DEPARTMENT OF MECHANICAL ENGINEERING

PROGRESS REPORT.

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Semi-Annual Report
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CHARACTERIZATION AND ENVIRONMENTAL
STUDIES OF POMPANO BEACH ANAEROBIC
DIGESTION FACILITY

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I. EXECUTIVE SUMMARY

1.1 Background

Anaerobic digestion of municipal waste has been demonstrated to be feasible in bench scale experiments by Pfeffer (1974). Approximately, fifty percent reduction in mass and production of 6000 cu ft of gas/ton have been estimated. The gas composition is estimated to be 50% methane and 50% carbon monoxide. The Department of Energy has sponsored Waste Management Inc. (WMI) to demonstrate the technical and economic feasibility of anaerobic digestion with an ultimate objective of commercialization.

A plant has been built at Pompano Beach, Florida on an existing shredding and landfill operation site. The plant design capacity is 100 tons/day. Two digestors have been constructed to be used in parallel. The process consists of primary shredding, metal separation, secondary shredding, air classification and digestion of light fraction. Sewage sludge was used to seed the initial mixture in the digester. The output slurry is vacuum filtered and the filter cake disposed on an existing landfill. The filtrate is recycled. Excess filtrate is sprayed on the landfill. At present the output gas is being flared. Fig.I-1 shows a flow chart for the plant.

It is imperative that environmental investigations be conducted on "new" energy technology prior to commercialization. The Resource Recovery Group at the University of Miami initiated a project to characterize all input and output streams and to assess the potential for ground water contamination by landfill disposal of effluents. Detailed chemical, biological

PROCESS FLOW CHART

FIG. 1.1 Process Flow-chart for Pompano Beach Anaerobic Digestion Plant.

and physical characterization efforts supported by leaching and modelling studies are being conducted to achieve the stated objectives. Some mutagenic studies were also conducted. The responsibility for trace analysis was assigned to Ames Laboratory. Fig.I-2 shows the sampling sites chosen.

The environmental investigations were started in August 1978. Sengupta et al (1979a) reported the first year's efforts. A quarterly report by Sengupta et al (1979b) described the work for the period August 1, 1979 to Oct. 31, 1979. This report presents the activities for the period August 1, 1979 to January 31, 1980. Therefore, there are repetitions of work summarized in the quarterly report.

1.2 Status Report

Plant Operation

1. The plant started producing gas in August 1978. An initial seeding of municipal sewage sludge was used with plans to add more sewage as needed. The plant operation has not dictated any further addition of sewage.
2. Since November, 1979, the plant has been shutdown for repair, modifications and cleaning. Therefore, no samples except for classification building particulate levels (background) have been investigated. Walter (1980) presented a report on the plant status. A summary from this paper is presented below. Detailed descriptions of plant operation are available in monthly reports by WMI to DOE.

Accomplishments

1. The digestors have produced gas on an intermittent basis since August, 1978.

FIG. 1.2 Schematic Drawing of Pompano Beach Plant Showing Sampling Sites.

2. The experiments are in the mesophilic range of $37 \pm 2^\circ\text{C}$. The pH has been kept in the 6.8 - 7.0 range by the addition of lime.
3. A feed rate of approximately 3.1 tons/day has been reached. This low feed rate has resulted in 3% total solids in the digestors and gas production of 5000-8000 cu ft per day.

Problems

1. The plant has suffered from numerous mechanical and operational problems; some of minor and others of major consequence. There have been conveyor breakdowns and digester water seal blow outs. Two explosions, one in the primary shredder and another in Digester #2, have occurred. There have been no injuries, although extensive facility damage has occurred.
2. Textile and plastic "stringers" on agitators in the premix tank and the digestors have been a problem.

Modifications are now underway to solve most of these problems.

Gas Characterization

1. Plastic, Saran and Tedlar bags have been tested as sample containers. Among these, Tedlar bags have been found to provide the least air contamination. Glass bulbs are better. Glass bulbs are used for syringe injection analysis and Tedlar bags for loop injection analysis.
2. Seventeen field trips were conducted and results indicate 55.2% CH_4 and 44.8% CO_2 . This agrees well with WMI plant data. Other compounds identified are H_2S , C_2H_6 and C_4^+ hydrocarbons. These are in the ppm range. Though carbon monoxide was detected during the first year it was not found during the last 6 month period.
3. The H_2S levels have dropped to 0 - 54 ppm. The gas meters have

malfunctioned owing to corrosion and H_2S is suspected as the cause.

4. In the next quarter GC/MS investigations will be conducted on gas samples to identify unknown peaks detected by the FID. They are tentatively suspected to be ethylene and propane. Attempts to identify the higher hydrocarbons, at present reported as C_4^+ , will also be initiated.

Particulates

1. An Andersen stack sampler for sampling particulates in the output gas stream has been obtained and is being tested.
2. A 4-stage Hi-volume Particulate Sampling System has also been acquired.
3. Preliminary sampling inside the classification building is being conducted to form a baseline data base. (The plant has not been in operation for the last two months).

Solid and Liquid Phase

1. Since July 25, 1979, 14 sampling trips have been conducted and 71 samples were collected and analysed at sampling locations shown in Fig. I-2. Sewage sludge (Site 3) and tipping floor wash (Site 10) were not collected owing to unavailability.
2. Ammonia and total organic nitrogen have shown near constant levels in input light fraction. Owing to decrease in nutrient addition, ammonia levels were lower in digester slurry, filtrate and filter cake. TON levels have remained at near constant levels in digester slurry and filtrate.
3. Nitrite-nitrogen levels are near constant in digester slurry and filtrate. There has been an increase of nitrite in the filter cake though

not to levels of environmental concern.

4. Nitrate-nitrogen levels showed an increasing trend in digester slurry and filtrate and a decreasing trend in the filter cake.
5. Vacuum filter cloth wash water output showed significant contamination by the four forms of nitrogen discussed above.
6. Total phosphorus has reached near constant levels during this quarter, in the input light fraction. Digester slurry had lower levels owing to reduced nutrient addition. Wash water contamination was also detected.
7. Chloride levels are near constant in input light fraction. Some buildup has been noticed in digester slurry, filtrate and filter cake. Chloride contamination of wash water was also detected.
8. The maximum level of sulfide was in the digester slurry (5.9 mg/l). This is lower than levels found during January through June, 1979.
9. The maximum BOD level was in the filtrate (2981 mg/l). This is significantly less than maximum levels found in landfill leachate.
10. COD levels showed an increasing trend with maximum level near 33000 mg/l in the digester slurry. Accumulation of non-biodegradable organic matter is the possible cause.
11. Stabilization of TOC levels in filtrate was reached with a maximum value near 1800 mg/l.
12. Significant variations in dissolved and suspended solids have been detected in digester slurry and filtrate.
13. The levels of carbon, hydrogen and oxygen in light fraction, and filter cake are close to theoretical values for cellulose.
14. From July to September, 1979, total and fecal coliform levels decreased

by an order of magnitude in all samples except wash water. The trend was reversed during October and levels the same as spring of 1979 were reached by November, 1979. Thermal stresses associated with heating to reach mesophilic range and subsequent stabilization is a probable explanation of this behavior.

15. Levels of metals have stabilized in all digester streams. However, measurements at Ames Laboratory has shown significant decreases. Adsorption of metal ions on glass walls of sample containers used for transport is a suspected explanation.
16. In complex samples interference and matrix effects can cause errors in analysis. A spiking study was conducted to evaluate analytical procedures used by the Miami group. Recovery rates for most parameters were between 80% to 150% with TOC at 65.9%, Kjeldhal nitrogen at 510%, this is not unusual as studies with landfill leachates have shown even negative recovery. Further investigations are ongoing.

Trace Analysis

This work is being conducted at the Ames Laboratory USDOE.

Emphasis has been placed in developing analytical techniques and detailed characterization of samples. Thus frequency of sampling has been kept to a minimum.

1. An ion exchange/gas chromatographic technique developed by Ames Laboratory has been used to identify acidic organic materials in the process filtrate. Over thirty organic acids including herbicide decomposition products have been found.
2. An adsorption technique for extracting and simultaneously fractionating organic materials on the basis of chemical functionality is being

developed. To date, this method has been found suitable for most phthalate esters and PAHS.

3. High performance liquid chromatographic procedure (HPLC) have proved successful on filtrate and filter cake.
4. Methods of extracting organic compounds from particulates are being investigated. Digester gas stream particulates and classification building dust will be sent to Ames by the University of Miami group during the next quarter.

Leaching

1. Characterization of Hallandale fine sand, plantation muck bottom, middle and top layer soils is complete. Organic content, pH, metals levels and cation exchange capacity were measured.
2. Batch experiments with all the soils at pH 6.8 were conducted. Experiments with plantation muck middle layer at pH 4.5 were completed. Langmuir isotherms were used to obtain attenuation coefficients for metals, various form of nitrogen, and phosphorous.
3. Batch column experiments or serial batch extraction experiments were conducted for Hallandale fine sand and plantation muck bottom layer.
4. In the next quarter the batch column studies will be completed and column studies for verification initiated.

Modelling

1. A one dimensional model was developed and parametric studies completed.
2. A two dimensional model was developed and boundary conditions were tested.
3. The two dimensional model was also executed using attenuation

coefficients determined from leaching studies.

4. A three-dimensional model was developed and solutions obtained using Langmuir constants from batch leaching studies.
5. These models were executed to steady state and time scales for clean up by rain after pollution source is removed were also investigated.

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II. GAS QUALITY

The objective of this phase of the contractual work is to evaluate the possible impact of the anaerobic digestion technology on the atmospheric environment. Before that can be done, it is necessary to first characterize the types and amounts of the major products in the digester gas stream regardless of their origin. Simple dispersion formulas will then be used to assist in predicting levels of the oxidized as well as the unoxidized products should they enter either the ambient or the working environment. Finally the resulting concentrations will be compared with the applicable National Ambient Air Quality Standards (NAAQS) as well as the Occupational Safety and Health (OSHA) standards.

The analytical instrumentation, sampling, and quality control procedures as well as preliminary results were presented in the first annual report of the project, Sengupta et al, (1979). A summary of the gas composition observed during that period is presented in Table 2.1.

It was noted that the concentrations compared favorably with those from ten landfill projects throughout the United States. However, H_2S concentrations in the Pompano digester were substantially higher than found in the landfill gas. It has been difficult to obtain an accurate trend on the H_2S levels because of so many blown air seals on the Pompano digester.

The performance objectives during the current phase of the contractual work specified continued H_2S Ecolyzer and G.C. analyses of the digester gas with further investigations of sample collection, handling, and analysis procedures during the first quarter; and a search for

TABLE 2.1

Gas Composition Observed 1 August 1978 - 31 July 1979,
Pompano Anaerobic Digester

Constituent	Concentration	Constituent	Concentration
O ₂	0-3%	1-Butane, 2-Butane	GC/MS Peak
N ₂	2.9-15.7%	Vinyl Chloride	0-9.6 ppb
CO	0-100 ⁺ ppm	Trichloroethylene	0-22.23 ppb
CH ₄	42.2-59.4%	Tetrachloroethylene	0-0.4 ppb
CO ₂	34.7-52.9%	Pentane	GC/MS Peak
Ethane	GC/MS Peak	Ar	GC/MS Peak
H ₂ S	0-500 ⁺ ppm (Average 100 ppm)	Ethylene	GC/MS Peak
		NH ₃	GC/MS Peak
Propane	GC/MS Peak		
Water	GC/MS Peak		
Butane	GC/MS Peak		

other possible pollutants including particulates in the gas stream (see Chapter III) during the second quarter. Although there was some equipment down-time associated with the G.C. malfunctioning, the major problems during the period were air leaks and down-time at the Pompano digester facility. There were eighteen entries of air seal and related problems in the WMI logs during the period August 1, 1979 to September 15, 1979 alone. Moreover, our last sample collection date was November 15, 1979 because the plant has not been operating essentially since late November 1979. It is still not operating as of this writing. Accordingly, we must await resumption of plant operation during the third quarter to complete those objectives.

2.1 Sample Collection and Handling

Four types of containers were used to collect gas samples during the period: plastic, Saran and Tedlar bags; and glass bulbs. Because of high leak rates, plastic bags have been rejected from further use. The best containers for minimal air contamination were the glass bulbs but they must be tested periodically for small, hard-to-find pin holes. The Tedlar bags contained slightly less air contamination than the Saran bags. Thus the glass bulb is used primarily for syringe injection analysis, and the Tedlar bag for loop injection analysis.

Because of column stripping and poisoning problems, we've been concentrating near the end of this period on "dry" gas samples which were collected downstream from a water trap. Analysis of the water trap condensate has not revealed sulfides but further tests are planned on that liquid next quarter.

As was the case during the previous period, field trips to collect G.C. gas samples were made once per week except when the plant was down.

H₂S levels were monitored at the site using the H₂S Ecolyzer.

2.2 Sample Analysis Procedure Using the G.C.

Prior to or while making a field trip, the G.C. columns were conditioned so that analysis could begin immediately upon return from the field. The current order of operation is summarized in Table 2.2, with approximate retention times shown in Table 2.3.

