaching 40%, while the coarser fractions had none. While the total OM is 20% by weight, this corresponds to close to 50% by volume.

Discussion. The high level of organic vegetative debris was expected because of the bioremediation which had previously taken place. The DARAMEND™ bioremediation employed an unidentified organic amendment to facilitate biodegradation. The majority of the visible (> 270 mesh) organic vegetative matter appeared to be chopped straw and other fibrous material. While the origin of all the vegetative matter is not possible to determine, it is assumed that the chopped straw was a result of bioremediation and not inherently present in the sediment as dredged. The origin of the finer organic matter is less obvious. If the DARAMEND™ treatment also added fine organic amendments, such as ground flours, starches, or saw dust, this

may contribute to the fine (<270 mesh) organic matter found. Otherwise, fine native degraded bio matter would be expected to exist in the fines fraction. Regardless of the origin, the organic vegetative matter fraction is significant (>20% by weight), and even more significant when measured by volume (approximately 50%). The eventual disposition of the organic matter will constitute a significant portion of a cleanup. As will be seen later (sections 4.2.4 and 4.4.1), the organic fraction contains significant metal concentrations and the prior use of biodegradation amendments will affect the distribution of metals in the sediment.

#### 4.2.4 Metal Concentration in Vegetation

A small sample of the vegetation was separated utilizing flotation in order to isolate it for preliminary metals analysis. A sample of sediment was placed in the bottom of a 250 mL graduated cylinder. A thin tygon tube connected to a water source was placed in the bottom of the cylinder so that water was delivered under the sediment. Water was then allowed to flow at a rate that caused the lighter material to float but allowed the heavier materials to remain in the container. The vegetation (with some fines that were swept over) was then filtered from the process water, dried and analyzed by XRF. Triplicate measurements were made on a single sample and the averaged results are shown in Table 5 below.

**Table 5.**  
**XRF Metal Analysis Data For Vegetation**

<b>Metal</b>	<b>Metal Concentration (ppm)</b>
As	BDL <sup>1</sup>
Cd	BDL
Cr	170
Cu	507
Fe	72,870
Pb	290
Mn	8,900
Ni	40
Zn	2,920

<sup>1</sup>Below Detectable Level.

Discussion. This XRF data suggests that there is a slightly higher concentration of most metals in the vegetation as compared to the whole sediment (comparison to XRF data in Table 2). These values are not as high as one might anticipate making it unclear as to whether removal of the vegetative material alone would substantially lower the metal concentrations in the remaining sediment. Further analyses on the vegetation were conducted later in the study during larger scale processing which show a more positive correlation of high metal values in the vegetative matter, reference section 4.4.1 for results.

#### **4.2.5 Sand Content**

A LaMotte classification test was conducted to estimate the sand content in the sediment. It was hoped that sand separated from vegetation and silt/clay would contain acceptable metal levels without further treatment. The LaMotte classification test separates soil into its three basic particle size fractions: sand, silt and clay based on settling time. This test was modified somewhat due to the sediment behaving differently than normal soil. Multiple steps involving decantation were conducted, as compared to the single step called for in the method, in order to make sure the vegetation was all separated from the sand. Approximately 30% of the sediment was found to be sand.

#### **4.2.6 Metal Concentration in Sand**

The sand separated in the LaMotte classification was measured by XRF to gain an estimate of the metal content in this fraction. A single sample was measured in triplicate and the averaged data is in Table 6 below.



**Table 6.**  
**XRF Metal Analysis Data**  
**LaMotte Separated Sand**

<b>Metal</b>	<b>Metal Concentration (ppm)</b>
As	BDL <sup>1</sup>
Cd	36
Cr	120
Cu	42
Fe	46,130
Pb	80
Mn	1,870
Ni	57
Zn	880

<sup>1</sup> Below Detectable Level.

Discussion. From this preliminary measurement it appeared that the sand with fines and vegetation removed still contained elevated levels for some metals. Therefore, a simple particle-size based separation of sand alone will not generate a fraction clean enough to meet the industrial landfill criteria. A more detailed look at different size sand fractions and their metal concentrations was conducted during larger scale processing, reference section 4.4 for results.

#### **4.2.7 Carbonate Content**

The sediment was found to have a pH of 7.8 and a very high carbonate/bicarbonate content. Titration of the sediment with hydrochloric acid was conducted to determine the carbonate/bicarbonate content and the general amenability of the sediment to any type of acidic leaching. Titration of the sediment with concentrated hydrochloric acid required ca. 22% of the material weight in HCl to maintain a pH of 1. This amounts to 6 meq/g acid neutralizing capacity. After titration approximately 50%wt of the sediment remained; approximately half of the material dissolved. During the acidification a large amount of carbon dioxide evolution was observed. The amount of carbon dioxide liberated was not specifically measured.

Titration was also conducted on separated sediment fractions (fines [ $<230$  mesh], sand and vegetative matter) individually. The fractions behaved similarly to the whole sediment, approximately 20 - 23% of the sample weight was required in HCl to maintain a pH of 1, and ca. 50% of each sample dissolved during titration. The high acid consumption is due to the elevated level of carbonate/bicarbonate contained in the sediment.

Sulfuric acid titration was conducted to determine if conversion of calcium carbonates to insoluble calcium sulfate (gypsum) would be feasible. Titration of the sediment fines ( $<230$  mesh) with sulfuric acid required 20% of the fines weight in concentrated sulfuric acid to achieve pH 3. The fines following titration had increased in weight by 10% and by volume 50%.

Both data supplied by WTC on pre-Treatability Study sediment and XRF data collected by COGNIS on the pre-treatment samples indicated that the concentration of calcium was 80,000 ppm or ca. 8%wt. This corresponds to 20% calcium carbonate or 32% calcium bicarbonate.

Discussion. Titration of the whole sediment as well as the separate sand and fines fractions consumed a very large amount of acid. The acid neutralizing capacity of the sediment can either be attributed to calcium bicarbonate or a mixture of calcium, magnesium and other carbonates. If the acid neutralizing capacity of the sediment is assumed to be a combination of calcium and magnesium carbonates only, this would predict about 25-30% of these carbonates in the sediment. If the neutralizing capacity of the sediment is assumed to be all calcium bicarbonate, this would amount to approximately 50% calcium bicarbonate. The exact source of the acid neutralizing species is likely to be complex and involve many types of species. In any case, this large acid consumption makes any acidic leaching operation unattractive both economically and with respect to the large amount of salt generated in neutralization. An acidic leaching attempt with an acid which reacts with calcium carbonate to produce a soluble salt, e.g. calcium chloride, will result in dissolving approximately half of the sediment. Therefore, any leaching operation with an acid which would produce soluble calcium salts (e.g. hydrochloric, nitric, acetic acid) was deemed not practical and was not further studied.

Reaction with sulfuric acid would avoid the soluble salt generation problem by producing an insoluble calcium sulfate byproduct. This approach was also not attractive because it resulted in a 10% weight increase and a 50% volume increase. The weight increase was expected if approximately 30% of the sediment is calcium carbonate (30% x 36% molecular weight increase in converting calcium carbonate (MW = 100 g/mol) to calcium sulfate (MW = 136 g/mol)). The volume increase was also not completely surprising as the calcium carbonate was likely present in a crystalline form while the calcium sulfate formation would result in amorphous calcium sulfate.

Primarily because of the very large volume increase, any sulfuric acid based leaching of the sediment did not appear to be practical and further studies were not conducted.

### 4.3 PARTICLE SIZE DETERMINATION

To obtain a more detailed analysis of the particle size distribution and how the vegetative material was partitioned in the sediment, further testing was conducted. Particle size determination was conducted in the COGNIS laboratory and a sample was sent to ETS (see section 4.2.3) for a parallel outside analysis.

#### 4.3.1 Internal Testing

Wet sieving was conducted on whole Hamilton Harbour sediment to determine the particle size distribution. A 500 gram sample of sediment was placed in a RoTap/Wet Sieve apparatus equipped with US sieve sizes 4, 10, 18, 100 and 230 mesh. Sieving was conducted for 20 minutes at a water flow rate of ca. 5 gallons/hour. Each fraction was collected, dried in a 60 °C oven and weighed. Results are shown in Table 7 below.

**Table 7.**  
**Results from COGNIS Particle Size Determination**  
**Whole Sediment**

Sieve Size	Fraction	% Weight	Description
> 4 mesh	Gravel	1.8	Clay Balls <sup>1</sup> and Gravel
4 - 10 mesh		15	Gravel and Vegetation
10 - 18 mesh	Sand	14	Sand and Abundant Vegetation
18 - 100 mesh		17	Sand and Vegetation
100 - 230 mesh		12	Fine Sand
< 230 mesh	Silt & Clay	40.2	Fines

<sup>1</sup>Clay balls formed during wet screening, without clay ball formation a majority of this material would have ended up in the <230 mesh fraction.

Discussion. This data shows that the silt/clay fraction is the largest. Visually it appeared that the 10 - 18 mesh fraction contained the most vegetative matter. Since much of the vegetation appears to be relatively

large (> 18 mesh), it should be readily removed from the inorganic fractions of the sediment by flotation and screening. Wet screening of the dried sediment generated few clay balls, which would indicate that deagglomeration of dried sediment should not be a particular problem on a larger scale. Pilot-scale deagglomeration in a trommel with wet screening should adequately generate a clean gravel fraction and allow separation of a silt and clay-free vegetative fraction.