The sequence shown in Table 2.2 requires at least 14 hours to perform assuming everything goes well. In addition, the analysis part of the sequence is often repeated to investigate possible concentration changes with time. Thus the analytical procedure is rather time consuming.

2.3 Analytical Results

A summary of the digester gas composition as analyzed throughout this period is presented in Table 2.4. While the air contamination in the samples is relatively high, it is felt that new containers have resolved most of that as of November 8, 1979. During November 1979, N₂/O₂ ratios were analyzed using the Molecular Sieve 5A column to determine if what we have been calling air contamination really was air, or perhaps excess nitrogen that registered as an air peak using the Porapak Q column. For ambient air containing 78.08% N₂ and 20.95% O₂ by volume, the N₂/O₂ ratio is 3.73. We obtained N₂/O₂ ratios ranging from 2.93 to 4.27 with the average less than 3.73 which implies greater-than-normal O₂ in the sample. Abeles et al (1980) obtained N₂/O₂ ratios averaging 4.88 from 13 farm digestors which does imply excess nitrogen. This will be checked further during the next quarter.

A comparative summary of the primary constituents is shown at the bottom of Table 2.4. It is noted that the actual U.M. data compare

TABLE 2.2 Order of Operation for G.C. Digestor Gas Analysis

WEEKLY

Porapak Q Column - Loop Injection:

1.	Calibrate Using Breathing Air	2 Runs
2.	" " CH ₄ and CO ₂	2 Runs
3.	Analysis, Dry Digestor Gas, Tedlar Bag, Prog 1	1 Run
4.	" " " Prog 2	1 Run
5.	" " " Prog 3	1 Run

Porapak Q Column - Syringe Injection:

6.	Calibrate Using Breathing Air	2 Runs
7.	" " CH ₄ and CO ₂	2 Runs
8.	Analysis, Ambient Air, Glass Bulb, Prog 1	1 Run
9.	" " " Prog 2	1 Run
10.	" " " Prog 3	1 Run
11.	" , Dry Digestor Gas, Glass Bulb, Prog 1	1 Run
12.	" " " Prog 2	1 Run
13.	" " " Prog 3	1 Run

Molecular Sieve 5A Column - Syringe Injection:

14.	Calibrate Using Breathing Air	2 Runs
15.	" " CH ₄	2 Runs
16.	" " CO ₂	2 Runs
17.	Analysis, Ambient Air, Glass Bulb, Prog 4	1 Run
18.	" , Dry Digestor Gas, " Prog 4	1 Run

Minimum of 25 Runs

ONCE PER MONTH

Calibrate C1-C6 Hydrocarbons 0-50 minutes
 " " " 0-15 minutes, backflush 15-30 minutes

PROGRAM IDENTIFICATION

1. TCD 0-5 min, FID 5-52 min, Backflush
2. TCD 0-15 min, Backflush 15-30 min Through FID
3. TCD 0-5 min, FID 5-15 min, Backflush 15-30 min Through FID
4. TCD 0-6 min, FID 6-10 min.

TABLE 2.3 G.C. Retention Times

Porapak Q Column*		Molecular Sieve 5A Column#	
Constituent	Retention Time (Min)	Constituent	Retention Time (Min)
Air	1.8	O ₂	1.5
CH ₄	2.2	N ₂	2.1
CO ₂	2.9	CH ₄	2.4
C ₂ H ₆	7.5	CO	8.6
H ₂ O	9.3		
C ₃ H ₈	13.1		
C ₄ H ₁₀	18.7		
C ₅ H ₁₂	28.9		
C ₆ H ₁₄	48		
* 12' x 1/8" Stainless Steel Porapak Q Column, 80/100 Mesh With Oven at 60°C, Programmed to 160°C After 5 Minutes at 10°C/min.		# 6' x 1/8" Stainless Steel Molecular Sieve 5A Column, 60/80 Mesh, With Oven Isothermal at 80°C.	

TABLE 2.4 Digester Gas Composition

1979 Collection Date	Air (%)	CH ₄ (%)	CO ₂ (%)	CO (ppm)	C ₂ H ₆ (ppm)	H ₂ S (ppm)	C ₃ H ₈ (ppm)	C ₄ ⁺ (ppm)	Type Container	No. of Runs
8/8	5.1	49.8	45.1	0	0	0	0	8.0	G.B.	3
8/15	2.0	51.0	47.0	0	24.3	0	0	0	G.B.	1
8/23	-	-	-	-	-	0	-	-	-	1
8/31	5.0	62.7	32.3	0	0	0	0	0	P.B.	1
9/14	3.3	57.9	38.8	0	0	17	0	3.6	P.B.	2
9/14	3.5	50.0	46.5	0	0	17	0	4.5	G.B.	2
9/20	1.7	55.8	42.5	0	0	54	0	4.3	P.B.	2
9/28	-	-	-	-	-	0	-	-	-	1
10/5	4.7	50.0	45.3	-	0	0	0	18.2	G.B.	10
10/18	0.1	55.6	44.3	0	0	41	0	8.5	G.B.	4
10/18	1.4	56.2	42.4	0	0	41	0	9.9	T.B.	12
10/18	3.3	54.9	41.8	0	0	41	0	14.5	S.B.	3
11/1	6.8	48.8	44.4	0	0	6	0	5.8	G.B.	2
11/1	6.7	49.5	43.8	0	0	6	0	1.2	T.B.	6
11/8	0.1	52.4	47.5	0	0	0	0	-	G.B.	1
11/8	0.8	52.7	46.5	0	0	0	0	10.1	T.B.	9
11/15	1.0	53.6	45.4	0	0	17	0	-	T.B.	3

Total 63

Average Data by Sampling Date During Period:

	Actual U.M.	Revised U.M.	WMI	13 Farm Digestors
Air (%)	3.2	Neglect	-	5.2
CH ₄ (%)	53.4	55.2	55.1	53.3
CO ₂ (%)	43.4	44.8	44.9	41.5
No. Dates	10	10	6	12 Wks.

well with that reported by Abeles et al (1980) from 13 farm digestors over a 12 week period. Since WMI does not report air in their results, and if one neglects the air from the U.M. results, the adjusted U.M. values agree very closely with those by WMI. All of those values fall within the range listed in Table 2.1 for the previous year.

Although CO was detected during the first year of the contractual work, it has not been detected yet this contractual year. Ethane was detected on one date early in the period but not afterward. Two unknown peaks frequently were observed at retention time 9.39 and 12.63 minutes using the FID. The former may have been ethylene and the latter possibly could have been propane but further testing is needed to be certain. A GC/MS run is scheduled as soon as digester gas is available in order to resolve this question, and to identify the higher hydrocarbons listed as C_4^+ .

Because of numerous air leaks, the H_2S readings cannot be considered to be representative. The levels immediately go to zero when a seal is blown. Excessive corrosion in the WMI gas meter suggests high corrosive action, perhaps related to H_2S and water forming sulfuric acid. The phenomenon is similar to corrosion in sewer lines with acidic compounds formed by H_2S . Schellenbach (1980) reported maintenance problems with her gas meter because of the H_2S corrosive action. She removes the H_2S using a Varac Scrubber.

2.4 Conclusions

It is premature to make definitive environmental impact assessments at this writing but no serious concerns have been obtained to date. Clearly the H_2S problem needs further study and several unknown constituents need to be identified during the next quarter.

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III. PARTICULATES

Along with characterizing the various gases produced by the anaerobic digestion technology, it is desirable to study the particulates which may be present in the gas stream, and those found in the classification building adjacent to the digestors. Because of extensive delays in installing a sampling port in the gas line, work on the former cannot begin until next quarter. Work on the latter was initiated at the end of the second quarter while the plant was down.

3.1 Sampling Equipment

During the period we obtained the following equipment to support the particulate sampling effort:

- 1) Christian Becker Analytical Balance (200 gram)
- 2) Precision Thelco Oven (0-200°C)
- 3) Stainless Steel Desiccating Cabinet
- 4) 4-Stage Hi-Volume Particulate Sampling System with Flow Controller and Andersen Particle Sizing Head
- 5) EPA Emission Parameter Analyzer (Andersen Stack Sampling System)

The Hi-Volume sampler is currently in position near the middle of the classification building at WMI. That particular building is open on all four sides. When the sampling port in the gas line is completed, the Andersen Stack Sampling System will be inserted into the line to sample particulates immediately prior to flaring the gas.

3.2 Sampling Schedule

Plans during the next quarter call for the following type of analyses

to be made monthly:

Particulates in the Digester Gas Stream

- a) Bacteria analysis
- b) Total amount of particulates per cubic meter of gas flow
- c) Particulate trace analysis by AMES laboratory

Particulates in the Classification Building

- a) Bacteria analysis
- b) Total amount of particulates stratified by the following ranges:
  - $\geq 7.0 \mu$
  - 3.3-7.0 μ
  - 2.0-3.3 μ
  - 1.1-2.0 μ
  - 0-1.1 μ
- c) Particulate trace analysis by AMES laboratory

The bacteria program will consider total plate count, i.e., number of colony forming units, and sub-culture studies.

3.3 Initial Results

Two field trips were made to Pompano in January 1980 to sample particulates in the classification building while the plant was not in operation in order to obtain background levels there. No coliform bacteria were found but fungus was observed. On future field trips we will also use settling plates to collect the particulate material as there is a possibility that the bacteria may be destroyed on the Hi-Volume Sampler filter because of the high air velocities.

The 24-hour particulate concentrations were $153.4 \mu\text{g}/\text{m}^3$ (during January 18-22, 1980) and $181.5 \mu\text{g}/\text{m}^3$ (during January 23-24, 1980). The 24-hour NAAQS for particulates is $150 \mu\text{g}/\text{m}^3$, and the 8-hour OSHA standard for inert or nuisance dust is $15 \text{ mg}/\text{m}^3$.

References

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2. Florida Administrative Code, "Air Pollution", Rules of the State of Florida Department of Environmental Regulation, Chapter 17-2.
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4. Occupational Safety and Health Administration, 1977, "Selected General Industry Safety and Health Standards," Federal Register, December 13, 1977.

IV. SOLID AND LIQUID PHASES

4.1 Objectives

A comprehensive task of characterization of the solid and liquid inputs and outputs of the RefCOM has been undertaken to evaluate the potential environmental impact of the anaerobic bioconversion of solid municipal waste to methane. Various sampling sites are indicated in the flow diagram (Figure 4.1). Samples have not been collected from sites number 3 (sewage and sludge) and number 10 (tipping floor wash) due to their unavailability. Table 4.1 lists dates of 14 sampling trips. The various samples preservation techniques have been reported in the Annual Report (Sengupta, et al, 1979).

4.2 Methods of Analysis

All physical, chemical and biological procedures used in the analysis of samples were taken from Standard Methods, 14th Edition. In some cases, however, modifications were made to accomodate the physical characteristics of the samples (Sengupta et al, 1979).

4.3 Results and Discussion

4.3.1 Nitrogen

Nitrogen appears in four forms; ammonia, organic, nitrite, and nitrate nitrogens. The status of these parameters, from July through December 1979 is discussed below.

Both ammonia and total organic nitrogens (TON) in the air-classified light fraction fluctuate about the means (.83 mg/g and .33 mg/g respectively) from sampling data recorded from July to December 1979. The data indicate a constant trend with minor fluctuations, in the levels of

A- MAKE-UP WATER
B- OVERFLOW

SITES

SAMPLE DESCRIPTION

1	Air Classified Heavy
2	Air Classified Light
5	Digester Slurry
7	Filter Cake
8	Filtrate
11	Vacuum Filter Wash Input
12	Wash Water Effluent

Fig. 4.1 Location of Sampling Sites

TABLE 4.1 Summary of Samples Collected

Date	Day Number*	Sites		
7/25	206	7		
7/30	211	5, 8, 11		
8/8	220	1, 2,	5, 7, 8,	11, 12
8/15	227	5, 8, 11		
8/23	235	2,	5, 7, 8,	11, 12
9/7	250	1, 2,	5, 7, 8,	11, 12
9/14	257	2,	5, 7, 8,	11, 12
9/20	263	2,	5, 7, 8,	11, 12
9/28	271	2,	5, 7, 8,	11, 12
10/11	284	1, 2,	5, 7, 8,	11, 12
10/19	292	2,	5,	11
11/1	305	1, 2,	5,	11
11/8	312	2,	5, 7, 8,	11, 12
11/15	319	2,	5, 7, 8,	11, 12

* Day from Jan.1, 1979

<u>Sites</u>	<u>Samples Discription</u>
1	Air Classified Heavy
2	Air Classified Light
5	Digestor Slurry
7	Filter Cake
8	Filtrate
11	Vacuum Filter Wash Input
12	Wash Water Effluent

the two nitrogens i.e. ammonia and TON in the air-classified light fraction since sampling has begun in January (Fig.4.2). This fluctuation is perhaps due to changes in the quality of the refuse or impurities associated with the refuse.

In digester slurry, the mean value of ammonia-nitrogen, from July to December, 1979, was 123.10 mg/l compared to the mean value of 191.56 mg/l, for the previous six month period (ie. Jan-June, 1979). This substantial difference is also characterized by less fluctuation in levels of ammonia as seen in Fig.4.3. The cause of this decreasing trend is the result of decreased nutrient addition (primarily diammonium phosphate and urea) to the digester (Matthew Streit, Pers. Comm.).