#### 4.3.2 External Testing

A sample of whole sediment was sent to ETS Laboratory for particle size determination. Wet sieving was conducted similarly to that done at COGNIS with slightly different screen sizes. Hydrometer testing was also conducted to determine precisely the sand, silt and clay distribution. Determination of the organic matter (OM) content already discussed in section 4.2.3 was evaluated at the same time. The results received are in Tables 8 and 9.

**Table 8.**  
**Results from ETS Particle Size Determination**  
**Whole Sediment**

Sieve Size	Fraction	Weight % of Total Retained	Weight % of Sediment Retained <sup>1</sup>	OM as % of Fraction	OM as % of Total
> 4 mesh	Gravel	1.1	1.4	0	0
4 - 10 mesh		8.5	10.9	0	0
10 - 18 mesh	Sand	14.2	12.8	29.8	4.2
18 - 35 mesh		12.5	9.7	39	4.9
35 - 270 mesh		23.5	26.2	13	3.1
< 270 mesh	Silt & Clay	40.2	39	24.2	9.7
TOTAL		100	100	-	21.9

<sup>1</sup> Sediment with organic matter removed.

Again the silt/clay fraction was found to be the largest. The sand fractions made up approximately 50% of the sediment. Results from internal and external testing agreed well.

The results from the hydrometer test are shown in Table 9 along with wet sieve data for comparison. The silt and clay values in the wet sieve data

column are calculated from the percentage found to be <270 and the ratio of silt vs. clay in the hydrometer test.

**Table 9.**  
**Sediment Classification Data from Wet Sieve and Hydrometer**

Sediment Fraction	Hydrometer Resulting % Weight	Wet Sieving Resulting % Weight
Gravel	-	12.3
Sand	55.5	48.7
Silt	25.7	22.5 <sup>1</sup>
Clay	18.8	16.5 <sup>1</sup>

<sup>1</sup> Calculated using <270 mesh wet sieve data and hydrometer results.

Discussion. The external particle size and organic matter determination verified the size distribution found by COGNIS. Approximately half of the organic vegetative matter was again shown to be in the coarse to medium sand-sized fractions (>35 mesh). Separation of this material should be relatively easy on any larger scale. The organic matter in the silt and clay fraction would not be easily separated because the settling properties of the organic matter and clay would be too similar. The <270 mesh organic matter should be considered to remain in the <270 mesh inorganic sediment fraction.

Table 9 showed that the silt:clay ratio is approximately 60:40. Because a majority of the fines fraction is in fact silt and not clay particles, settling of a flocced fines fraction on a larger scale should not be particularly troublesome and should give a suitably thickened and dried fines fraction. The high percentage of fines in the total sediment does mean that the fines handling equipment on full-scale will have to appreciably scaled up to maintain fast throughput.

#### **4.3.3 Metal Concentrations in Light vs. Dense Fractions**

An experiment was conducted to determine whether there was a difference in metal concentration between light material and heavy material in the fines fraction. The fines fraction obtained from the wet sieving experiment (internal) described in section 4.3.1 was used for this purpose. Samples of this <230 mesh fraction were placed in a centrifuge for 10 minutes at 3,000

rpm. After centrifugation the bottom and the top of the pellet were separated from the rest of the sample. These top and bottom portions were then measured by XRF. This experiment was conducted in duplicate, each fraction measured on the XRF in triplicate (averages presented in data table) and the data are summarized in Table 10 below.

**Table 10.**  
**Metal Analysis Data**  
**Light and Heavy Fractions of <230 mesh Fines / XRF**

Metal	Metal Concentration (ppm)								
	As	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Pellet Top	43	BDL <sup>1</sup>	190	640	111,000	820	2,350	20	4,780
Duplicate	BDL	BDL	370	550	115,467	1,010	2,870	BDL	5,090
Pellet Bottom	60	BDL	170	BDL	99,100	240	1,440	140	1,570
Duplicate	BDL	40	110	100	105,130	310	1,380	70	1,810

<sup>1</sup>Below Detectable Level

The top of the pellet had noticeably higher concentrations of copper, lead, manganese and zinc, while a slightly lower concentration of nickel. Iron was quite evenly distributed.

Discussion. This separation of lighter and heavier material within the fines fraction showed that the metals are not evenly distributed throughout all particle types in the fines fraction. Most contaminant metals were somewhat concentrated in the lighter fines material. This effect was most noticeable for copper, lead, and zinc. The lighter fines material would be the organic matter which still constitutes 24% of the fines fraction. The metals concentration in the lighter material was not deemed high enough to warrant further attempts to remove this material from the fines. Depending on the outcome of the pilot-scale demonstration and exact full-scale processing and disposal needs, separation of the lighter fines material could be further studied and implemented. Separation of the lighter material in the fines would depend on the final concentration of copper, lead, and zinc in the fines fraction, since these are the metals most concentrated in the lighter material.

#### 4.4 MULTI-PROCESS TREATMENT

A set of experiments was conducted on a slightly larger scale (1 Kg) in order to obtain a comprehensive mass balance of all sediment components and to estimate what portion of the sediment could be cleaned to meet residential or industrial fill requirements. Figure 1 outlines the processes conducted in this series of experiments and each is described in detail in the following sections. Table 11 contains a mass balance summary with fraction weights and metal analysis data.

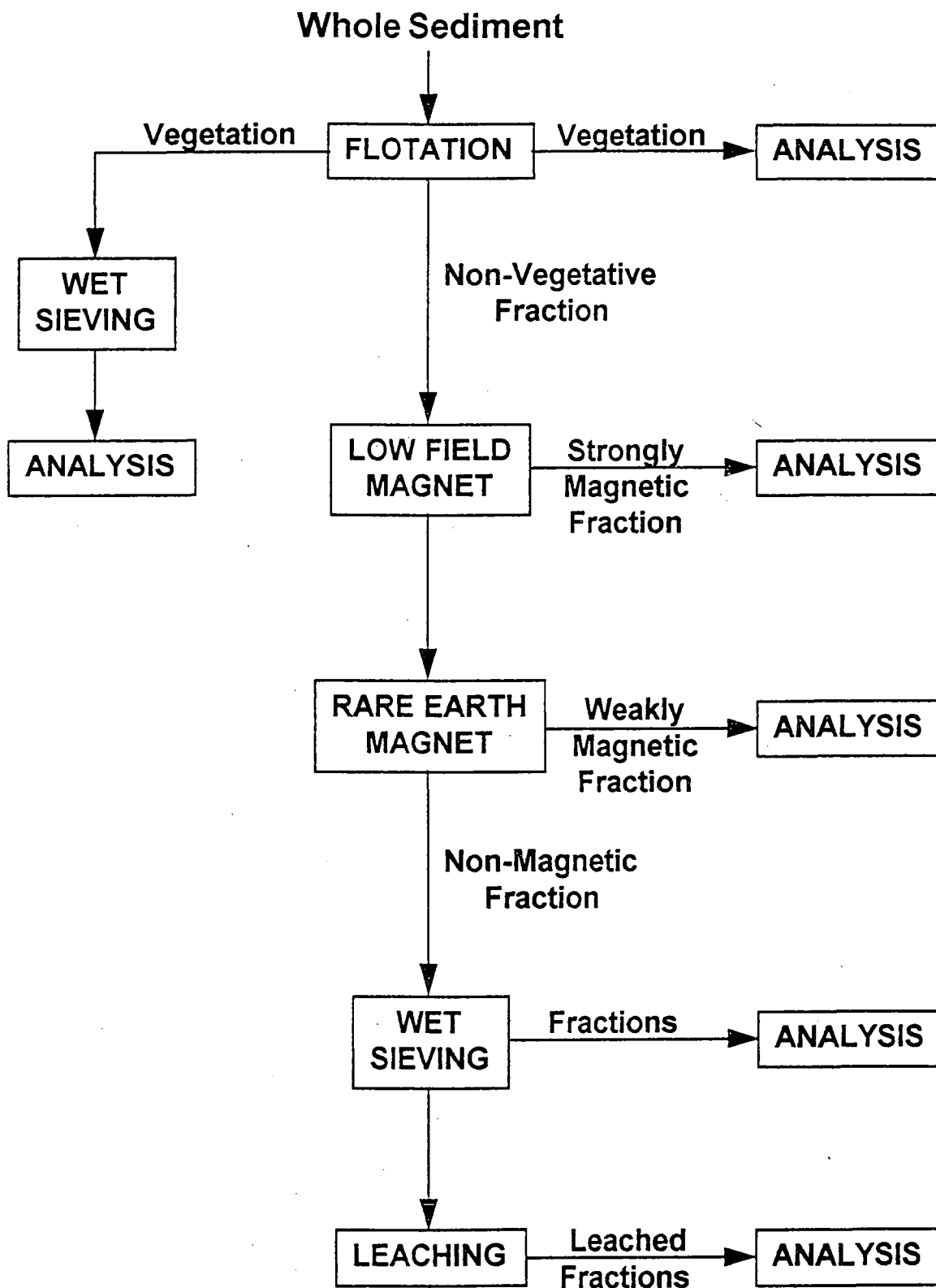


FIGURE 1.



**Table 11.**  
**Large Scale Processing Data Summary**

SAMPLE	WEIGHT %	Metal Concentration (ppm) from Digest/ICP								
		As	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Vegetation	4.9	20.7	5.5	57.7	29.5	59,000	347	5,340	< 11.4	2,840
Strongly Magnetic Fraction	1.9	27.4	10.0	198	87.4	263,000	439	3,560	< 11.4	2,310
Weakly Magnetic Concentrate	8.5	21.3	6.1	111	103	83,800	450	2,850	< 11.4	2,580
> 18 Mesh Gravel/Coarse Sand	19.4	< 19	< 1.4	< 12.7	39.1	13,400	< 9.7	877	< 11.4	126
18 - 35 Mesh Sand	10.2	< 19	< 1.4	< 12.7	40.4	10,400	< 9.7	796	< 11.4	166
35 - 100 Mesh Sand	8	< 19	< 1.4	17.7	53.9	11,000	30.3	779	< 11.4	325
100 - 230 Mesh Sand	11.4	< 19	< 1.4	20	63.6	15,000	84.7	674	< 11.4	580
< 230 Mesh Silt/Clay	35.7	19.1	4.4	76.6	112	54,600	428	1,250	< 11.4	2,070

#### 4.4.1 Flotation

A kilogram of whole sediment was charged to a Denver D12 Flotation cell and run for 10 minutes to remove the vegetation. In the flotation procedure air was bubbled through a water/sediment slurry. Water was slowly added to the cell and the vegetation allowed to flow over the cell weir leaving the heavier components behind. The vegetation was collected, filtered from the process water, dried in a 60 °C oven and retained for further analysis.

Analysis. Samples of the vegetation were analyzed for metals concentrations utilizing digest/ICP. The results are shown in the first data row in Table 11.

Particle Size Determination. The vegetation collected from flotation was wet sieved to determine its particle size distribution. US sieve sizes 10, 18, 35, 60, and 100 mesh were used for this procedure. The results are shown in Table 12.

**Table 12.**  
**Particle Size Data for Vegetation**  
**Determined by Wet Sieving**

Fraction	Weight %
> 10 mesh	15
10 - 18 mesh	27
18 - 35 mesh	12
35 - 60 mesh	5
60 - 100 mesh	2
< 100 mesh	39

A majority of the vegetation was found to be < 100 mesh.

Analysis of Fractions. The largest (>10 mesh) and the smallest (<100 mesh) vegetation fractions were analyzed by digest/ICP to determine whether there was any correlation between vegetation particle size and metal concentrations. The results are shown in Table 13.

**Table 13.**  
**Metal Analysis Data for Vegetation Fractions by DIGEST/ICP**

Vegetation Fraction	Metal Concentration (ppm)								
	As	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
> 10 mesh	20.5	3.8	292	353	49,600	560	4,800	114	2,600
< 100 mesh	26.2	6.1	151	524	86,200	531	1,780	58	2,880

There seemed to be no substantial difference in metal concentration between the largest and smallest sizes of vegetative matter.

Discussion. Removal of vegetative organic matter by flotation worked well as a unit operation on the bench-scale and should be convertible to pilot-scale with no difficulty. Consistent with prior organic separations, over half of the vegetation is in the >35 mesh size fraction. In defining the particle size of the vegetation one must remember that all the vegetation consists of rod-shaped pieces of straw or fibrous material, and so separation by screening will allow some material to fall vertically through a screen and appear as a smaller particle size fraction while other pieces lay flat and report to a larger size fraction.

Both the larger and smaller particle size fractions of vegetation contain high levels of most contaminant metals. Because of this there would be no reason to try to segregate the vegetation fractions based on particle size. On the pilot-scale all separable vegetation would be removed and collected as a single fraction.

#### **4.4.2 Low Field Magnetic Separation**

Following flotation and vegetation removal the sediment slurry was run over a low field magnetic sheet. This was done to determine what fraction of the sediment could be segregated by a very low field magnetic separation and to measure the metal concentration in the material retained on the magnet. A small fraction (ca. 2%) of the sediment was retained on the low field magnet.

Analysis. Analysis of the collected magnetic material was conducted by digestion/ICP; the results are shown in the second data row in Table 11. .

The weak magnetic concentrate had a substantially elevated level of iron, as well as slightly elevated cadmium, chromium, copper, lead, manganese and zinc.

Discussion. Removal of a strongly magnetic fraction was designed to remove any iron or steel filings which may be present due to steel mill processing and any strongly magnetic iron oxides which may be present again from steel mill processing, or as imported iron ore which may have spilled into the Harbour, or native iron oxides in the sediment. The strongly magnetic material which was removed was highly enriched in iron (>26% iron or 38% iron oxides). This material was also substantially higher in all other measurable contaminant metals (cadmium, chromium, copper, lead, manganese, and zinc) than the remaining non-magnetic sand fractions of the sediment. Removal of the strongly magnetic fraction would be planned as part of the pilot- and full-scale operations. This material should be considered for recycle within the steel mills as feedstock. The high iron content should make this attractive. The magnetic material will contain other contaminant metals, and their behavior within the steel mill processing equipment will dictate how cost effective recycling will be.

#### 4.4.3 Rare Earth Magnetic Separation

A higher field rare earth magnet was used to separate an additional magnetic fraction from the sediment slurry. This was conducted to determine what fraction of the sediment would be separated with a higher field magnet and to measure the metal concentration in this material. Approximately 8% of the sediment was separated in this fraction (after the strongly magnetic fraction had already been separated).

Analysis. The metal concentration results are shown in the third data row of Table 11.

Discussion. The higher field magnetic separation generated a larger weight fraction (8%) than the low field magnet (2%). This larger fraction also contains highly elevated levels of most contaminant metals, although the iron content in this fraction dropped to about 8% iron. The concentration of copper, lead, manganese, and zinc remained as high as in the smaller low field magnetic fraction. While the cadmium and chromium levels remained higher than in the non-magnetic sand fractions, the levels in the higher field magnetic fraction were not quite as high as in the low field magnetic fraction.

Separation of a higher field magnetic fraction is not proposed for inclusion in the pilot-scale demonstration but it could be included if deemed useful after discussion of overall project goals. This fraction would somewhat lower the iron content of the magnetic fraction isolated for recycle, but it would substantially lower the residual contaminant metals in the sand fraction of the sediment. Removal of a larger magnetic fraction which is recyclable will increase the amount of material which can be recycled and lower the amount of material which would require disposal in a landfill. If

the level of contaminant metals in the magnetic fraction causes processing concerns, these concerns can and should be addressed later.

#### 4.4.4 Particle Size Separation

The sediment following removal of the vegetation and the two magnetic fractions was wet sieved to create five particle size fractions. This was conducted in order to measure the metal concentration in the different fractions once the large vegetation and the magnetic materials had been removed. US mesh sieve sizes 18, 35, 100, and 230 were used for this purpose. The resulting weight percents in each fraction are shown in Table 11.

Analysis of Fractions. Each of the particle size fractions was digested and the digest solutions measured utilizing ICP to produce the data shown in the last five data rows of Table 11.

Discussion. The sand fractions show a general trend toward higher metal concentrations in the finer size fractions with the exception of manganese which shows the reverse trend. A number of the metals were below reporting limits in all the sand fractions (arsenic, cadmium, and nickel).

All the sand fractions meet the Ontario Draft Fill guidelines for urban industrial fill use and meet the guidelines for most metals for urban residential use, after removal of vegetation and magnetic material. The metals which pass the urban residential use guidelines are chromium, copper, lead, and nickel. The sand fractions meet urban industrial fill guidelines for arsenic and cadmium. The analytical reporting limits for arsenic and cadmium are above the residential landfill guidelines, and so no definitive statement can be made about this requirement for these two metals. Iron and manganese do not have Ontario Draft Fill guidelines; however, their levels are significantly reduced from their original levels. The iron concentration is reduced to about one quarter of the original and the manganese to about half the original levels. Zinc is the only metal for which the sand does not clearly meet the urban residential fill guideline, but it does meet the urban industrial fill guideline.

The fines (<230 mesh) fraction meets the urban industrial guideline for chromium, copper, and nickel, but does not meet this guideline for arsenic, cadmium, lead, and zinc. Again, there are no guidelines for iron and manganese. The iron and manganese content of the fines fraction, however, is considerably higher than in the sand (1.5 times higher in manganese and four times higher in iron). The fines fraction does not meet fill guidelines, and because neutral or ammonia leaching did not reach the fill guidelines for lead or zinc (see section 4.4.5), leaching treatment of this fraction so that it does meet all the guidelines is not possible. This material

must be handled as controlled landfill material or reused in some other way.

Therefore in conclusion, physical separation of the vegetative fraction and the magnetic fraction from the sediment allows the sand fraction to meet all the Ontario Draft Fill Guidelines for urban industrial use. The fines fraction does not meet the urban industrial usage criteria and would require controlled landfill or reuse in some other fashion. The vegetative and magnetic fractions should be recyclable within the steel mill for their metal value.

#### 4.4.5 Leaching

The COGNIS bench-scale leaching process was conducted on small (1-2 gram) samples of sediment. This scale allowed the leaching and acid digestion data to be gathered on the exact same sample so that no sampling errors were introduced. In this way the amount of metal leached from the sediment plus the residual metal remaining in the sediment could be added together to give the amount of metal initially in the sediment and the percentage of leachable metal calculated with confidence. Leaching with both neutral and basic leachants was conducted. Acid leaching experiments were not tested due to the high acid consumption behavior of the sediment (discussed in section 4.2.7).

The fines fraction was considered the most likely fraction of the sediment to require leaching and therefore it was tested first.