In filter cake and filtrate, similar noticeable drop of ammonia has occurred, from July to December 1979, probably for the same reason as for digester slurry. These trends are illustrated in Figs.4.4 and 4.5.

The mean value of ammonia-nitrogen in wash-water output (Fig.4.7) is approximately twice that of wash-water input (1.63 mg/l and .83 mg/l respectively Fig.4.6). This is an appropriate indicator of contamination of the wash-water input. The levels of contamination of ammonia-nitrogen vary due to the fact that the wash-water output stream sometimes contains filtrate overflow.

Total organic nitrogen (T.O.N.) values for the digester slurry and filtrate, during July through December 1979, have remained close to the levels determined from January through June 1979. In digester slurry the T.O.N. mean value for January through June 1979 was 63.83 mg/l, for July through December 1979 the mean was 61.85 mg/l T.O.N. In filtrate the mean value for T.O.N. was 44.11 mg/l for the January through June

FIG.4.2 Concentration of Ammonia-Nitrogen and Organic Nitrogen vs Time in Air Classified Light Fraction.

FIG. 4.3 Concentration of Nitrogen from Four Compounds vs Time in Digester Slurry.

FIG. 4.4 Concentration of Nitrogen from Four Compounds vs Time in Filter Cake.

FIG. 4.5 Concentration of Nitrogen from Four Compounds
vs Time in Filtrate.

FIG. 46 Concentration of Nitrogen from Four Compounds vs Time in Wash Water Input.

FIG. 4.7 Concentration of Nitrogen from Four Compounds vs Time in Wash Water Effluent.

1979 period, whereas, for the July through December 1979 period the mean T.O.N. value was 64.4 mg/l. Filter cake shows less concentration of T.O.N. than previously reported for January through June 1979 (.30 mg/g and .49 mg/g respectively). Total organic nitrogen values for the wash water input and wash water output once again indicate contamination of wash water input with respect to nitrogen due to washing of the vacuum filter cloth.

Mean nitrite-nitrogen values, from July through December 1979, remain at about the same level in digester slurry and filtrate reported for January through June 1979 (digester slurry mean values .027 mg/l and .037 mg/l respectively; filtrate mean values .029 and .018 respectively). In filter cake the mean level of nitrite-nitrogen has increased from the previous mean value of .0014 $\mu\text{g/g}$ to this period's mean value of .247 $\mu\text{g/g}$. While these values indicate a large relative increase of nitrite levels, the absolute increase as micrograms per gram ($\mu\text{g/g}$) is not alarming. Again, the mean value for the wash water output is noticeably higher, indicating contamination of the wash water input.

Mean nitrate-nitrogen values, from July through December 1979, are noticeably higher than the previous period, from January to June 1979, in digester slurry (5.8 mg/l and 2.77 mg/l respectively) and filtrate (5.40 mg/l and 2.70 mg/l respectively). Filter cake mean values of nitrate indicate a major drop in concentration this period (July-December 1979) as compared to the previous period (January-June 1979). The value dropped from .85 mg/g to .04 mg/g. Comparison of wash water input and output mean values for nitrate-nitrogen indicate contamination of wash water input.

During the period of July to December 1979 nitrogen levels have decreased due to low nutrient additions as mentioned above. Environmentally it can be seen that wash water input is contaminated in the process of washing the vacuum filter cloth.

4.3.2 Total Phosphate-Phosphorus

In the air classified light fraction total phosphorus varied less widely from July to December 1979 compared to January through June, 1979 as shown in Fig.4.8 (0.29-1.16 mg/g compared to 0.1-4.0 mg/g). Thus a slightly reduced amount of phosphorus is entering the system through air classified light. The mean value for this period is 0.78 mg/g whereas previously it was, 1.10 mg/g. Digester slurry showed a marked decrease in phosphate from 250 mg/l to 180 mg/l (Fig.4.9). This reduction is due in part from the lower phosphate input with the air classified lights and from reduced nutrient addition of diammonium phosphate. However, filter cake and filtrate show a slight increase of phosphate levels over the previous values, as shown in Figs.4.10 and 4.11, respectively. Furthermore, wash water input and wash water effluent also show increase in phosphate levels as indicated in Figs.4.12 and 4.13.

4.3.3 Chloride

Although the chloride entering the system through air classified light (Fig.4.8) follows the same pattern as reported in the Annual Report; however, chloride values have increased almost steadily in digester slurry, filter cake, and filtrate (see Fig.4.9, 4.10, 4.11). This build-up of chloride ion may be due to the recirculation of the filtrate back to the digester. Chloride levels are observed once more consistently higher in the wash effluent (Fig.4.13) than in the wash input (Fig.4.12).

FIG. 4.8 Concentration of Total Phosphorus, Chloride
vs Time in Air Classified Light Fraction.

S VALUES x 10

FIG. 4.9 Concentration of Total Phosphorus, Chloride and Sulfide vs Time in Digester Slurry.

FIG. 4.10 Concentration of Total Phosphorus and Chloride
vs Time in Filter Cake.

S VALUES X 10

FIG. 4.11 Concentration of Total Phosphorus, Chloride and Sulfide vs Time in Filtrate.

S VALUES X 10
 P VALUES X 100

FIG. 4.12 Concentration of Total Phosphorus, Chloride and Sulfide vs Time in Wash Water Input.

S VALUES X 10
 P VALUES X 10

FIG. 4.13 Concentration of Total Phosphorus, Chloride and Sulfide vs Time in Wash Water Effluent.

4.3.4 Sulfide

The sulfide concentration has been monitored in the digester slurry, filtrate, wash water input and wash water effluent. During July through November the sulfide concentration in the digester slurry varied from 3.6 to 5.9 mg/l (Fig.4.9) and during January through June it varied from 1.9 to 9.06 mg/l. The sulfide level in filtrate was lower than that in the digester slurry and varied from 2.6 to 4.9 mg/l (Fig.4.11) during July through November. During January through June, sulfide level in the filtrate varied from 1.52 to 5.33 mg/l. It is observed that the wash water input has a sulfide concentration varying from 1.02 to 2.4 mg/l (Fig.4.12) as found between July through November. The sulfide level slightly increased in the wash water effluent due to contribution from impurities left over in the cloth of the vacuum filter. The levels varied between 1.45 to 2.7 mg/l (Fig.4.13) during July through November; the corresponding levels found during January through June were between 1.2 to 6.1 mg/l.

4.3.5 BOD, COD, TOC

During the period July through November 1979, BOD of the digester slurry varied between 233 to 2345 mg/l (Fig.4.15) with the levels found in November lying close to the upper value found during this period. During the earlier period (January through June 1979) the average BOD of the digester slurry was about 3000 mg/l (Sengupta et al., 1979) which indicate a fairly uniform trend during the year 1979. The BOD of the filtrate varied from 313 to 2981 mg/l (Fig.4.17) during July through November with the levels in the first half of the year ranging between 500 to 2500 mg/l (Sengupta; et al., 1979)

FIG. 4.14 Concentration of COD vs Time in Air Classified Light Fraction.

FIG. 4.15 Concentration of BOD and COD vs Time in Digester Slurry.

FIG. 4.16 Concentration of BOD and COD vs Time in Filter Cake.

FIG. 4.17 Concentration of BOD, COD and TOC vs Time in Filtrate.

FIG.4.18 Concentration of BOD,COD and TOC vs Time in Wash Water Input.

FIG. 4.19 Concentration of BOD, COD and TOC vs Time in Wash Water Effluent.

which also shows a uniform range of values throughout the year. The BOD levels of filter cake, wash water input and wash water effluent have been quite low and the results obtained have been shown in Figs. 4.16, 4.18 and 4.19 respectively. It is interesting to note that the BOD levels of leachate obtained from different sanitary landfills indicate values varying between 1550 to as high as 33,600 mg/l as reported in a comprehensive report by EPA (Chian and De Walle, 1977a). The levels of BOD found in the filtrate of the digester as mentioned above indicate much lower values compared to that found in leachate from sanitary landfill as reported by various studies. The reason for obtaining lower BOD values in the filtrate than those found in leachate of sanitary landfill is that the raw waste in the digester is better metabolized by the microorganisms under control conditions which lowers the level of BOD remaining in the filtrate. In the case of landfill, conditions for anaerobic biodegradation vary to a great extent depending on various factors like weather, method of landfilling operations, possibilities of aeration during landfilling etc. which ultimately affects the efficiency of the sensitive anaerobic process. As a result very high BOD levels could remain in the leachate. This variation of environmental conditions for the biodegradation process taking place in a landfill is also reflected by the wide fluctuation of BOD levels found in the leachate (Chian and De Walle, 1977a).

The COD level of the air classified light fraction varied between 750 and 1600 mg/g (Fig. 4.14) which reflects a fairly uniform quality of the raw material fed to the digester. The COD of the digester slurry varied between 7500 to 33000 mg/l (Fig. 4.15) during July through

November 1979 which indicates an increasing trend compared to that found in the period January through June 1979 when the level varied between 14000 to 29000 mg/l (Sengupta et al, 1979). One of the reasons for this increase in COD level in the digester slurry could perhaps be attributed to the continuous recycling of the filtrate over a long period which is causing a gradual build up of the non biodegradable organic matter. The filtrate also shows an increasing trend in COD ranging from 2500 to 10,000 mg/l (Fig.4.17) when compared to the values during January through June when it varied between 1700 to 8500 mg/l (Sengupta et al, 1979).

Gradual build up of non-biodegradable matter is taking place continuously and so this may be expected to show up in the increasing trend of COD values found in digester slurry. A comparison of COD values of leachate reported in a study which show COD levels ranging from 40 to 89,520 mg/l indicate a tremendously large variation and much higher levels than that found in the filtrate of the digester under study. Another study by Chian and De Walle (1977b) on leachate characteristics from an experimental lysimeter indicated COD value of 49,300 mg/l which is also much higher than that found in filtrate of the digester under study. The COD levels of air classified light fraction, filter cake, wash water input and wash water effluent are much lower compared to that found in the digester slurry and filtrate and are indicated in Figs.4.16, 4.18,4.19 respectively.

The TOC levels of the filtrate have remained quite uniform during July through November 1979 the values ranging from 1365 to 1800 mg/l (Fig.4.17). The levels in the earlier period January through June 1979 showed a larger variation in values ranging from 700 to 2000 mg/l

(Sengupta et al., 1979). Chian and De Walle (1977b) have reported TOC values of 17060 mg/l from leachate of sanitary landfill which is much higher than that found in the filtrate of the digester under study.

It is observed that the concentration of the above pollutants show a considerable variation on a day-to-day basis which has also been noted in other research studies (Chian and De Walle, 1977a). It is therefore more meaningful to study the ratio of different parameters instead of their absolute values. In the digester slurry the BOD/COD ratio varied between 0.03 to 0.07 during July through November which indicate a fairly uniform quality of the slurry as compared to that found during January through June when it varied between 0.09 to 0.24. In case of filtrate, however, the BOD/COD ratio varied from 0.13 to 0.30 during July through November but was uniform at a value of 0.29 during the earlier period January through June. Miller et al. (1974) found that the BOD/COD ratio of leachate from sanitary landfill decreased from 0.47 to 0.07 over a period of twenty-three years. Similar studies on leachate conducted by EPA (Chian and De Wall, 1977a) demonstrated that the BOD/COD ratio decreased from 0.8 to 0.048 over a period of seventeen years. In both cases, however, it was clearly observed that the BOD/COD ratio decreased considerably with the increasing age of the landfill. The COD/TOC ratio of the filtrate varied between 1.9 to 5.5 during July through November and from 2.4 to 4.3 during January through June which indicates a similar range of values during the whole year. Chian and De Walle (1977a) observed that COD/TOC ratio of a leachate from sanitary landfill decreased from 3.3 to 1.16 with the age of landfill. Rickert and Hunter (1971) found that the maximum possible

COD/TOC ratio for several organic compounds is 4.0 and it can be as low as 1.3 for organics containing carboxyl groups.

4.3.6 Solids

The total dissolved solids in the digester slurry varied from 0.27 to 1.56 g/l and that in the filtrate varied from 18.36 to 36.6 g/l during July through November. Corresponding values observed during January through June were 2.0 to 9.5 g/l and 0.5 to 4.2 g/l respectively. The suspended solids in digester slurry varied from 10.7 to 21.2 g/l during July through November and that in the filtrate varied between 11.6 to 16.3 g/l. Corresponding levels of suspended solids observed during January through June in digester slurry and filtrate were between 14.0 to 27.0 g/l and 1.8 to 5.1 g/l respectively.

4.3.7 Elemental Analysis

Twelve samples of air classified light fraction, collected from August through November 1979, and one sample of filter cake were analyzed for carbon, hydrogen and nitrogen contents, on a per cent by weight basis. These results, along with the theoretical levels for cellulose, are summarized in Table 4.2. There is little difference between the air classified light fraction, the filter cake, and the theoretical cellulose values of carbon, hydrogen and oxygen levels. The slightly higher levels of carbon and hydrogen and the slightly lower levels of oxygen in the air classified light fraction and filter cake compared with cellulose are probably due to the presence of plastics.