Neutral Leaching: Duplicate samples of the <230 mesh silt/clay fraction from wet sieving were tested under neutral leaching conditions. Four different leachants were tested in a 5:1 liquid to solid weight ratio. EDTA was not examined due to high cost and anticipated nonselectivity. Five fifteen minute contacts at room temperature were carried out. The results are shown in Table 14. The pH in each case stayed fairly constant. Each contact solution, after separation from the sediment, was weighed and analyzed for the nine project metals. Using this data, along with the starting sediment weight, the concentration of each metal removed was calculated. In Table 14 this data is presented as a percentage of the starting concentration removed (using values obtained earlier for the <230 mesh fines). The amount of metal removed by neutral leaching was negligible. For this reason the residual leached solids were not analyzed.

**Table 14.**  
**Results from Neutral Leaching / <230 mesh Fines**

Leachant	Initial pH (#1 Contact)	Ending pH (#5 Contact)	Approximate % Removal <sup>1</sup>								
			As	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Initial Conc. In Fines (ppm)			19.1	4.4	76.6	112	54,600	428	1,250	<11.4	2,070
1	7.1	7.7	BDL	BDL	BDL	BDL	BDL	BDL	1%	BDL	<0.1%
1 (dup.)	"		BDL	BDL	BDL	BDL	BDL	BDL	1%	BDL	<0.3%
2	6.8	7.1	BDL	BDL	16%	BDL	BDL	BDL	2%	(20 ppm) <sup>2</sup>	1%
2 (dup.)	"		BDL	BDL	6%	BDL	BDL	BDL	2%	(5 ppm) <sup>2</sup>	1%
3	8.2	8.9	BDL	BDL	BDL	25%	<0.5%	BDL	2%	BDL	2%
3 (dup.)	"		BDL	BDL	BDL	27%	<0.5%	BDL	2%	BDL	3%
4	7.5	7.9	BDL	BDL	BDL	BDL	BDL	BDL	<0.5%	BDL	BDL
4 (dup.)	"		BDL	BDL	BDL	BDL	BDL	BDL	<0.5%	BDL	BDL

<sup>1</sup>In all cases the metal leached was removed gradually over the five contacts.

<sup>2</sup>Concentration of metal removed. Not able to calculated % removal of <11.4 ppm.

BDL = Below Detection Limit (Metal concentration in leachants was below detection at each contact)

Discussion. Neutral pH leaching seemed to be ineffective in leaching metals from the fines, in each case only a fraction if any of the metal was removed from the sediment. No further attempts at neutral leaching were conducted. Because of the large volume of sediment to eventually be treated in Hamilton Harbour, complex and expensive leaching systems were not studied. Because the results of neutral leaching on fines were so unproductive, sand leaching was not investigated.

#### Basic Leaching

Leaching with an ammonia based solution was also tested. Both the recombined >230 mesh sand and the <230 mesh fines fractions from wet sieving were tested. The same leaching conditions described for neutral leaching were employed, five fifteen minute contacts at room temperature with a 5:1 leachant to sediment ratio. Results are shown in Tables 15 and 16 below. In this case both leachate solutions and residual solids were analyzed for metals. Tables 15 and 16 contain data for zinc, copper and lead. Only these metals were present in high enough concentration to demonstrate leaching behavior reliably. The ammonia leaching was anticipated to be most effective on zinc and copper.

**Table 15.**  
**Leaching<sup>1</sup> of >230 mesh Sand**

Metal	Cumulative % Metal Leached					Initial <sup>2</sup>	Final <sup>3</sup>
	Leaching Contact #					[Pb]	[Pb]
	1	2	3	4	5	(ppm)	(ppm)
Zn	16	30	35	41	44	340	192
Zn (duplicate)	19	25	32	36	40	360	217
Cu	27	38	44	49	53	65	31
Cu (duplicate)	29	39	46	51	56	62	28
Pb	0	2	5	7	10	43	39
Pb (duplicate)	3	3	3	5	7	49	46

<sup>1</sup>Data is from five consecutive contacts of sand samples with leachant.

<sup>2</sup>Based upon the total metal detected in leachant plus metal retained in sand as determined by nitric acid digestion.

<sup>3</sup>Based upon EPA acid digestion of treated sand.



**Table 16.**  
**Leaching<sup>1</sup> of <230 mesh Fines**

Metal	Cumulative % Metal Leached					Initial <sup>2</sup>	Final <sup>3</sup>
	Leaching Contact #					[Pb]	[Pb]
	1	2	3	4	5	(ppm)	(ppm)
Zn	12	20	26	31	35	2,281	1,490
Zn (duplicate)	11	19	24	28	31	2,269	1,560
Cu	18	30	36	41	44	129	72
Cu (duplicate)	18	29	37	42	46	132	72
Pb	0	1	1	1	2	387	380
Pb (duplicate)	0	1	1	1	1	394	389

<sup>1</sup>Data is from five consecutive contacts of fines samples with leachant.

<sup>2</sup>Based upon the total metal detected in leachant plus metal retained in fines as determined by nitric acid digestion.

<sup>3</sup>Based upon EPA acid digestion of treated fines.

Ammonia leaching was somewhat effective for zinc and copper, removing 30 - 50% with five consecutive contacts. This leaching was less effective for lead, removing less than 10%.

Additional leaching experiments were conducted with longer leaching times (one hour instead of fifteen minutes) to determine whether better removal could be achieved. There was no improvement with the longer leach contacts.

Discussion. Ammonia leaching was conducted primarily to remove zinc. Ammonia leaching was tried because it would not be adversely affected by the high carbonate content of the sediment (sand or fines fractions) as acid leaching would. The residual level of zinc in the sand fraction after removal of the vegetation and magnetic fraction marginally meets the Ontario Draft Guidelines for industrial fill (Table 15). If the vegetation and magnetic separations are not quite so effective, and the zinc level ended up above the guideline, removal of zinc by leaching may be required. The ammonia leaching for zinc in the sand was quite effective (removing 42%), and it lowered these particular samples to 204 ppm, comfortably under the industrial fill guideline of 280 ppm, although not attaining the residential fill guideline of 140 ppm. Ammonia leaching of zinc from the fines was not so effective. It resulted in a lower percent removal (33%) and only attained a

residual average concentration of 1,500 ppm. Because longer leaching contact times did not yield any better results, substantially better zinc leaching results do not appear likely without greatly increasing the ammonia concentration, which is possible but more costly. In summary, ammonia leaching for additional zinc removal could be performed on the sand, but incorporation of a leaching step for removal of essentially one metal would be costly for the benefit.

Zinc leaching from the magnetic fraction was not investigated. If the high zinc level in this magnetic fraction makes its recycle within the steel mill difficult, it may be possible to selectively remove zinc from this iron-rich material for improved recyclability.

## **4.6 LARGE SCALE MAGNETIC SEPARATION**

### **4.6.1 Sampling**

A second sediment sample was obtained in order to have a larger scale magnetic separation conducted at an outside vendor. The magnetic separations were conducted in bench-scale equipment known to give results that can be reproduced in pilot and full-scale equipment. The sample was homogenized as described in section 4.1 and analyzed for metal concentrations to compare to the first sample received. The results are shown in Table 17, and they compare closely to those already reported in Table 2 for bucket #1.

**Table 17.**  
**Metal Analysis Data for Whole Sediment: Bucket #2**

Metal	Metal Concentration (ppm)				
	XRF	DIGEST/ICP			
		#1	#2	#3	Avg.
As	50	<19	<19	<19	<19
Cd	BDL <sup>1</sup>	2.5	2.4	2.5	2.5
Cr	185	94.4	92.8	95.7	94.3
Cu	45	50.5	49.8	54.8	51.7
Fe	82,840	41,600	43,800	45,600	43,667
Pb	255	258	267	248	258
Mn	2,240	1,360	1,380	1,350	1,363
Ni	20	35.8	35.6	35.6	35.7
Zn	1,935	1,310	1,270	1,320	1,300

<sup>1</sup>Below Detectable Level.

After homogenization of the sample, 20 lbs was sent to ERIEZ Magnetics in Erie, Pennsylvania. ERIEZ, together with a COGNIS engineer conducted a larger scale magnetic separation of the sediment with varying magnetic strengths. After magnetic separations were complete the separated fractions were returned to COGNIS for analysis. Figure 2 outlines the processes carried out and the steps in the process are described in detail in the following sections. Table 18 contains a summary of the mass balance and metal concentration data collected at COGNIS after receipt of the isolated fractions.

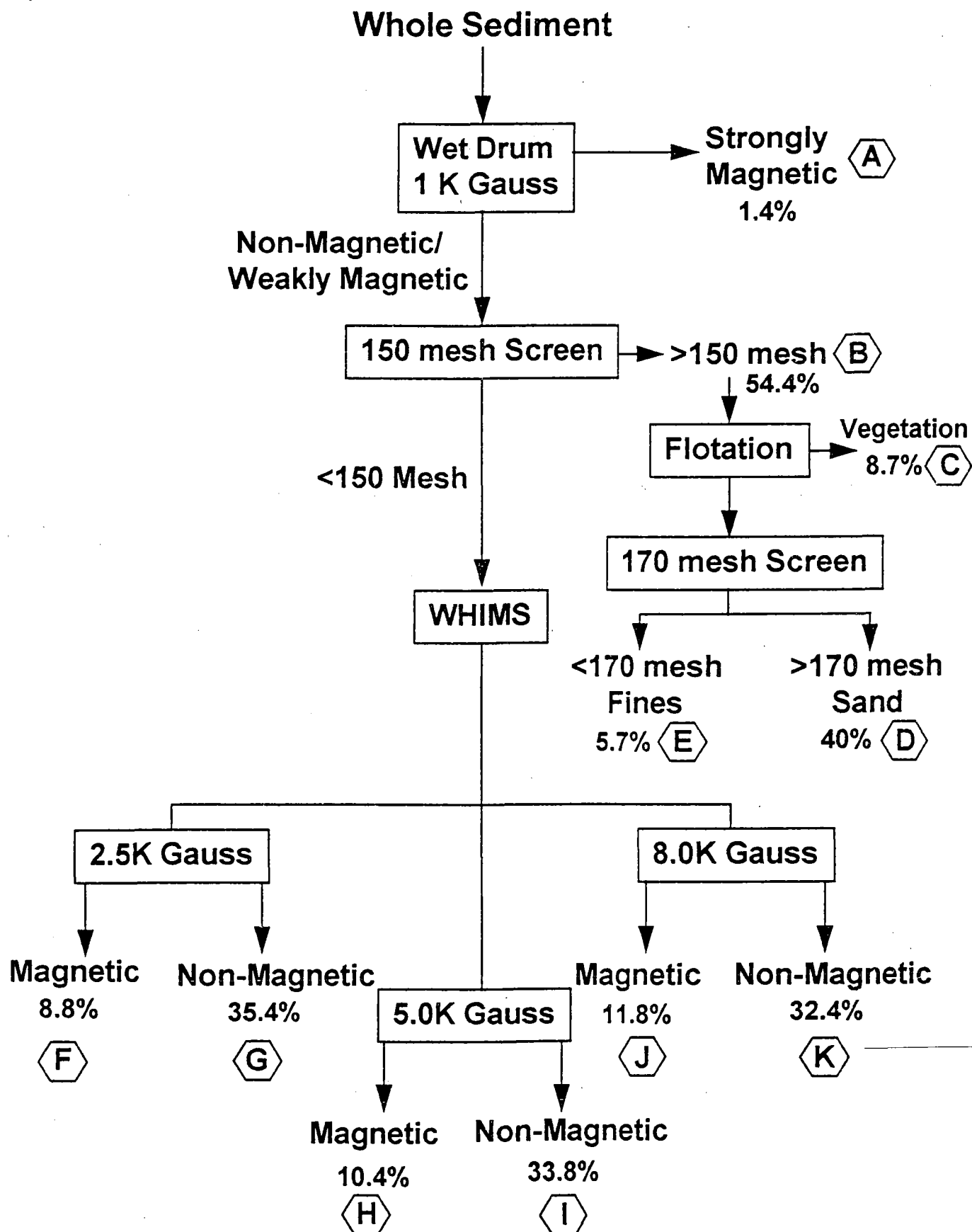


FIGURE 2.

**Table 18.**  
**POST LARGE SCALE MAGNETIC SEPARATION SAMPLES : DIGEST/ICP RESULTS**

Sediment Fraction	Key	% of Feed <sup>1</sup>	Metal Concentration (ppm)								
			As	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Wet Drum, 1K Magnetic	<b>A</b>	1.4	31.8	11.8	284	93	372,000	539	4,760	47.9	2,840
> 150 Mesh Non-Magnetic	<b>B</b>	54.4	< 19	< 1.4	14.4	34.8	15,300	59	1,110	< 11.4	432
Vegetation	<b>C</b>	8.7	Not Analyzed								
> 170 Mesh NonMagnetic, Non Organic Sand <sup>2</sup>	<b>D</b>	40	< 19	< 1.4	< 12.7	41.6	12,300	31.9	853	< 11.4	214
			< 19	< 1.4	< 12.7	40.6	11,200	17.1	794	< 11.4	153
			< 19	< 1.4	< 12.7	41.3	11,100	23.9	789	< 11.4	178
< 170 Mesh NonMagnetic, Non Organic Fines	<b>E</b>	5.7	Not Analyzed								
2.5K Magnetic (< 150 mesh)	<b>F</b>	8.8	32.9	7	97.1	91.9	152,000	579	2,920	101	3,530
2.5 Non-Magnetic (< 150 mesh)	<b>G</b>	35.4	20.7	2.1	32.1	64.2	40,200	355	1,210	32.2	1,900
5K Magnetic (< 150 mesh)	<b>H</b>	10.4	28.0	6.6	83.8	88.5	144,000	545	2,840	45.8	3,380
5K Non-Magnetic (< 150 mesh)	<b>I</b>	33.8	< 19	1.6	22.7	56.2	34,500	292	1,030	17.5	1,590
8K Magnetic (< 150 mesh)	<b>J</b>	11.8	32.6	6.2	77	85.9	144,000	506	2,760	46.5	3,200
8K Non-Magnetic (< 150 mesh)	<b>K</b>	32.4	< 19	1.4	47	54.9	33,300	280	983	19.5	1,580

<sup>1</sup>The > 150 mesh was further treated with flotation to remove vegetation (C) and an additional screening to separate < 170 mesh fines (E) from the vegetation free > 170 mesh (D) sand. Fractions C + D + E equal 54.4%, the percentage of > 150 mesh material.

The < 150 mesh material was split into three portion and a portion was magnetically treated at 2.5K, 5K, or 8K gauss. The fractions F + G, H + I, and J + K equal 44.2% when combined with the +150 fractions A + B, the sum equals 100%.

<sup>2</sup>Sample measured in triplicate to determine homogeneity.

#### 4.6.1 Wet Drum

Approximately 5 gallons of slurry was prepared by combining water with whole sediment to about 10% solids. This slurry was used as feed to a ca. 6" wide by ca. 9" diameter concurrent wet drum separator with ceramic magnets providing a 1,000 gauss field. The strongly magnetic fraction collected had the appearance of the magnetic fraction obtained from the low field magnetic separation on the bench-scale (reference section 4.4.2). This 1K gauss magnetic fraction (A) represented a very small fraction of the whole sample (1.4%wt). A sample of the magnetic fraction (A) was digested and analyzed by ICP, the results are shown in Table 18.

Discussion. The wet drum separation was conducted before the high magnetic field separations to ensure prior removal of any highly magnetic particles which can interfere with the proper operation and cleaning of the high field magnetic equipment. In addition to this protective measure it also is a low-cost way to generate a highly magnetic fraction which should be suitable for recycle within a steel mill.

The 1K gauss wet drum magnetic separation was found to be very similar to the low field magnetic separation reported in section 4.4.2 in all respects. Visually the material was similar. It consisted of fine grained black mineral particulates. No evidence of iron/steel filings or metal debris was observed. The amount of strongly magnetic material removed in this step (1.4%) is close to the 2% removed previously in the low field magnetic separation. The strongly magnetic fraction obtained has a slightly higher metal content than that observed previously. The iron content in the wet drum magnetic fraction is actually about 40% higher than observed before.

The wet drum magnetic separation proved to effectively remove a small fraction of material which greatly lowered the metal content of the non-magnetic and weakly magnetic fractions. Pilot-scale sediment treatment would include this separation step.

#### 4.6.2 Screening

The next magnetic separation step involved a wet high intensity magnetic separator (WHIMS). Design of the WHIMS is such that feed must all pass a 35 mesh screen. Therefore, the tailings from the wet drum separator were wet screened on a 150 mesh screen before being fed to the WHIMS. A 150 mesh screen size was chosen to correspond to a screen cut similar or equal to that used on the pilot-scale to separate sand and fines. The sand/fines cut-off point in the pilot plant can be varied. The >150 mesh fraction (B) was collected from the screen, dried and weighed. This fraction representing 54.4% of the sediment was analyzed (see B in Table 18) and saved for further processing (reference sections 4.6.3 and 4.6.5).

#### 4.6.3 Flotation and Additional Screening

The >150 mesh non-magnetic sand fraction was then put through a flotation step to remove the vegetation (C). The vegetation equalled 8.7%wt of the feed (16.1% of the 54.4% >150 mesh sand) and it was not analyzed.

The vegetation free >150 mesh sand was then screened with a 170 mesh screen to remove additional fines. The pre-WHIMS 150 mesh screening was carried out to separate out large materials before feeding to the WHIMS. Here the objective was to carefully remove any fines that might have been retained in the sand during this preliminary screening. The <170 mesh separated fines fraction (E) equalled 5.7%wt of the feed (10.5% of the original 54.5% >150 mesh sand) and it was not analyzed for metal concentration. The fines and vegetation free >170 mesh sand (D) equalled 40%wt of the feed, a sample of this was digested and analyzed by ICP, see results in Table 18. Removal of the vegetation and additional fines dropped the zinc, lead, manganese and iron levels substantially.

Discussion. The >150 mesh sand fraction (B) directly after 1K gauss wet drum magnetic treatment was significantly lower in metal content than before magnetic treatment, and still contained vegetative materials which were known to be very high in metals. Fraction B with organic vegetation still present meets the residential and industrial fill guidelines for all project metals (arsenic, cadmium, chromium, copper, lead) except zinc. Iron and manganese do not have guidelines, but these values were also reduced by about 66% and 20% respectively. The residual zinc level (432 ppm) remained above the urban industrial fill guideline of 280 ppm.