The chief difference between these samples lies in the level of nitrogen. Pure cellulose has no nitrogen. Therefore, the levels of nitrogen in the air classified light fraction must be due to the impurities adsorbed into

TABLE 4.2 Elemental Analyses* - Air Classified Light Fraction,
Filter Cake, Cellulose.

ELEMENT	AIR CLASSIFIED LIGHT		FILTER CAKE	CELLULOSE (C ₆ H ₁₀ O ₅)***
	MEAN	RANGE		
CARBON	46.23	42.82-51.92	48.41	44.45
HYDROGEN	6.40	5.92-7.80	6.30	6.22
NITROGEN	.43	0.17-0.77	0.86	0
OXYGEN**	46.94	40.11-50.94	44.43	49.34

* All data reported as g/100 g dry weight

** Calculated by difference:

Per. cent Oxygen=100-(per cent Carbon+per cent Hydrogen+per cent Nitrogen)

*** C: (6)(12.011) = 72.066

H: (10)(1.008) = 10.080

O: (5)(15.9994) = 79.997

Total =162.143

C: 72.066/162.143 = .4445 or 44.45%

H: 10.080/162.143 = .0622 or 6.22%

O: 79.997/162.143 = .4934 or 49.34%

the paper. The level of nitrogen in the filter cake is about twice that of the air classified light fraction. This increase in nitrogen level in filter cake can be associated to high levels of nitrogen in digester slurry.

4.3.8 Bacteriology

From July to mid-September, 1979, the levels of total and fecal coliforms appeared to decrease by an order of magnitude in all samples except wash water input and output (Fig. 4.20 through 4.22). This trend was reversed during October and November 1979. At the time of plant shut-down in mid-November, the total and fecal coliform levels were back up into the range they had been last spring (Sengupta et al., 1979). Evidently, the fluctuating levels relate to changing temperatures, since the digester temperature was being raised from ambient to mesophilic at the time of the initial decrease. When the bacterial population was acclimated to the higher temperatures, the bacterial counts increased to their original levels.

Another possible reason is fluctuation in the levels of coliforms in the air classified light input. An attempt was made to measure coliform levels in the air classified light fraction, by the multiple tube technique. All dilutions showed positive results, so no measurement was possible; the level was in excess of 10^6 coliforms/100 g. It is hypothesized that coliforms would be present in air classified light fraction primarily as contaminants from disposable diapers and pet litter boxes.

Total and fecal coliform levels found in wash water input and output are illustrated in Fig. 4.23 and 4.24, respectively. Bacterial counts of less than one per 100 ml are reported as 10^{-1} . The increase in bacterial level from the wash input to output is due to both contamination from

FIG. 4.20 Concentration of Total and Fecal Coliforms
vs Time in Digester Slurry.

FIG. 4.21 Concentration of Total and Fecal Coliforms
vs Time in Filter Cake.

FIG. 4.22 Concentration of Total and Fecal Coliforms
vs Time in Filtrate.

FIG. 4.23 Concentration of Total and Fecal Coliforms
vs Time in Wash Water Input.

FIG. 4.24 Concentration of Total and Fecal Coliforms
vs Time in Wash Water Effluent.

the filter cloth as well as overflow from the filtrate tank.

4.3.9 Heavy Metals

Results of heavy metal analyses performed on samples collected from July through November are summarized in Table 4.3. Data are reported as means and ranges of the 14 samples collected. As in the last quarterly report, little differences have been found with levels reported previously (Sengupta et al., 1979) except for manganese. Again, the levels of most metals appear to have stabilized in the various digester streams.

The high levels of manganese continued at their elevated levels throughout October and November. Thus it seems that the previously observed trend is real; manganese levels were approximately twice as high in the second half of 1979 as they were in the first half. Reasons for this are unclear at the present time.

A comparison of heavy metal concentrations in the filtrate as performed by the Miami team with one performed by the Ames team revealed major differences in levels of cadmium, chromium, cobalt, copper, iron, manganese and zinc, with the levels reported by Ames approximately one order of magnitude lower than those reported by the Miami team. This difference is surprising since no appreciable differences have been found previously (Sengupta et al., 1979). Furthermore, the levels reported by Miami are similar to those reported earlier, while the Ames results have dropped an order of magnitude. Since the Ames results are based on only one sample, it is most probable that those levels are in error, owing to adsorption of the metal ions onto the glass walls of the sample container. In the future, samples sent to Ames for heavy metal analyses will be sent in plastic bottles; samples for organic analyses will continue to be

TABLE 4.3 Concentration of Heavy Metals (Mean) Range*

METAL	DIGESTOR SLURRY	FILTRATE	WASH WATER INPUT	WASH WATER
CADMIUM	(.16) 0.11-0.19	(.13) 0.06-0.18	(.07) 0.01-0.10	(0.11) 0.01-0.17
CALCIUM	(525) 360-705	(279) 201-410	(184) 160-219	(172) 160-205
CHROMIUM	(.81) 0.50-1.51	(.48) 0.27-0.83	(.17) 0.04-0.46	(.25) 0.04-0.81
COBALT	(0.14) 0.1-0.4	(.17) 0.1-0.4	(0.07) N.D.-0.2	(.14) N.D.-0.3
COPPER	(2.40) 1.47-3.66	(1.29) 0.90-1.69	(.49) 0.10-0.96	(.64) 0.10-1.31
IRON	(98) 75-118	(32) 26-38	(1.6) 1.0-2.1	(2.5) 1.6-10.1
MANAGANESE	(11.3) 7.1-14.7	(7.29) 6.56-8.56	(.07) 0.05-0.12	(.41) 0.10-5.1
NICKEL	(.48) 0.31-0.70	(.35) 0.25-0.71	(.14) 0.06-0.24	(.18) 0.09-0.29
SILVER	(0.06) 0.03-0.07	(0.03) N.D.-0.06	(N.D.)	(N.D.) N.D.-0.03
ZINC	(21) 13-29	(11) 6.1-27	(.55) 0.40-0.81	(.95) 0.56-10.1
BARIUM	(5.1) 3.0-7.2	(2.8) 1.5-4.2	(0.2) 0.1-0.3	(0.3) 0.1-1.2

* All data reported as mg/l.

N.D. = Not detectable.

sent in glass.

4.4 Spiking Study

Whenever a new type of sample is analyzed, the reliability of the method of analysis is open to question. Analytical procedures can be affected by sample constituents other than the one of interest. These "matrix effects" can either artificially raise or lower the the measurement of the parameter of interest. If free chlorine is present, for example, an attempt to measure nitrate ion by the cadmium-reduction method will yield results which are lower than actual nitrate levels. In atomic absorption analysis, on the other hand, certain metals will give higher readings in the presence of easily activated metals, such as sodium or potassium, than in their absence. These types of interferences also apply to other parameters of interest. Since the samples collected at the Pompano Beach facility are not well characterized, a study was undertaken to determine the reliability of the analytical methods used in determining parameters of interest. It was the aim of this study to determine how much of a constituent actually present was "recovered" by the method of analysis used for that parameter.

Two different types of studies can be performed in order to determine how much a given technique is susceptible to matrix effects in the samples. The first of these calls for the analysis of a synthetic sample. This type of study can be performed only if the complete composition of the sample is known, since it requires synthesizing an artificial sample from reagent grade chemicals. This type of study is not possible at present due to the complex nature of the samples.

The second type of study requires the addition of known amounts of the parameter of interest (called "spikes") to actual samples. The

resulting mixture is then analyzed in the usual manner (see Sec. 4.2 above). This type of study is similar to one used by De Walle et al. (1979) in comparing the results of analyses of landfill leachate performed by various laboratories.

4.4.1 Method

In this study, process filtrate was spiked in amounts varying from zero to approximately 1.5 times the amount of the chemical normally present. In order to facilitate this, the concentration in the spiking solution was usually kept at about 50 times the amount normally present in filtrate, with the volume of spike varying from 0 through 1, 2 and 3 ml per 100 ml of filtrate. In some cases, however, other volumes and concentrations were used. Furthermore, an appropriate amount of distilled water was added to keep the final volume constant. All additions were performed prior to any pretreatment steps. The spiked samples were then analyzed by the methods normally used. Most of the spiked samples were analyzed in duplicate. As an example, the volumes of filtrate, spiking solution, and water used in the Ammonia spike are listed in Table 4.4.

4.4.2 Analysis of Data

Data generated by these analyses can be examined in a variety of ways. The slope, intercept, and correlation coefficient of the least-squares straight line can be calculated for concentration found in the spiked sample vs amount of spike added. The intercept value represents the most people (based on all the data) value for the unspiked filtrate sample. The correlation coefficient indicates whether the least-square line is a statistically proper description of the data. The slope indicates the recovery of the method. These results, along with the theoretical 100% recovery line, are presented in Figures 4.25 through 4.44. The

TABLE 4.4 SAMPLE CALCULATION - SUBTRACTION OF SPIKE

VOLUME FOR MIXTURE (ml)			CONCENTRATION OF AMMONIA (mg/ℓ)		
Filtrate	Spike*	Water	Found in Mixture	Spike**	Calculated for Filtrate ***
100	0	50	91.1	0	136.7
			107.9	0	161.9
100	10	40	126.4	42.2	126.3
			123.4	42.2	121.8
100	20	30	167.2	84.4	124.2
			166.6	84.4	123.3
100	30	20	203.1	126.6	114.8
			204.3	126.6	116.6
MEAN					128.2
§ Absolute Standard Deviation					15.1
§§ Absolute Standard Error					5.4

* Spiking Solution: 633 mg/l

** Conc. from Spike (ml/l) = $\frac{(633 \text{ mg/l})(\text{ml of Spike})}{(150 \text{ ml})}$

*** Conc. in Filtrate (mg/l) = $\frac{(\text{Conc. in Mixture} - \text{Conc. for Spike})(150 \text{ ml})}{(100 \text{ ml})}$

§ Absolute Standard Deviation = $\sqrt{\frac{\text{Sum of all (a Value} - \text{Mean Value)}^2}{\text{Number of Values} - 1}}$

§§ Absolute Standard Error = $\frac{\text{Absolute Standard Deviation}}{\sqrt{(\text{Number of Values})}}$

Relative Standard Deviation = $15.1/128.2=0.118$ or 11.8%

Relative Standard Error = $5.4/128.2=0.042$ or 4.2%

FIG.4.25 Ammonia Spike with Least Squares Line; $r=0.9899$
Recovery=84.1%.

FIG.4.26 Kjeldahl Nitrogen Spike with Least Squares Line $r=.9750$
Recovery=510%.

FIG.4.27 Nitrite Nitrogen Spike with Least Squares Line $r=.9999$
Recovery=949%.

FIG.4.28 Nitrate Nitrogen Spike with Least Square Line $r=.9983$
Recovery=282%.

FIG. 4.29 Total Phosphorus Spike with Least Squares Line $r=.9791$
Recovery=158%.

FIG. 4.30 Chloride Spike with the Least Squares Line $r=.9921$
Recovery=104%.

FIG.4.31 COD Spike with Least Squares Line $r=.9937$
Recovery=122%.

FIG.4.32 TOC Spike with the Least Squares Line $r=.9719$
Recovery=65.9%.

FIG.4.33 Sulfide Spike with Least Squares Line $r=.9618$
Recovery=80.0%.

FIG. 4.34 Bacterial Spike with the Least Squares Line. $r=1.000$
Recovery=111%.

FIG.4.35 Zinc Spike with the Least Squares Line. $r=.9959$
Recovery=87.4%.

FIG. 4.36 Copper Spike with Least Squares Line, $r=.9849$
Recovery=129%.

FIG.4.37 Chromium Spike, with Least Squares Line, $r=0.9833$
Recovery=114%.

FIG.4.38 Cobalt Spike with Least Squares Line, $r=.9863$, Recovery=154%.

FIG.4.39 Cadmium Spike with Least Squares Line $r=.9673$, Recovery=160%.

FIG. 4.40 Manganese Spike with Least Squares Line, $r=.9988$.
Recovery=85.1%.

FIG.4.41 Nickel Spike with the Least Squares Line, $r=.9918$.
Recovery=127%.

FIG. 4.42 Calcium Spike with Least Squares Line, $r=.9861$
Recovery=174%.

FIG. 4.43 Iron Spike with Least Squares Line, $r=.9966$, Recovery=86.0%.

FIG. 4.44 Silver Spike Observed Behaviour is Probably Due to Precipitation of Excess Silver with Chloride.

percent recovery is calculated by dividing the least-squares slope by the theoretical 100% slope, and expressing the result as a percent. The relative recovery for various analyses found in this study is compared with those values found by De Walle et al. (1979) in Table 4.5.

In the case of ammonia, for example, filtrate, a spiking solution of 633 mg ammonia-nitrogen/l, and water were mixed as reported in Table 4.4. Each mixture was analyzed in duplicate; the results are also listed in Table 4.4 and plotted in Figure 4.25, along with the least-squares line. In addition, the theoretical recovery line is also plotted, with an intercept equal to that of the least squares line, and a slope calculated by dividing the fifth column of Table 4.4 by the second column. The slope of the least-squares line divided by that of the 100% recovery line is the relative recovery, expressed as a percent.