Removal of the vegetative matter and additional fines by flotation/screening to produce fraction D resulted in the expected further decrease in certain metal concentrations, particularly in iron, lead, manganese, and zinc. The residual zinc concentration (162 ppm average) was now below the urban residential fill guideline (280 ppm) and approached the urban residential fill guideline (140 ppm). Combined wet-drum magnetic separation and vegetation flotation produced a sand fraction which met all urban industrial fill guidelines.

#### 4.6.4 Wet High Intensity Magnetic Separator

For the bench-scale testing the WHIMS was operated in a batch mode whereby the non-magnetic/weak magnetic slurry passes through the device and the magnetic material is held within the WHIMS. At the end of a batch run, the magnetic fraction is removed. In pilot or full-scale operation the magnetic fraction recovery can be done continuously. Portions of the <150 mesh slurry were fed to the WHIMS at three different field strengths: 2,500, 5,000, and 8,000 gauss respectively. Magnetics and tailing slurries were

collected for each run. The tailings were tan-clay colored while the magnetics slurries were noticeably gray.

The weakly magnetic and non-magnetic fraction slurries were filtered and dried. The weight percentages of each magnetic/non-magnetic fraction are listed in Table 18 along with the metal content of each fraction. The three high magnetic fields separated increasingly larger amounts as a magnetic fraction, 2.5K gauss retained 19.9% (8.8% of feed) magnetic material (F), 5K gauss 23.5% (10.4% of feed) (H), and 8K gauss 26.7% (11.8% of feed) (J). At all three magnetic fields, the magnetic fraction contained more contaminant metals than the non-magnetic fraction.

Discussion. The goal of the three WHIMS experiments was to remove sufficient contaminant metals from the <150 mesh fine material so that it could meet the urban industrial fill guidelines. Despite removing approximately 25% of the <150 mesh material, this goal was not achieved. The residual lead (280 ppm) and zinc levels (1,600 ppm) remained above the urban industrial fill guidelines. The magnetic fractions are enriched in all the project metals and include 14% iron.

Whether high field magnetic treatment of the <150 mesh material is conducted depends on the most cost-effective option. The options are: 1.) do not magnetically treat the fines fraction and dispose of this material in a hazardous waste landfill, or 2.) magnetically treat the fines to generate a magnetic fraction for recycle within the steel mill. If the high field magnetically separated material (approximately 10% of the total sediment) is recyclable within the steel mill, this will reduce the volume of sediment fines which require disposal.

#### **4.6.5 Sand Fraction**

An additional magnetic separation was conducted on a portion of the >150 mesh fraction to determine what percentage of the sand fraction would be separated with a higher intensity magnetic field. A 35-150 mesh sand fraction was created from the non-magnetic >150 mesh wet drum effluent. This fraction was put through a 5K gauss magnet to produce 40% magnetic and 60% non-magnetic material. The results from metal analyses are shown in Table 19.



**Table 19.**  
**Analysis of Large Scale Magnetically Separated Sand**

	% of Feed	As	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
5K Magnetic (35-150 mesh)	40	<19	2.6	77.1	67.3	47,000	254	2,220	19.3	1,720
5K Non-Magnetic (35-150 mesh) <sup>1</sup>	60	<19 <19	<1.4 <1.4	<12.7 <12.7	20.1 18.1	7,720 7,190	57.7 48.6	722 596	<11.4 <11.4	364 328

<sup>1</sup>Sampled in duplicate to determine homogeneity.

Discussion. High field magnetic treatment of the >150 mesh sand (still containing vegetation) further lowers the metal contaminant levels relative to the feed material, fraction B. However, this treatment produced a very large magnetic fraction (40%) which would not be as valuable an iron feed stock (4.7% iron), and the non-magnetic fraction was not brought down to less than the urban residential fill guidelines. Therefore, no significant benefit was observed by performing this step, and it would not be recommended for inclusion in a pilot-scale process.

## 5.0 SUMMARY

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### 5.1 SUMMARY OF RESULTS

#### 5.1.1 Analysis of Waste Stream Characteristics

The Hamilton Harbour sediment after bioremediation of the organic contaminants was a very fine grained material. Particle size distribution was 0% oversize (>4 mesh), 10% gravel (4-10 mesh), 50% sand (10-270 mesh), and 40% silt and clay (<270 mesh). Of the 50% sand sized material, inorganic sand was 38% and organic vegetation made up 12% of the material. The fines (silt and clay) were also high in organic matter (10%) with 30% inorganic material. The high level of organic vegetation is the result of the amendments used in the DARAMEND™ bioremediation which destroyed the PAHs and tarry organic contaminants.

The metal contamination reported by WTC, the average concentration found in this study in the untreated sediment and the Ontario Draft Guidelines for urban industrial fill are compared below in Table 20. The metals which failed to meet the guidelines are cadmium, lead and zinc. Iron and manganese do not have standards, but are at greatly elevated levels and need to be lowered. Zinc and iron were the two metals which required the greatest level of reduction.

**Table 20.**  
**Comparison of Initial Metal Concentrations**  
**with Ontario Industrial Fill Guideline<sup>1</sup>**

Metal Contaminant	Metal Concentration (ppm)		
	WTC Data Supplied <sup>2</sup>	Average Found	Urban Industrial Guideline
Arsenic	5.7	< 19	20
Cadmium	4.9	2.4	1.7
Chromium	49	40	120
Copper	43	41	130
Iron	38,000	45,000	---
Lead	300	194	200
Manganese	1,635	1,350	---
Nickel	27	< 11	76
Zinc	1,790	1,150	280

<sup>1</sup>Data compiled from Tables 1 and 2.

<sup>2</sup>Pre-Treatability Study data.

### 5.1.2 Analysis of Treatability Study Data

Metals were found in all the particles size fractions and in both the organic vegetative matter and the inorganic sediment. A combination of attrition, particle size separation, flotation to remove organic vegetation, and magnetic treatment was found to generate four fractions: vegetation, magnetic material, treated sand, and fines. The treated sand met the Ontario Draft Guidelines on urban industrial fill for all metals, and the iron was reduced by 75% and the manganese by 40%. The treated sand met the urban residential fill guideline for all metals except zinc (182 ppm achieved, 140 ppm is guideline). The other three fractions isolated were all well above the fill guidelines and will require disposal or recycle. The magnetic fraction should be recyclable in the steel mill. The vegetation and fines fractions will likely require controlled landfill disposal. Reuse of these materials should be investigated.

**Table 21.**  
**Summary of Metal Concentrations in Separated Fractions<sup>1</sup>**

<b>Metal Contaminant</b>	<b>Metal Concentration (ppm)</b>			
	<b>Vegetation</b>	<b>Magnetic Fraction</b>	<b>Treated Sand</b>	<b>Fines</b>
Arsenic	21	32	<19	19
Cadmium	6	12	<1.4	4
Chromium	58	284	<13	77
Copper	30	93	41	112
Iron	59,000	372,000	11,500	54,600
Lead	350	539	24	428
Manganese	5,300	4,760	811	1,250
Nickel	<11	48	<11	<11
Zinc	2,800	2,840	182	2,070

<sup>1</sup>Data selected from Tables 11 and 18.

### 5.1.3 Comparison to Test Objectives

The project goal was to generate as large a sediment fraction as possible which met the Ontario Draft Guideline for urban industrial or residential fill.

Specific objectives were as follows:

- (1) investigate the distribution of contaminants among the sediment fractions
- (2) determine the effect of physical treatment on the sediment
- (3) determine the effect of leaching treatment on the sediment.

The goal was obtained with a sand fraction which had been physically treated by flotation to remove the light organic vegetative material and by magnetic separation to remove the magnetic material, both of which were high in metal contaminants.

The objectives were achieved in support of this goal.

- (1) Metal contaminants were found to be principally associated with the organic vegetative matter, the magnetic fraction, and the sediment fines. Pieces, fragments, filings, or shavings of metal were not observed. Slag or other debris associated with metal working were not observed. Iron was

fraction also contained the highest concentrations of all metals in any fraction isolated. Surprisingly, the vegetation fraction was very high in all project metals despite the fact that most vegetation present had been added to the sediment only during the bioremediation within the past two years. Thus within a relatively short period of time, migration of over half of the total metals present into the vegetation (or adsorbed biomass) had taken place.

(2) The physical treatment steps tested and found to be useful were particle size separation, flotation of light organic vegetative matter and low field magnetic separation. Density separation was investigated briefly, but found to give mixed results. Some metals were slightly concentrated into the lighter fraction, while others were slightly concentrated into the denser fraction. In no case was a significant effect observed. High field magnetic separation was also investigated, and it always resulted in concentration of metals into the magnetic fraction. However, the effect was again small relative to a low field magnetic separation, and the generation of a much larger magnetic fraction was not deemed to be particularly helpful. High field magnetic separation would only be useful if recycle of this lower iron content magnetic fraction proved feasible. In this case, approximately 10% more fine material could be recycled rather than disposed.

(3) Leaching was considered under acidic, neutral, and basic conditions. The high carbonate content of the sediment ruled out acidic leaching with any acid which would generate soluble calcium salts. Leaching with sulfuric acid to produce an insoluble calcium sulfate, would increase the volume of the sediment by about 50%, while still not achieving the fill guidelines at a high cost. Neutral leaching was shown to be completely ineffective. Ammonia leaching was moderately effective for removing zinc and copper. Zinc removal may be of some benefit, as ammonia leaching of the sand fraction could generate a product which met the urban residential fill guidelines instead of the industrial fill guidelines. The extra cost of ammonia leaching may not be worth this slight improvement.

Comparison of the final metal concentrations achieved with the urban residential and industrial fill guidelines are shown below in Table 22.

**Table 22.**  
**Comparison of Treated Sand with Ontario Industrial Fill Guideline<sup>1</sup>**

Metal Contaminant	Metal Concentration (ppm)		
	Treated Sand	Urban Residential	Urban Industrial
Arsenic	< 19	17	20
Cadmium	< 1.4	0.84	1.7
Chromium	< 13	62	120
Copper	41	65	130
Iron	11,500	---	---
Lead	24	98	200
Manganese	811	---	---
Nickel	< 11	38	76
Zinc	182	140	280

<sup>1</sup>Data selected from Tables 1 and 21.

## 5.2 PROPOSED PILOT-SCALE PROCESS

The proposed pilot-scale process will duplicate the separation stages found to be effective in this Treatability Study in cleaning a sand fraction to meet the Ontario Draft Guidelines for urban industrial fill. The major separation stages are particle size separation, vegetation flotation, and magnetic material removal.

The unit operations in the pilot-plant include the following:

1. Feed system (feed hopper and conveyor)
2. Trommel (deagglomeration)
3. Oversize separation (screen)
4. Particle size separation (sand and fines separation)
5. Flotation (organic vegetation removal)
6. Wet Drum magnetic separation (magnetic fraction removal)
7. Sand dewatering
8. Fines dewatering
9. Misc. dewatering (magnetic and vegetation fraction)
10. Water handling, pumps, misc.

The pilot-plant is assembled and ready for shipment from Santa Rosa, CA to the Wastewater Technology Centre when it is needed and final agreement has been reached with the WTC on the pilot-plant unit operations to be demonstrated. The magnetic separation equipment will be rented for the duration of the pilot-scale demonstration.

Additional unit operations could be tested if deemed necessary, i.e. higher field magnetic separation for additional magnetic material removal, and ammonia leaching of the sand fraction for additional zinc removal. Also, if deemed necessary to allow recycle of the magnetic fraction(s), zinc removal from the iron-rich magnetic material could be studied in the laboratory and implemented if proven effective.

The goal of the pilot-scale demonstration remains the same: to generate as large a fraction as possible of material which meets the urban industrial fill guidelines and to recycle as much other material as possible with a minimum amount of material requiring controlled landfill. Treatment costs should be kept at a minimum and allow maximum in-kind-services by stakeholders.

If recycling of the magnetic or vegetative fractions require additional characterization or specific contaminant removal, such characterization and treatment can be conducted as additional contracted work. The recyclability determination must be made together with relevant stakeholders in the cleanup. Likewise, if discussions with stakeholders are required to maximize their in-kind-services, these can be arranged.

## 6.0 REFERENCES

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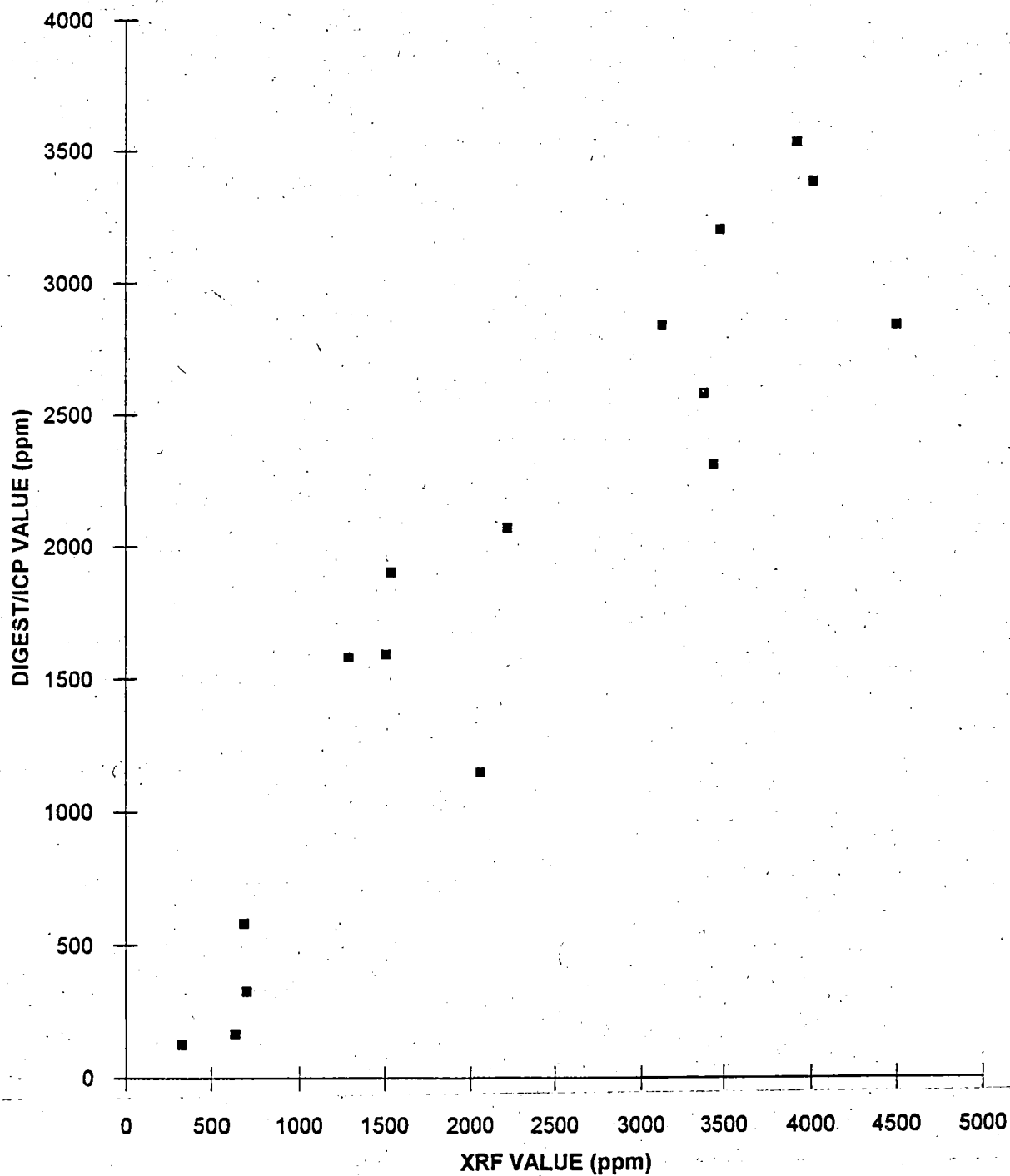
1. T. Mayer and P.G. Manning. *Environmental Impact of Hamilton Harbour on the Nearshore Area of Western Lake Ontario*. Lakes Research Branch, National Water Research Institute. NWRI Contribution No. 90-36.