In all cases except for silver the correlation coefficient indicates that the least-squares line is a statistically valid description of the data. In the case of silver, (Fig. 4.44), however, the concentration found reaches an asymptote at 0.11 mg/l. This is probably due to precipitation by chloride. This precipitation, however, is not likely to affect results at the normal levels of 0.05-0.06 mg/l found in filtrate.

There is another technique to analyze the data. If it is assumed that all of the spike that was added to the filtrate sample was measured in the resulting mixed sample, then subtracting the amount of the chemical added by the spike from the amount found in the mixed sample for each replicate, results in an estimate of the concentration for the original unspiked sample. The mean, standard derivation and standard error for all replicates of each analysis can then be calculated. These are

TABLE 4.5 RESULTS OF RELATIVE RECOVERIES

PARAMETER	FOUND IN THIS STUDY ON FILTRATE (%)	FOUND BY DE WALLE ET AL (1979) ON LEACHATE (%)
Kjeldahl Nitrogen	510	-
Ammonia Nitrogen	84.1	245
Nitrite Nitrogen	949	-
Nitrate Nitrogen	282	-126
Total Phosphorus	150	-31.5
Chloride	104	172
COD	122	32.9
TOC	65.9	137
Sulfide	80	-
Zinc	87.4	11.7
Calcium	174	8.7
Iron	86	-8.4
Manganese	85.1	-
Nickel	127	96.7
Cobalt	154	-
Cadmium	160	314
Copper	129	14.3
Chromium	114	25.5

listed, both as absolute and relative values, in Table 4.6. Relative values are calculated by dividing the absolute by the mean, and are expressed as a percent. A sample calculation for ammonia-nitrogen is performed in Table 4.4. These calculations, as well as the concentration found directly and that calculated from the intercept of the least-squares line are listed in Table 4.6. The values have been adjusted to reflect concentration in original filtrate.

4.4.3. Discussion and Conclusion

There appear to be few similarities between the relative recoveries found in this study and those reported by De Walle et al. (1979) for landfill leachate (Table 4.5). Relative recoveries in this study ranged from 65.9% (TOC) to 949% (Nitrite-nitrogen). De Walle et al. (1979) reported values between -138% (lead) and 328% (potassium). In no case were negative recoveries found. This is perhaps due to the fact that De Walle et al. (1979) added all spikes to a single solution, whereas each test was conducted on separately spiked samples in this study. Those parameters whose relative recoveries are in excess of 100% will be rechecked to make sure that errors in and contamination of the spiking solutions were not a problem.

While the recovery calculations elucidate the accuracy of the analytical methods, the standard deviations reflect the precision of the work. In general, the results are excellent. The relative standard deviations (or coefficients of variation) are on the order of 15% for most of the parameters analyzed (Table 4.6). This is quite reasonable and in good agreement with those values found in Standard Methods (14th ed.). De Walle et al. (1979) found coefficients of variation ranging between 32% for COD to 210% for

TABLE 4.6 CONCENTRATION IN UNSPIKED SAMPLE

TEST	FOUND DIRECTLY*	INTERCEPT OF LEAST-SQUARES STRAIGHT LINE*	CALCULATION BY SUBRATION OF SPIKE				
			MEAN*	STANDARD DEVIATION		STANDARD ERROR	
				ABSOLUTE*	RELATIVE	ABSOLUTE*	RELATIVE
Kjeldahl Nitrogen	180.2	180.1	197.4	14.3	7.23%	5.04	2.56%
Ammonia	149.2	143.3	128.15	15.1	11.8%	5.35	4.2%
Total Phosphorus	89.8	95.5	115.1	17.24	15.0%	8.62	7.5%
Chloride	239	251	190.4	49.5	26%	17.5	9.1%
COD	5640	5210	6030	820	13.6%	335	5.6%
Nitrite	0.577	0.576	0.705	0.109	15.5%	0.039	5.5%
Nitrate	9.92	9.78	12.21	1.95	15.9%	0.688	5.6%
TOC	62.2	57.6	43.1	15.2	35.2%	5.7	13.3%
Zn	6.8	6.5	5.52	0.88	16.1%	0.31	5.7%
Ca	402	393	481	76	15.7%	27	5.6%
Fe	19.4	19.9	16.8	2.8	16.4%	0.97	5.8%
Mn	1.75	1.79	1.52	0.22	14.5%	0.78	5.1%
Ni	0.23	0.22	0.26	0.037	14.2%	0.013	5.0%
Co	0.14	0.15	0.19	0.036	18.6%	0.013	6.5%
Cd	0.08	0.055	0.10	0.044	43.7%	0.015	15.5%
Cu	0.70	0.78	0.93	0.15	16%	0.05	6%
Cr	0.20	0.24	0.28	0.06	21.7%	0.02	7.7%
S ⁻²	0.64	0.602	0.56	0.05	9.8%	0.03	5.6%

cadmium. In general, the levels found here are much lower than those reported by them. This is in keeping with their finding that differences between laboratories are greater than differences within a laboratory. While they note that their data indicate "that the parameters such as sulfate and nitrate are most difficult to determine precisely," in this study, the largest relative standard deviation was found for cadmium (44%), with nitrate at 15.9%.

It can be concluded that the results indicate relatively good precision in the analytical and recovery techniques used. The accuracy, however, is much more variable. Further checks on the large recoveries, as noted above, are necessary before any reliable conclusion can be drawn about the accuracy.

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V. TRACE ANALYSIS

5.1 Progress

The digestors at the Refcom Facility at Pompano Beach are not presently in a stable operation condition. Because of their unstable operation, the concentrations of contaminants in potential effluents are not representative of the levels likely to be encountered in normal operation. Routine monitoring of contaminant concentrations has, therefore, been deferred in favor of placing greater emphasis on characterization of constituents and improving analytical procedures.

Acidic Compounds

The Ames Laboratory developed ion exchange/gas chromatographic procedure has been used to determine acidic organic materials in process filtrate. This procedure consists of using a special ion exchange resin to isolate organic acids selectively from an aqueous sample. Isolated acids are esterified and separated and identified by gas chromatography/mass spectrometry. Compounds identified by this procedure in process filtrate are listed in the accompanying table.

Acids Detected in Pompano Beach Process Filtrate by the Ion Exchange/ Gas Chromatographic/Mass Spectrometric Procedure

---

Acetic	Benzeneacetic
Propionic	Benzenepropionic
Dimethylbutanoic (2)	Benzenebutanoic
4-Methyloctanoic	Tolyacetic (2)
Octanoic	(Dimethylbenzene) acetic
7-Methylnonanoic	3-Methylbenzoic

Acids Detected in Pompano Beach Process Filtrate by the Ion Exchange /
Gas Chromatographic / Mass Spectrometric Procedure

Tetramethylpentanoic	4-Methylbenzoic
3,6-Dimethyloctanoic	3,5-Dimethylbenzoic
2-Ethylbutanoic	2-Hydroxy, 3-Methylbenzoic
2,2-Dimethylbutanoic	2-Methyl, 3,4-Dihydroxybenzoic
Hexadecanoic	Butanedioc
3-Octenoic	2-Methoxy, 2-Pentendioc
	a. 1,4-Dicarbonxylic
Trimethyl-2-pentenonoic	4-Methylphthalic
2-Methylcyclohexanoic	Abiatic
4-Methylcyclohexanoic	Dibutylphosphoric or diisobutylphosphoric
4- (1,5-Dimethyl-3-Oxohexyl) -cyclohexanoic	2- (4-Chlorophenoxy) , 2-methylpropanoic*

*herbicide decomposition products

Concentration of Organic Compounds

An adsorption technique is being developed for concentrating organic materials from aqueous solutions such as process filtrate and simultaneously fractionating the concentrated materials on the basis of chemical functionality. The procedure makes use of commercially available, disposable adsorption columns loaded with silica, ODS bonded to silica or magnesium silicate. Depending on the packing material different organic materials are accumulated on these columns from aqueous solution. Retained materials are eluted sequentially with solvents of increasing polarity. Thus far,

this procedure has proven to be applicable to the recovery of most phthalate esters and PAHs from aqueous solutions. The potential advantages of this technique include greater convenience than fractionation procedures based on solvent extraction and less sample handling which reduces the potential for constituent losses.

Fractionation of Organic Materials by HPLC

Capabilities for fractionating complex organic mixtures have been improved by the adoption of normal phase, high performance liquid chromatographic procedures. The procedures basically consist of separating aliquots of isolated organic materials on a semi-preparatory scale NH_2 or Diol HPLC column using a gradient from a non-polar solvent such as hexane to a polar solvent such as methylene chloride. Alkanes are eluted first followed by aromatic compounds of increasing numbers of fused rings. Polar organic compounds are eluted last. This technique has been successfully applied to organic materials isolated from process filtrate and filtercake, as well as to organic materials from synthetic fuels.

Isolation of Organic Materials from Particulates

Particulates formed during the combustion of organic fuels including digester gas contain absorbed organic compounds. A large body of information exists describing partially successful procedures for isolating organic materials from particulates. In preparation for work aimed at characterizing organic materials absorbed on particulates in digester gas or formed during the combustion of digester gas, a new "brute force" technique is being developed for improving the recovery of organic materials from particulates. This procedure involves the treatment of particulates with hydrofluoric acid before extraction. The rationale for

this treatment is that isolation difficulties are partially caused because particulates contain alumina and silica adsorbents. The alumina can be deactivated and the silica dissolved by HF. Preliminary studies indicate that PAHs can be recovered from bag ash to a greater extent after HF treatment. Preliminary studies also indicate that the HF treatment leads to the recovery of a large amount of non-gas chromatographable material that is not recovered to any appreciable extent without use of HF. Because these compounds have not been characterized, there is a possibility they may be impurities from the HF or products of a reaction involving HF, but they could also be a previously unidentified major constituent of stack particulates.

5.2 Status

Future work will continue to be directed toward characterizing constituents of potential effluents from the Pompano Beach facility and toward improving analytical methods for determining those constituents. In the near future samples from the plant and particulates isolated from the digester gas will be sent to Ames for component characterization.

VI. LEACHING

6.1 Introduction

Prediction of pollutant migration patterns through soil and ground water aquifer requires a thorough understanding of the various mechanisms governing the behaviour of the pollutant media and media through which it moves. The interaction of the pollutant species with the matrix medium is a strong function of certain pertinent properties of the pollutant and matrix medium such as porosity, pH, initial concentration of the pollutant species, cation exchange capacity and organic content of the matrix medium and initial concentration of pollutant species & pH of the pollutant medium. As such the prediction techniques are site specific and have to be determined by direct experimentation with the particular pollutant and matrix media.

The first half of the first year was spent in defining the guidelines to be followed for achieving the required goals. Literature survey was carried out to understand the direction of work undertaken by other researchers in this area.

In the work carried out by U.S. Army engineers at the Environmental Effect Laboratory (5) the attenuation properties of soil under a landfill was verified by actually measuring the extent of pollution in the groundwater system.

Metry (7) characterized the mechanisms in a soil leachate system by laboratory simulation of a landfill in a lysimeter. Holland (8) carried out column studies to understand the mechanisms which play an important role in the interaction between a soil leachate systems.

Griffir (9) determined the capacity of different soils for removing

heavy metals by performing batch studies and then fitting Langmuir isotherms to the results. This survey helped in defining our areas of interest and the guide line set forth were

- a) Characterization of the matrix media through which the pollutant migrates.
- b) Characterization of the pollutant media.
- c) Characterization of the physical, chemical and biological phenomena dictating the interaction between the pollutant and matrix media.

In the second half of the first year, the physical, chemical and biological processes were identified and experimental procedures were formulated to determine the parameters necessary to express these phenomena mathematically. Batch experiments were designed to eliminate the effects of physical processes such as convection and diffusion and provide information solely on chemical adsorption and/or precipitation.

The first set of batch experiments were carried out with four different types of commercial soils. The soils were composed from commercially available components. These studies were carried out to obtain better understanding of the differences between sandy and clayey soils. They also helped in improving and optimising the experimental techniques. To cover a wider spectrum of soils the experiments were performed under three different pH values. The batch experiments with the site specific soils (four types: (i) Hallandale fine sand (ii) Plantation muck top layer (iii) Plantation middle layer (iv) Plantation muck bottom layer) were carried out for the pH level of 6.8, which is the natural hydrogen ion concentration (pH) in the filtrate.

This half was also utilized in the characterization of the pollutant media. The characteristic pollutant media in these experimental studies is in fact a composite filtrate from the plant. The composite filtrate was obtained by mixing portions of the filtrate collected from the plant over a period of several months between February and May 1979. Owing to logistic problems of storage under refrigeration, there was insufficient characteristic leachate left over to carry out experiments this year. As such new composite filtrate was prepared. This change does not really affect the results as the ultimate values are expressed in a non-dimensional form using the characteristic leachate concentration as the reference quantity.

During the first half of this year, progress in this area has been as follows:

- (i) Characterization of the pollutant transport media/matrix media.
- (ii) Batch experiments for the four Pompano Beach soils at pH 4.5 (unbuffered).
- (iii) Batch column studies at neutral pH (unbuffered) for Hallandale fine sand and plantation muck bottom layer.

6.2 Soil Characterization

To characterize the soil, the following experiments were performed.

- (i) Organic content of soil.
- (ii) pH of Soil.
- (iii) Initial concentration of metallic species in soil.
- (iv) Soil cation exchange capacity (C.E.C.)

6.2.1 Organic Content of Soil

The organic content of the four site specific soils were found by loss of ignition method. A known weight of sundried soil was ashed

in a muffle furnace at 550°C to constant weight. The loss of weight due to ashing gave the organic content of the soil. The results are tabulated in Table 6.1.

SOIL	ORGANIC CONTENT (g/g)
Hallandale fine sand	14.5
Plantation muck bottom layer.	27.9
Plantation muck middle layer.	670.7
Plantation muck top layer	705.2

Table 6.1

6.2.2 pH of the Soils

Each kind of soil was saturated with carbon dioxide free distilled water. After 30 minutes, the pH of the soil water paste was measured with a digital pH meter. The average of two experimental results are shown below.

SOIL	AVERAGE pH
Hallandale fine sand	8.20
Plantation muck bottom layer.	7.30
Plantation muck middle layer.	7.20
Plantation muck top layer	7.10

Table 6.2

All the soils are basic in nature. This is expected as Florida soil contains a high percentage of limestone.

6.2.3 Initial Concentration of Metallic Species in Soil

The total concentration of the various metal species of interest in soil was determined by a batch extraction process. The same soil was extracted several times until the extract showed negligible amounts of the metal.

Ten grams of soil was shaken with 100 ml of 7.5 N nitric acid for 24 hours. The bottles were allowed to sit for 30 min and the supernatant poured out. Another 50 ml of 7.5 N nitric acid was added to the residue and the bottle shaken again.

The supernatant was dried on a steam table heated in an oven at 100°C and finally ashed in a muffle furnace at 500°C for 4 to 6 hours. The ashed residue was dissolved in 25 ml concentrated nitric acid, filtered through Wattman No.3 filter paper and the filtrate brought to 100 ml. The solution was analyzed on an Atomic Absorption spectrometer for the eleven metals of interest. The process of shaking and analyzing the supernatant was carried out until it showed negligible amounts of all the metals. The concentration of a particular metal species in the soil was found by multiplying the reading of each extraction with the volume of the extract and dividing the sum by the weight of the soil.

The results are tabulated in Table 6.3.

SOIL	METAL CONCENTRATION $\mu\text{eq/kg}$									
	Cu	Zn	Fe	Mn	Ni	Cd	Cr	Ca	Ag	Co
Hallandale Fine Sand	.031	.192	5.52	.185	.139	.056	.271	4.72	0.0	.006
Plantation Muck Bottom Layer	.056	.177	16.67	.208	.204	.055	.300	46.65	0.0	.067
Plantation Muck Middle Layer	.173	.327	1021.7	1.36	.422	.088	1.19	1185.5	.005	.37
Plantation Muck Top Layer	.173	.293	223.8	.442	.629	.058	.819	893.5	0.0	.203

Table 6.3 Initial Concentration of Cations in the Soil.

For all the four soils, the concentration of calcium is highest. Presence of limestone and other calcium bearing rocks account for this. Besides calcium, the level of iron is also very high. Since the soil is basic, iron is bound very strongly to the soil sites in the form of iron hydroxide. In this form it is unsuitable for plant uptake. Moreover alkaline pH decreases the mobility of the element, Allaway (4). This attributes to the high concentration level of the metal. Concentrations of all the cations in plantation muck middle and top layer are much higher than that in plantation muck bottom layer and Hallandale fine sand. Both of these layers have very high clay content. Clayey soil compared to sandy soils are known to have very high cation concentrations, reference (5). Figs. 6.1, 6.5, 6.6 and 6.7 indicate selective desorption of the cations copper, nickel, cadmium and chromium for Hallandale fine sand. These cations are extracted only after the higher concentration. Cations like zinc, iron and calcium have desorpted out.

Plantation muck bottom layer, which is basically sand, behaves very similarly to Hallandale fine sand. Figs. 6.2, 6.5, 6.6 and 6.7 indicate selective desorption of cations, zinc, nickel, cadmium and chromium for this soil. These metals are extracted after the sites containing the more mobile cations copper, iron and calcium have been replaced by hydrogen ions.

Plantation muck middle and top layers behave very similarly. It can be seen from Fig. 6.1 to 6.10 that none of the cations show selective desorption. This may be because of the high concentration levels of all the cations.

6.2.4 Determination of Soil Cation Exchange Capacity

A two step procedure for determination of soil C.E.C. was used.

reference (1).

- 1) The cation-exchange sites of the soil (4-5 g) were saturated by equilibrating it with four successive 33 ml aliquots of pH 8.2, 60% ethanol solution of 0.4 N NaOAc - 0.1N NaCl. Equilibration were achieved by shaking the soil solution mixture for 5 min. The exhausted solution were decanted after centrifugation.
- 2) The saturated samples were extracted with three 33 ml aliquot of 1.0 N, MgNO_3 solution at pH 7. Both sodium (Na_t) and chloride (Cl_t) were subsequently determined in both solutions and in the combined extract. Chloride was determined so that the soluble sodium (Na_{sol}) from the excess saturating solution carried over from the saturation step to the extraction step may be deducted from the total sodium to obtain exchangeable sodium (Na_{exch}).

$$\text{Thus, CEC} = (\text{Na}_t - \text{Na}_{\text{sol}}) = \text{Na}_t - [\text{Cl}_t (\text{NaCl})_{\text{saturating solution}}],$$

where (Na/Cl) saturating solution is the ratio of Na to Cl in the saturating solution.

SOIL	C.E.C. $\frac{\mu\text{eq}}{\text{g}}$
Hallandale Fine Sand	1.13
P.M. Top Layer	4.53
P.M. Middle Layer	4.09
P.M. Bottom Layer	1.58

Table 6.4

It can be seen that the C.E.C. for the Hallandale fine sand is about the same value as that for plantation muck bottom layer, which is mainly sand. The C.E.C.'s for the plantation muck top and middle layers are very similar as both are mainly clay.

6.3 Batch Experiments

Batch experiments for all the four Pompano Beach soils at pH 4.5 were performed. The experiment with plantation muck middle layer at pH 6.8 was repeated since the behavior to iron and calcium could not be explained.

6.3.1 Experimental Procedure

- (i) 0.5 g, 1 g, 2 g, 5 g and 10 g of soil was mixed with 100 ml of the characteristic filtrate in five separate 250 ml bottles. The pH of the filtrate was either kept at its natural level of 6.8 or initially adjusted to the required level of 4.5 or 9.5 by addition of 15 N concentrated nitric acid.
- (ii) The bottles were shaken for the length of the equilibrium time, as determined by the equilibrium rate studies (6).
- (iii) The contents of the bottle were filtered through 2 micrometer millipore filter paper in an ultrafiltration unit.
- (iv) The filtrate was evaporated on a steam table, dried in an oven at 100°F and finally ashed in a muffle furnace at 1000°F.
- (v) The residue was dissolved in 25 ml of concentrated nitric acid and filtrated through Whatman 3 paper. The volume of the filtrate was brought upto 100 ml with distilled water.
- (vi) The solution was analyzed on an atomic absorption spectrometer for

	COPPER	ZINC	IRON	MANGANESE	NICKEL	CADMIUM	CHROMIUM	CALCIUM	COBALT
<u>HALLANDALE FINE SAND pH = 6.8</u>									
K ₁	-1.462	-.485	-.080	-.554	-4.336	-17.976	-10.824	-.003	-6.220
K ₂	-0.0001	-0.0001	-.001	-0.0004	-.002	-.002	-.001	-.458	-.027
<u>PLANTATION MUCK TOP LAYER pH = -6.8</u>									
K ₁	-1.682	-.509	-.063	-.586	-5.361	-6.657	-3.176	-.003	C=0
K ₂	-0.0004	-.001	-.012	-.001	-0.0005	-.003	-.001	-.168	C=0
<u>PLANTATION MUCK MIDDLE LAYER pH = -6.8</u>									
K ₁	-1.507	-.502	-.098	-1.05	-5.107	-4.862	-7.360	-.003	-118.54
K ₂	-0.0003	-.001	-.006	-.041	-.001	-.004	-.001	-.215	.001
<u>PLANTATION MUCK BOTTOM LAYER pH = 6.8</u>									
K ₁	-1.682	-.487	-.084	-.581	-4.967	-4.714	-12.34	-.002	2.491
K ₂	-.001	-0.0003	-.003	-0.0003	-.001	-.006	-.001	-.36	.054

TABLE 6.5 Langmuir Coefficients.

the eleven heavy metals.

6.3.2 Results

The Langmuir isotherms are shown in Figs. 6.11 through 6.19. The Langmuir constants were obtained by least square fit from the plot of $1/(X/M)$ vs $1/C$.

where

X/M = amount of cations adsorbed per unit mass of the soil.

C = concentration of the cation in the liquid at equilibrium with the soil.

The batch experiment with Hallandale fine sand at pH 4.5 was performed by initially adjusting the pH of the composite filtrate to 4.5 by addition of concentrated nitric acid. No buffer solution was added to hold the pH at this level. During the process of shaking the pH of the solution rose because of the basic nature of the soil. (The pH of the solution was measured after the mixture had been shaken). Due to this change in pH of the mixture, the results obtained do not show a particular trend. As such Langmuir constants were not determined for these values since they would not have much chemical significance.

The coefficients for all the four soils at pH 6.8 have been modified to take into consideration the fact that a large amount of the metallic cations which do not react with the soil are retained by the membrane during filtration. Since the composite filtrate is very inhomogenous containing large solid particles, these particles are removed during the process of filtration. They carry with them the unreacted cations and it apparently seems as if these cations have been adsorbed by the soil. To modify the results, the composite filtrate with some amount of a particular

soil was ultrafiltered and the filtrate was analyzed. The difference between the initial concentration of a particular cation and the concentration in the filtrate was added to each concentration value obtained previously. The modified concentration values were used to calculate the new constants.

6.4 Batch Column Experiments

The migration of chemical substances through soil is usually studied in the laboratory using columns packed with soil. Continuously leached column experiments provide information as to the ability of a soil to remove chemical substances. However, an important limitation of this method is the time and effort required to obtain and analyze a sufficient number of samples to make predictions of migration rates. This usually takes months and may even take years. However, batch extraction of the soil with leachate can provide much of the same information, Houle and Long (3). These experiments are rapid compared to continuous column experiments. If the volume of liquid used in a batch experiment can be related to the same volume of liquid passing through the soil over a period of time, sequential batch extractions can be the basis for an accelerated testing of flow of leachate through soil.

6.4.1 Experimental Procedure

- (i) 1000 g of soil was mixed with 1000 ml of composite filtrate in a bottle. The bottle was shaken for the length of the equilibrium time (48 hours for Hallandale fine sand and plantation muck bottom layer N.S.; 72 hours for plantation muck middle and top layers).
- (ii) The contents of the bottle was filtered through 2 micrometer millipore filter paper in an pressure ultrafiltration unit.
- (iii) 100 ml of the filtrate was separated for analysis.
- (iv) The remaining filtrate was mixed with new soil such that the ratio

TABLE 6.6 Flow Chart for Batch Column Experiment.

of the volume of the filtrate to the weight of the soil was 10:1.

- (v) The soil obtained as residue from the filtration process was mixed with new filtrate in the same ratio.
- (vi) Steps (i) to (ii) were repeated for each bottle.
- (vii) This process was continued till twenty four different samples were obtained.
- (viii) All the samples were stored at pH below 2.0 and analyzed as per steps (iv) - (vi) of the batch experiments.

The flow chart for the experiment is shown in Table 6.6.

For this purpose the composite mixture of cations and anions will be referred to as the composite mixture.

The notations used are:

L_{IJ} = Filtrate obtained by filtering a mixture of soil, which has already been challenged I times by composite mixture, and composite mixture which has challenged soil (J-1) times.

S_{IJ} = Residue obtained by filtering a mixture of soil, which has been challenged (I-1) times by the composite mixture and composite mixture, which has challenged soil (J-1) times.

A_{IJ} = 100 ml of aliquot for analysis, obtained on filtration of the contents of bottle B_{IJ}

L_{11} through L_{16} represent the flow of the composite mixture through six different soil layers in a continuous column experiment. A_{11} through A_{16} represent samples taken out at the interface of each layer as a certain volume of the composite mixture flow down the column. L_{21} through L_{26} represent flow of fresh composite mixture through the same six soil layer which have already been challenged with composite mixture previously.

6.4.2 Interrelation between Batch Column and Continuous Column

In a continuous column experiment, sample ports are located at different heights of the column and samples of a particular volume are collected at certain intervals of time. In a batch column experiment, a certain weight of soil is shaken with a certain volume of the leachate for the length of equilibrium time. The same soil is reshaken with new or already used leachate, and the same leachate is reshaken with new or already used soil. Correlation between the two experiments essentially consists of interrelating the weight of the soil and volume of the leachate used in the batch column experiment with the location of the ports and time interval between each sample collection of the continuous column experiment.

Let X = weight of the soil.

V = volume of composite filtrate.

A = area of the column for continuous column experiments.