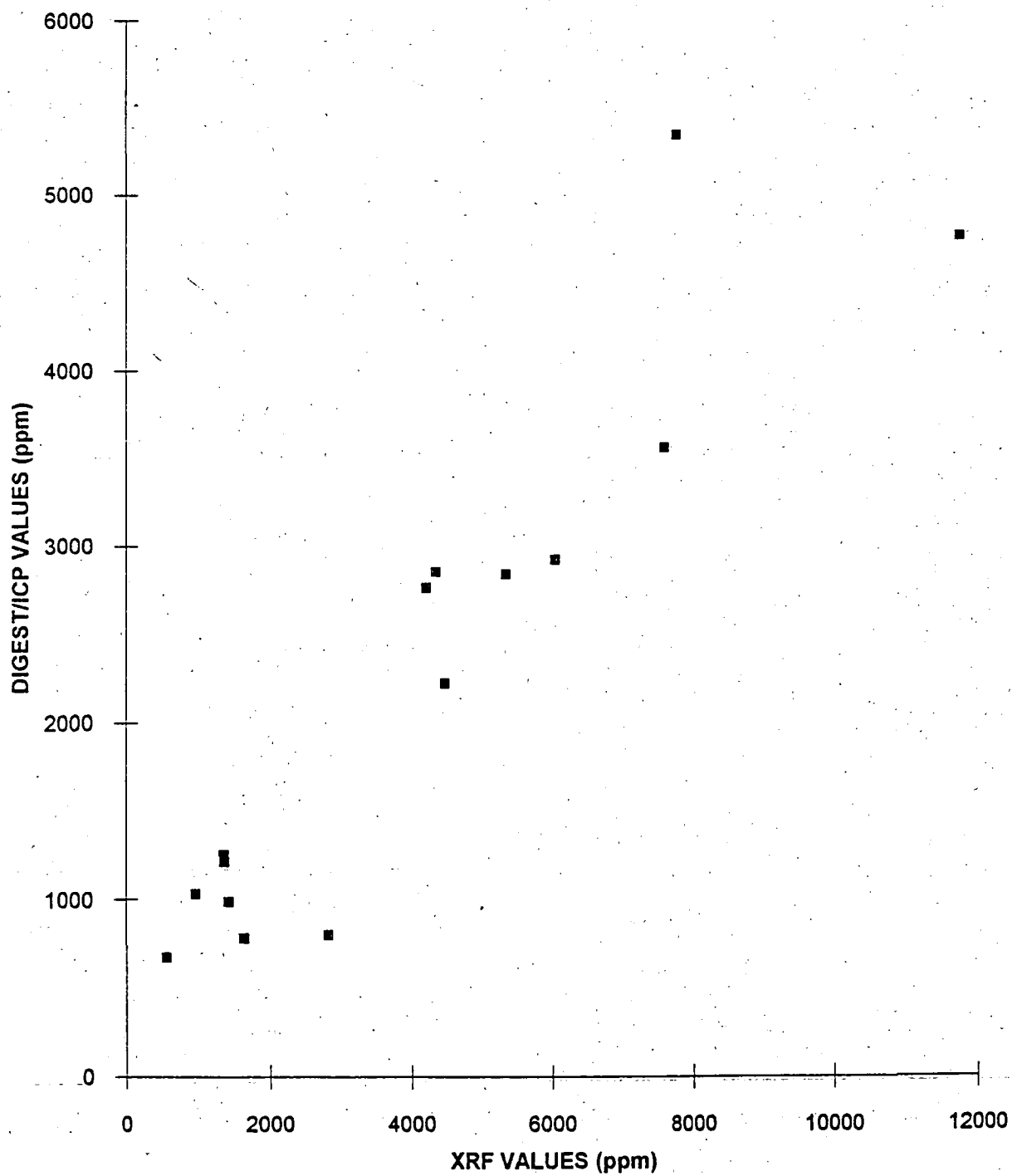
## APPENDIX A

### COMPARATIVE DATA : XRF vs. DIGESTION/ICP

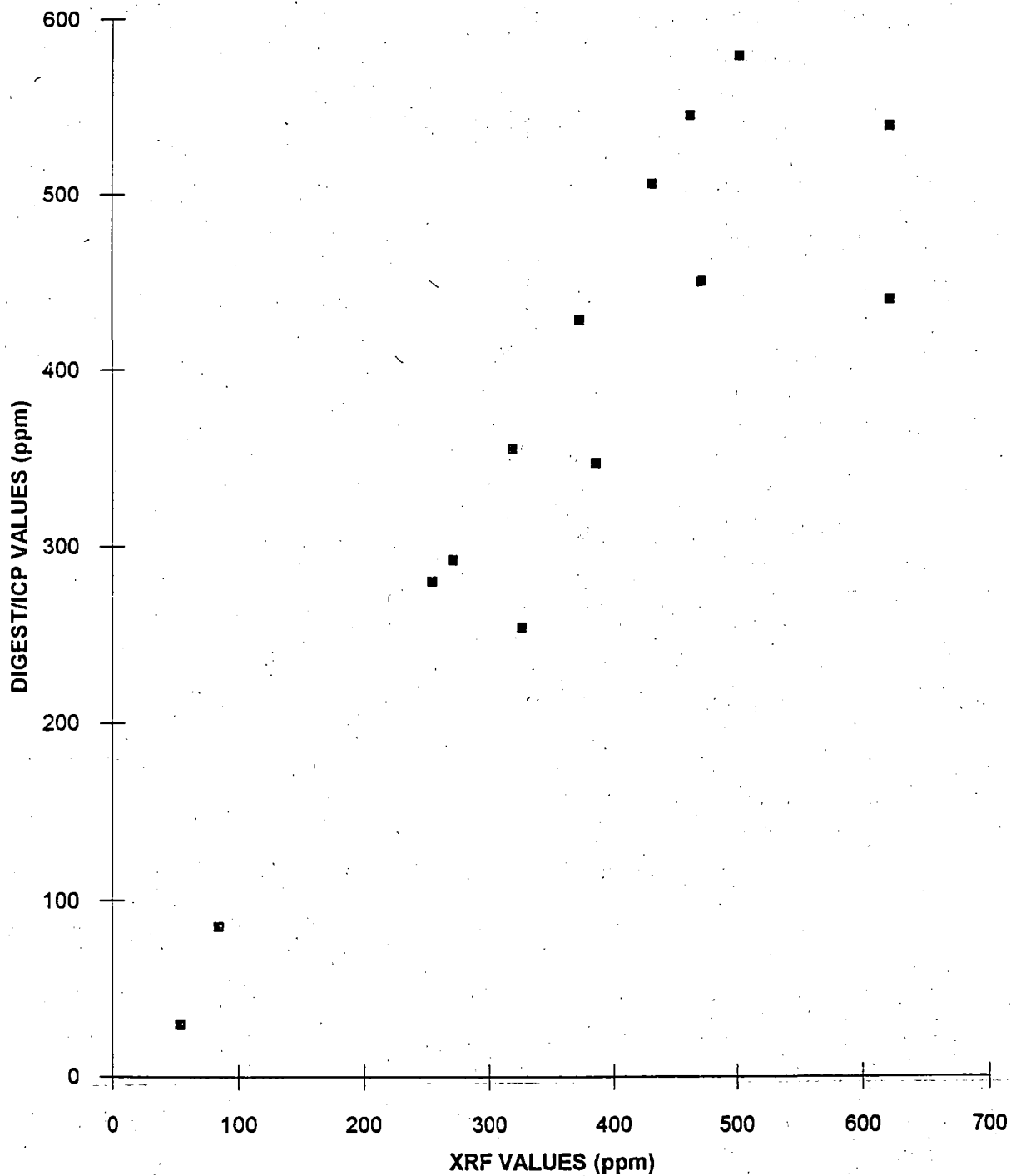
## ZINC: XRF vs. DIGEST/ICP VALUES



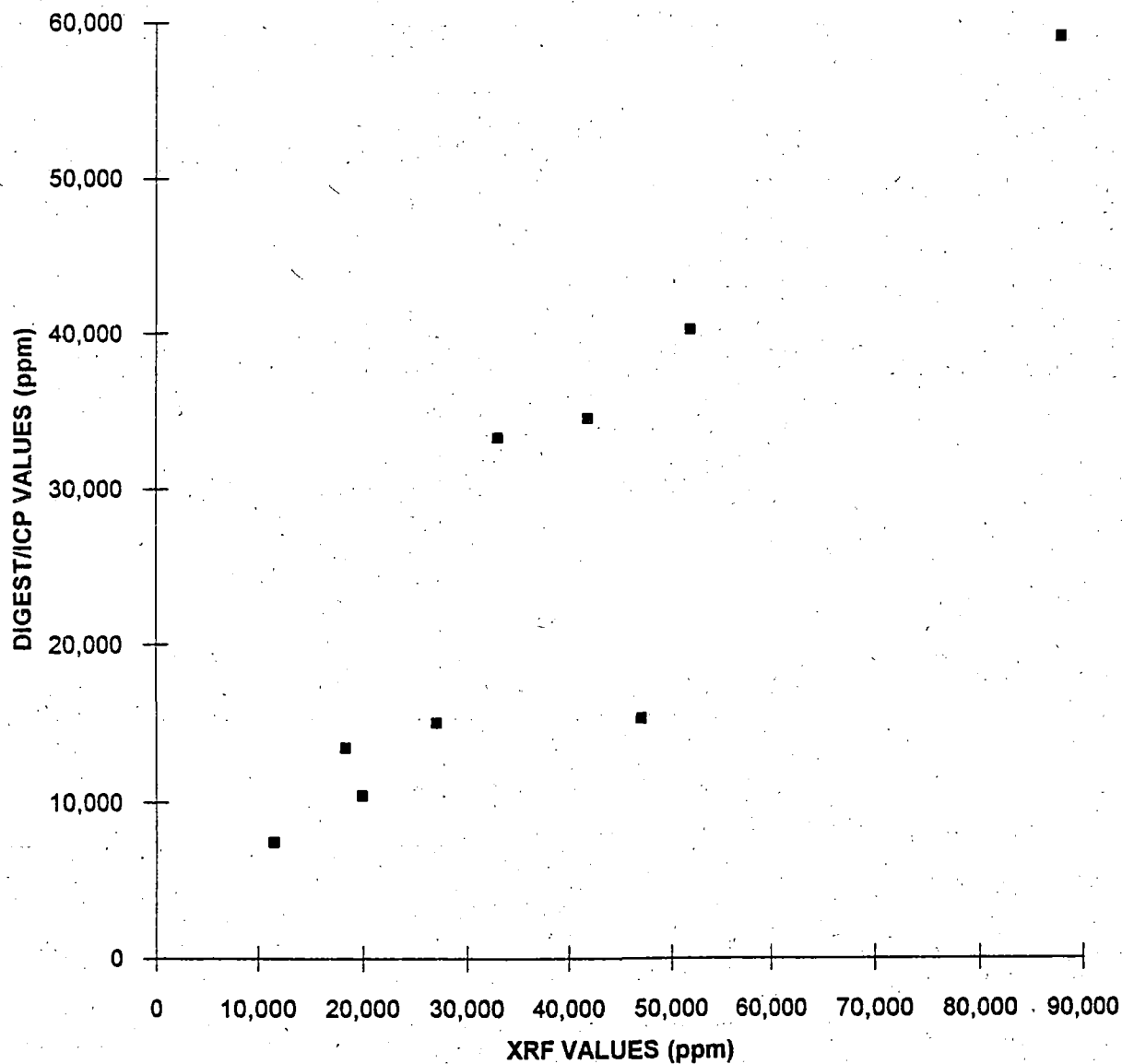
## MANGANESE: XRF vs. DIGEST/ICP



## LEAD: XRF vs. DIGEST/ICP VALUES



## IRON: XRF vs. DIGEST/ICP



## IRON: XRF vs. DIGEST/ICP