L = length of each soil layer at which the sampling points.

are located in the column.

ρ_b = bulk density of the soil.

W = pore water velocity.

The time taken by the composite filtrate to travel length " L " of the column = $\frac{L}{W}$

The time needed to collect volume " V " of the composite filtrate at the first sampling point = $\frac{V}{W A}$

Length " L " of the column for it to contain weight " X " of soil of bulk

density $\rho_b = \frac{X}{\rho_b A}$

Thus if volume "V" of composite filtrate is mixed with weight "X" of soil, the composition of the filtrate after it has been shaken is equivalent to collecting the sample at the ports of the continuous column over a period of time equal to $\frac{V}{W A}$.

6.4.3 Results

The plots of variation of concentration with depth for the nine cations, nitrite-nitrogen, nitrate-nitrogen, ammonia-nitrogen, total organic nitrogen-nitrogen and phosphate-phosphorus in Hallardale fine sand and plantation muck bottom layer are shown in Figs. 6.25 through 6.35.

These plots represent the variation in concentration of the various species of interest in a particular volume of the filtrate as it flows through different soil layers in a column.

Comparing Figs. 6.25 and 6.28, it is seen that cations copper, zinc, managanese and chromium behave very similarly for both the soils. This is expected as the difference between the two soils is their organic content. Zinc and manganese show a gradual decrease with depth. The first extraction indicates a drastic fall in the concentration of copper, zinc and manganese while concentration of chromium goes above its initial concentration level. This trend indicates that sites occupied by chromium in the soil are first replaced by copper, zinc and managanese. The next extraction shows a rise in the concentration of copper while that of chromium falls and zinc and managanese remain low. This indicates copper being replaced by the other three cations.

Fig. 6.29 indicates that nickel, cadmium and cobalt get gradually

adsorbed with depth for plantation muck bottom layer.

For Hallandale fine sand the trend is very erratic indicating both adsorption and desorption. This is seen in Fig. 6.26.

6.5 Tasks for the Second Half

The plans for the next half are:

- (a) Completion of batch studies at neutral pH (unbuffered) for plantation muck top, middle and bottom layer for the anions.
- (b) Completion of batch column studies at neutral pH (unbuffered) for plantation muck top and bottom layer for the cations.
- (c) Starting the column studies.

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FIG. 6.1

FIG. 6.2

FIG. 6.3

FIG. 6.4

EXTRACTION FOR NICKEL

- (1) PLANTATION MUCK TOP LAYER □
 (2) PLANTATION MUCK MIDDLE LAYER ☆
 (3) PLANTATION MUCK BOTTOM LAYER △
 (4) HALLANDALE FINE SAND *
- TIME BETWEEN EACH EXTRACTION - 24 HRS.
 EXTRACTION MEDIUM: 7.5(N) NITRIC ACID

FIG. 6.5

FIG. 6.6

FIG. 6.7

FIG. 6.8

FIG. 6.9

FIG. 6.10

FIG. 6.11

FIG. 6.12

FIG. 6.13

ADSORPTION ISOTHERM FOR MANGANESE

(1) PLANTATION MUCK TOP LAYER $\square$

(2) PLANTATION MUCK MIDDLE LAYER $\diamond$

(3) PLANTATION MUCK BOTTOM LAYER $\triangle$

(4) HALLANDALE FINE SAND $\times$

EQUILIBRATION TIME (1)72(2)72(3)48(4)48HRS.

FILTRATE P.H=6.9

FIG. 6.14

FIG. 6.15

FIG. 6.16

FIG. 6.17

ADSORPTION ISOTHERM FOR COBALT

(1) PLANTATION MUCK TOP LAYER $\square$

(2) PLANTATION MUCK MIDDLE LAYER $\star$

(3) PLANTATION MUCK BOTTOM LAYER $\triangle$

(4) HALLANDALE FINE SAND $\times$

EQUILIBRATION TIME (1) 72 (2) 72 (3) 48 (4) 48 HRS.
FILTRATE P.H=6.9

FIG. 6.18

FIG. 6.19

FIG. 6.20

FIG. 6.21

FIG . 6. 22

FIG. 6.23

FIG. 6.24

FIG, 6.25

FIG. 6.26

FIG. 6.27

FIG. 6.28

FIG. 6.29

FIG. 6. 30

FIG 6. 31

FIG. 6. 32

FIG. 6, 33

FIG. 6.34

FIG. 6. 35

VII. MODELLING

7.1 Introduction

In waste disposal operations, it is important to be able to predict pollutant migration in the soil. This predictive capability is important as the soil is the ultimate receptacle of the waste. Work in this area of pollutant migration includes references (1-7).

Fuller, 1977, (1-3) essentially uses the Lapidus-Amundson model, 1952, ref.(6). The problem with the Lapidus-Amundson model is that it apparently refers to point-wise property values of the phases. If one considers a point, P, and move this point all over the system, there would be regions where the point P is in the solid and other regions where it is in the fluid. In this case, the statement of point-wise property values presents a conceptual problem. However, a statement of volume averaged properties centered about a point, would not present a conceptual problem.

7.2 Summary

The approach to the problem advocated here is the volume averaging technique. This technique involves taking a suitable volume average of the microscopic equations as has been done by Wong, 1976, 1978, (8,9). In the next section, the volume averaged transport equations are written down for easy reference. These equations have been derived in the August 1979 Annual Report Sengupta, et al. 1979, (11).

The volume average transport equation apply to a single chemical species within a complex mixture. The equations are formulated in terms of Langmuir coefficients, which were experimentally found for a complex mixture, as described in the previous chapter. The Langmuir coefficients are then used in the equations which predict the migration of heavy

metal pollutants in a landfill.

7.3 Volume Averaged Transport Equation

The volume averaged transport equation for an element through saturated soil is

$$\phi \frac{\partial \gamma}{\partial t} + \text{div}(\phi C_a \vec{v}) - D \phi \text{div}(\nabla \gamma) + (1-\phi) \frac{K_1 K_2 \rho_s}{(1+K_1 \gamma)} \frac{\partial \gamma}{\partial t} = 0 \quad (7.3.1)$$

where C_a = mass concentration of component 'a'

ϕ = porosity

$\vec{v}$ = velocity vector

D = diffusivity

K_1, K_2 = Langmuir constants

ρ_s = bulk density of solid (soil)

γ = intrinsic average of component 'a' concentration

in the fluid

$$= \frac{1}{V_f} \int_{V_f} C_a dV$$

The complete derivation of the above equation is given in Sengupta, et al., 1979, (11). Suffice it to say that in the derivation, the Langmuir adsorption equation has been assumed i.e.,

$$\beta = \frac{K_1 K_2 \gamma}{1+K_1 \gamma}$$

where β = intrinsic average of component 'a' concentration in the solid

$$= \frac{1}{V_s} \int_{V_s} C_a dV$$

For low velocities, $\frac{E}{Re} \ll 1$ and viscous dissipation may be neglected.

Under such conditions, the two dimensional form of eqn.(7.3.1) is

$$\begin{aligned} & [\phi + (1-\phi) \frac{K_1 K_2 \rho_s}{(1+K_1 \gamma)^2}] \frac{\partial \gamma}{\partial t} + \phi (u \frac{\partial \gamma}{\partial x} + v \frac{\partial \gamma}{\partial y}) \\ & - D \phi (\frac{\partial^2 \gamma}{\partial x^2} + \frac{\partial^2 \gamma}{\partial y^2}) = 0 \end{aligned} \quad (7.3.2)$$

The one dimensional form of eqn. (7.3.1) is

$$\phi \frac{\partial \gamma}{\partial t} + \frac{Q}{A} \phi \frac{\partial \gamma}{\partial Z} - D \phi \frac{\partial^2 \gamma}{\partial Z^2} + (1-\phi) \frac{K_1 K_2 \rho_s}{(1+K_1 \gamma)^2} \frac{\partial \gamma}{\partial t} = 0 \quad (7.3.3)$$

7.4 Parametric Studies with the One Dimensional Model

The three independent variables in eqn. (7.3.3) are the averaged concentration γ , depth Z and time t . These three variables have been nondimensionalized with respect to three reference quantities.

γ_0 = initial concentration of the pollutant

$\frac{Q}{A}$ = pore water velocity

and L = total depth of the soil Layer

The nondimensional form of eqn. (7.3.3) is

$$\frac{\partial \gamma'}{\partial t'} + \frac{K_2'}{(1+K_1' \gamma')^2} \frac{\partial \gamma'}{\partial t'} + \frac{\partial \gamma'}{\partial Z'} - D' \frac{\partial^2 \gamma'}{\partial Z'^2} = 0 \quad (7.4.1)$$

where $K_1' = K_1 \gamma_0$

and $K_2' = \left(\frac{1-\phi}{\phi}\right) K_1 K_2 \rho_s$ are dimensionless Langmuir constants, and are a measure of the affinity of the chemical species to the solid phase

$$D' = \frac{AL/Q}{L^2/D}$$

$$= \frac{\text{Time for Convection}}{\text{Time for Diffusion}}$$

Thus D' is the ratio of time taken by the pollutant to convect through a particular distance to the time taken by the pollutant to diffuse through the same distance.

The initial condition used to solve eqn. (7.4.1) is that there is no pollutant in the soil initially, i.e., $\gamma'=0$ at $Z'>0$ at time $t=0$.

Table 7.1 1-D Parametric Studies

	D'	K_1'	K_2'	Steady State Time	$\gamma'(Z'=1)$ at Steady State
(i)	100	100	100	0.0243	0.99
(ii)	100	100	0.15	0.0195	0.99
(iii)	100	0.15	100	0.9760	0.99
(iv)	100	0.15	0.15	0.0114	0.99
(v)	0.15	100	100	2.7210	0.50
(vi)	0.15	0.15	100	115.55	0.50
(vii)	0.15	100	0.15	1.0306	0.50
(viii)	0.15	0.15	0.15	1.928	0.50

The boundary condition at the top of the soil layer ($Z'=0$) is $\gamma'=1$ ($\gamma=\gamma_0$) for all $t>0$. The other boundary condition at the soil aquifer is taken to be that whatever diffuses out of the bottom of the top-soil layer is collected away by the aquifer. A mass balance gives

$$D' \frac{\partial \gamma}{\partial Z'} + (V_a - \frac{Q}{A})\gamma' = 0 \text{ at } Z'=1, t'>0$$

7.4.1 Results

To obtain a better understanding of the different physical phenomena like convection, diffusion, chemical adsorption and/or precipitation which affect the movement of chemical specie through the soil, the non-dimensionalized form of the finite difference model representing the one dimensional pollutant equation was computed under eight different combinations of the three nondimensional groups.

The highest value of the nondimensional group was taken as 100.0 and the lowest value as 0.15. Before experimentally determined coefficients were found, this range was estimated to include physically determined coefficients. As a hind sight, the lower limit investigated should have been taken to be smaller than 0.15.

Parametric studies were performed with eqn. (7.4.1). Values of the parameters D' , K_1' and K_2' are listed in Table 7.1. The steady state time for each of the eight cases investigated are listed, and so are the values for $\gamma'(Z'=1)$ at steady state. Compared to the analytical steady state solutions, the numerical steady state solutions were good to $\pm 6\%$. Steady state is defined as a percentage concentration change of no more than a fixed amount everywhere within the domain, in a fixed time period.

The transient and steady state profiles for each of the eight cases investigated are also attached. Figures 7.1-8 correspond to cases (i) - (viii) in Table 7.1.

Figures 7.1-8 are plots of concentration of a particular cation, γ , with the dimensionless depth, Z/L . The transient profiles are concentration profiles at various times. As should be expected, there are only two steady state profiles for the 8 cases investigated, these correspond to $D'=100$ and $D'=0.15$. The steady state profiles for Figures 7.1-4 are identical, and those for Figures 7.5- 8 are the same.

The largest steady state time is 115.55 dimensionless units for case (vi) in Table 7.1. This corresponds to the case of least mobility. The shortest steady state time is 0.0114 dimensionless units for case (iv) in Table 7.1. This is the case of greatest mobility.

Case (iv) corresponds to a condition of convection dominating over diffusion and the overall low affinity of the pollutant to the solid phase ie. $\frac{K_2'}{(1+K_1'\gamma')^2} = \frac{0.15}{(1+0.15\gamma')^2}$ is small ($0 \leq \gamma' \leq 1$). Case (vi) corresponds to a condition of diffusion dominating over convection and the overall high affinity of the pollutant to the solid phase ie.

$$\frac{K_2'}{(1+K_1'\gamma')^2} = \frac{100}{(1+0.15\gamma')^2} \text{ is large } (0 \leq \gamma' \leq 1).$$

7.5 The Two Dimensional Model

The two dimensional model was studied as the next step towards developing a physical three dimensional model.

The nondimensional form of eqn. (7.3.2) is

$$\left[1 + \frac{K_2'}{(1+K_1'\gamma')^2} \frac{\partial \gamma'}{\partial t'} + (u' \frac{\partial \gamma'}{\partial x'} + v' \frac{\partial \gamma'}{\partial y'}) - D' \left(\frac{\partial^2 \gamma'}{\partial x'^2} + \frac{\partial^2 \gamma'}{\partial y'^2} \right) \right] = 0 \quad (7.5.1)$$

where $x' = \frac{x}{L}$, $y' = \frac{y}{L}$

Table 7.2 Boundary Conditions Used for the 2-D Model

(A)
(B)
(C)

$$u' = \frac{u}{u_{\text{ref}}} , \quad v' = \frac{v}{v_{\text{ref}}}$$

The initial condition used to solve eqn.(7.5.1) is that there is no pollutant in the soil initially ie. $\gamma'=0$ at $x'>0$, $y'>0$, $t'=0$.

The boundary conditions used are shown in Table 7.2. For all three cases shown, the pollutant enters the top surface i.e. at $y'=0$. For case (A), the flow is in the vertical direction, and the boundary condition at the bottom surface $y'=1$ is that whatever diffuses out is convected away by the underlying aquifer. For cases (B) and (C), the flow is in the horizontal direction, and the bottom surface is

$$\text{ie. } \frac{\partial \gamma'}{\partial y'} = 0$$

For all three cases, the sides (ie. $X'=0$, $X'=1$ for (A) and (B) and $x'=4$ for (C)), are considered to be so distant that there is no longer significant changes in the concentration of the pollutant.

7.5.1 Results

The boundary conditions used to solve eqn.(7.5.1) are as shown in the figure attached. The corresponding results showing the transient and steady state concentration contours are attached. The values of the parameters D' , K_1' , and K_2' are shown on the Figures 7.9-1.3 and have been chosen as a test case.

Figures 7.9 and 7.10 are the results for case (A) in Table 7.2. The concentration contours have been plotted for various times, and also for the steady state time. The boundary conditions dictate symmetrical solution about the median line parallel to the y-axis, and the computed solutions show that this is so.

Figure 7.11 and 7.12 are the results for case (B) in Table 7.2. The plots have been made for various times, and also for the steady state time. With a specified velocity field of constant magnitude in the x-direction, the plume is expected to be skewed. This skewing is apparent in the plots.

Figures 7.13 gives the results for case (C) in Table 7.2. The results are presented for two different times and also for the steady state time of $t=1.585$. The plume is skewed as in case (B) above. This is because the same specified velocity field has been used. The difference between case (B) and case (C) is that in case (C), the ratio of the length to breadth of the domain is 4, whereas the domain is square for case (B).

7.5.2 Experimentally Determined Coefficients

The 2-D model is also solved for boundary condition (C) shown in Table 7.2, but with experimentally determined values of K_1' and K_2' . It is assumed that the diffusion coefficient in the longitudinal direction (x-direction) is different from that in the transverse direction (y-direction). The values of the dimensionless coefficients used for Fig.7.14 are as follows:

$$D_1' = \frac{D_1}{U_r L_1} = 6.214 \times 10^{-2}$$

$$D_2' = \frac{D_2}{U_r L_2} = 1.0936 \times 10^{-1}$$

$$K_1' = K_1 \gamma_o = -1.31436 \times 10^{-1} \quad (K_1 = -3.651 \text{ } \mu\text{/mg})$$

$$K_2' = \left(\frac{1-\phi}{\phi}\right) K_1 K_2 \rho_s = 30.182 \quad (K_2 = -0.003 \text{ mg/g})$$

In evaluating the coefficients above, realistic values of velocity and porosity (which are applicable to an actual plant site) have been used. The values of K_1 , K_2 are for Hallandale fine sand and cadmium (as a typical heavy metal), obtained by experiments described in the chapter on leaching work. The domain looked at is .1 mile in length and 150 ft deep. It is assumed that the domain contains only Hallandale fine sand, a top soil.

Actually, the top soil may only be about 6 to 10 ft deep, below which is bedrock, mainly coral. The pollutant metal would be more mobile in the bedrock than in the top soil, so one should expect the computational results to show less pollutant mobility than the actual case. Less mobility manifests itself as less skewness in the pollutant plume as the flow field is defined as a constant velocity in one direction.

Figure 7.14 shows the pollutant plume at various times. Steady state is reached after 497 years, but as discussed, the plume in the physical case would be more skewed than that shown in the figure.

Figure 7.15 shows what happens to the plume in Fig. 7.14 if after steady state is reached, no more pollutant is added, instead the pollutant is washed away by a constant uniform flow of water. It can be seen that at the end of 989.8 years (i.e. about 492.8 years after pollution has been discontinued) the domain is almost completely free of pollutant.

7.6 The Three-Dimensional Model

Equation (7.3.1) as it stands is difficult to solve. A simplifying assumption is that velocities are low enough such that $\frac{E}{Re} \gg 1$, which means viscous dissipation terms may be neglected. In addition, it is assumed that there are small fluctuations of velocity in an averaging volume.

With the assumptions stated above, the nondimensional form of eqn. (7.3.1) may be written as

$$\begin{aligned} \left[1 + \frac{(1-\phi)}{\phi} \frac{K_2'}{(1+K_1'\gamma')} \right] \frac{\partial \gamma'}{\partial t} + (u' \frac{\partial \gamma'}{\partial x'} + v' \frac{\partial \gamma'}{\partial y'} + w' \frac{\partial \gamma'}{\partial z'}) \\ - D \left(\frac{\partial^2 \gamma'}{\partial x'^2} + \frac{\partial^2 \gamma'}{\partial y'^2} + \frac{\partial^2 \gamma'}{\partial z'^2} \right) = 0 \end{aligned} \quad (7.6.1)$$

where $x' = \frac{x}{L}$, $y' = \frac{y}{L}$, $z' = \frac{z}{L}$

TABLE 7.3 Boundary Conditions for the 3-D Model.

$$u' = \frac{u}{u_{\text{ref}}}, \quad v' = \frac{v}{v_{\text{ref}}}, \quad w' = \frac{w}{w_{\text{ref}}}$$

If the diffusion coefficient in the longitudinal direction is different from that in the y- and z-direction, eqn. (7.6.1) may be written as:

$$\begin{aligned} & \left[1 + \frac{(1-\phi)}{\phi} \frac{K_2'}{1+K_1'(\gamma')^2} \right] \frac{\partial \gamma'}{\partial t} + (u' \frac{\partial \gamma'}{\partial x'} + v' \frac{\partial \gamma'}{\partial y'} + w' \frac{\partial \gamma'}{\partial z'}) \sigma \\ & - (D_1' \frac{\partial^2 \gamma'}{\partial x'^2} + D_2' \frac{\partial^2 \gamma'}{\partial y'^2} + D_2' \frac{\partial^2 \gamma'}{\partial z'^2}) \sigma = 0 \end{aligned} \quad (7.6.2)$$

where $\sigma = \text{scaling factor} = \frac{L_1}{L_2}$, $D_1' = \frac{D_1}{u_r L_1}$, $D_2' = \frac{D_2}{u_r L_2}$

The initial condition used to solve eqns (7.6.1) and (7.6.2) is $\gamma'=0$, at $x'>0$, $y'>0$, $z'>0$, $t=0$ ie. there is no pollutant in the domain of interest initially.

7.6.1 Results

The domain investigated in Figs. 7.16-7.18 is 1 mile long x 150 ft wide x 150 ft deep. The experimental values used for K_1 and K_2 are for cadmium (as a typical metal) and Hallandale fine sand. It is assumed that the whole domain is made up of Hallandale fine sand. The values of the dimensionless coefficients used are

$$D_1' = 6.214 \times 10^{-2}$$

$$D_2' = 1.0936 \times 10^{-1}$$

$$K_1' = -1.3436 \times 10^{-1} \quad (K_1 = -3.651 \text{ L/mg})$$

$$K_2' = 30.182 \quad (K_2 = -0.003 \text{ mg/g})$$

The boundary conditions used for Figs. 7.16 and 7.17 are shown in Table 7.3. These conditions indicate that pollutant enters the region in the top surface. The bottom surface is impervious. The sides are

considered to be so distant that there is no larger significant changes in the concentration of the pollutant.

Figure 7.16 shows the pollutant plume in the 3-D domain after 6.171 years. The boundary condition at $Z'=0$ is $\gamma'=1.0$ for a 0.1 mile length in the center of the plane, and $\gamma'=0$ everywhere else. Because of the symmetrical boundary conditions, the profile is the same at $y'=0$ as it is for $y'=1.0$. Also, the pollutant plane is less skewed than it should be because it is assumed that the whole domain consists of top soil, instead of top soil and bedrock where the pollutant is much more mobile.

Figure 7.17 shows the pollutant plume at steady state after 9.503 years. Figure 7.18 shows what happens to the plume in Fig. 7.17 if after steady state is reached, no more pollutant is added, instead the pollutant is washed away by a constant uniform flow of water. Figure 7.18 shows the condition after 15.5 years i.e. about 6 years after pollution is discontinued).

In Figs. 7.19 and 7.20, the 3-D domain is the same as for Figs. 7.16-7.18, and the boundary conditions used are as shown in Table 7.3. The experimental coefficients used, K_1' and K_2' , are also the same. However, the values used for the dimensionless coefficients D_1' and D_2' are

$$D_1' = 6.214 \times 10^{-4}$$

$$D_2' = 1.09936 \times 10^{-3}$$

These values of D_1' and D_2' are two orders of magnitude lower than those used in the previous three figures. This has been done as

Freeze and Cherry, 1979, (10), discusses a discrepancy in the values of the diffusion coefficients, to as much as two orders of magnitude.

In Fig. 7.21, the 3-D domain is 1 mile long x 150 ft deep x 600 ft. wide. The coefficients used are the same as for Figs. 7.19 and 7.20. The figure shows the pollutant plume at steady state after 16.51 years.

Compared to the two dimensional model, the steady state time is stated for the three dimensional model of equal length and depth. This is as expected because for the same coefficients, grid-size and time increment, the three dimensional finite difference equation would converge faster than the equivalent two dimensional finite difference equation.

Steady state is defined here as a percentage concentration change of no more than a fixed amount (say 0.01%) everywhere within the domain, in a fixed time period (say 0.0005 dimensionless time unit or 0.031 years if the reference time is 61.7 years).

7.7 Tasks for the Second Half

The first task would be to apply the experimentally determined Langmuir coefficients to the 1-D model. In doing this, the mobility of the various ions in the different soils may be established.

The second task would be to couple the 1-D and 2-D models as a predictive tool, using experimentally determined coefficients. Actual land sites may be investigated in this part of the work.

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CONCENTRATION, γ

FIG.7.1 One Dimensional Model

CONCENTRATION, γ

FIG.7.2 One Dimensional Model

FIG.7.3 One Dimensional Model

FIG.7.4 One Dimensional Model

FIG.7.5 One Dimensional Model

FIG.7.6 One Dimensional Model

FIG.7.7 One Dimensional Model

FIG.7.8 One Dimensional Model

FIG. 7.9 Concentration Contours

$$D'=1, \quad K_1'=1, \quad K_2'=1$$

$t=0.5$

$t=1.0$

FIG. 7.10 Concentration Contours

$$D'=1, K_1'=1, K_2'=1$$

$t=1.5$

Steady State $t=1.5295$

$$\epsilon=0.00001$$

$\gamma=0 \quad \gamma=1 \quad \gamma=0$

A square domain with boundary conditions $\frac{\partial \gamma}{\partial x} = 0$ on the left and right sides, and $\frac{\partial \gamma}{\partial y} = 0$ on the top and bottom sides. A downward arrow labeled v is shown in the center of the square.

$$D' \frac{\partial \gamma}{\partial y} + a\gamma = 0$$

FIG. 7.11 Concentration Contours

$$D'=1, K_1'=1, K_2'=1$$

$t=0.5$

$t=1.0$

FIG. 7.12 Concentration Contours

$$D'=1, \quad K_1'=1, \quad K_2'=1$$

Boundary conditions for the concentration contours:

$$\begin{aligned} \gamma=1 & \text{ at } y'=0 \\ \gamma=0 & \text{ at } x'=0 \text{ and } x'=1 \\ \frac{\partial \gamma}{\partial x} &= 0 \text{ at } x'=0 \text{ and } x'=1 \\ \frac{\partial \gamma}{\partial y} &= 0 \text{ at } y'=0 \text{ and } y'=1 \end{aligned}$$

FIG. 7.13 Concentration Contours

$$D'=1.0, K_1'=1.0, K_2'=1.0$$

$$t=.5$$

$$t=1.0$$

$$t_s=1.1585$$

FIG. 7.14 Concentration Contours.

FIG.7.15 Concentration Contours.

FIG. 7.16 Migration of Cadmium in Hallandale Fine Sand, Pompano Beach Plant Site.

FIG. 7.17 Migration of Cadmium in Hallandale Fine Sand, Pompano Beach Plant Site.

$t=0.2514$ (15.5 yrs)

FIG.7.18 Clearing of Pollutant Plume (Cadmium, in Hallandale Fine Sand).

FIG.7.19 Migration of Cadmium in Hallandale Fine Sand, Pompano Beach Plant Site.

$t_s = 0.556$ (34.308 Yrs)

x' (1 Mile)

$Y' = 0$

$Y' = 0.5$

$Y' = 1$

FIG.7.20 Migration of Cadmium in Hallandale Fine Sand, Pompano Beach Plant Site.

FIG. 7.21 Migration of Cadmium in Hallandale Fine Sand.