DOE/EV/10133-1

MASTER

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Annual Report

CHARACTERIZATION AND ENVIRONMENTAL
STUDIES OF POMPANO BEACH ANAEROBIC
DIGESTION FACILITY

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PREFACE

This report presents the findings during the second year of characterization and environmental studies of an anaerobic digestion plant at Pompano Beach. This 100 ton/day proof of concept plant which produces methane from municipal waste is operated by Waste Management Inc. under contract from the United States Department of Energy.

The work described here was conducted with funding from the Pollutant Characterization and Safety Research Division of the United States Department of Energy through DOE contract #DE-AS05-78EV10133.

ACKNOWLEDGEMENTS

The support from several institutions and individuals was necessary in pursuing the ongoing investigations reported in this document. We wish to acknowledge our gratitude to Dr. Robert Wood, and Dr. Gerald Goldstein of USDOE for their continued support. Dr. V. Fassel of Ames Laboratory has contributed in initial planning and liaison with investigators at his laboratory. Mr. Donald Walter of U.S.DOE has helped in liaison with Waste Management Inc. Office.

The continued co-operation of the officers of Waste Management Inc. is gratefully acknowledged. Mr. Peter Ware, Mr. Charles Perron and Mr. Matthew Streit have helped make sampling at the plant site possible.

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I. EXECUTIVE SUMMARY

1.1 Background

The rapid depletion of sources of fossil fuels has prompted a concerted effort to develop non-conventional renewable energy sources and resource recovery technologies. Material and energy recovery from municipal wastes has a dual payoff in resource conservation and in reducing environmental pollution.

Energy recovery systems that have been explored to various degrees of commercialization include, mass combustion, refuse derived fuel, pyrolysis and bioconversion. A report from the Office of Technology Assessment [1] presents the status of these technologies.

In the last few years numerous municipalities have built resource recovery plants, and many more are under construction. It is revealing to note that a report by Freeman [2] in 1978 stated that installed capacity of resource recovery plants in the United States was only 6,730 tons per day, while Dade County, Florida is constructing a 3000 ton/day plant, with early 1981 as a start date, with a possible future capacity of 6000 tons/day. Resource recovery is a growing industry in the United States.

While the increase in capacity has been significant the total capacity is still small compared to that in Europe where shortage of land has been a great incentive for resource recovery from solid wastes. The relatively high cost of fossil fuels in Europe has also served to make resource recovery economically viable [3]. The technology most favored in Europe has been mass burning.

1.2 Anaerobic Digestion Plant at Pompano Beach

In the United States a wide range of energy recovery technologies are being investigated. A summary of these technologies are presented in the proceedings of the U.S. EPA Resource Recovery Conferences [4,5].

Anaerobic Digestion of municipal solid wastes to produce methane has been demonstrated to be feasible in bench scale by Pfeffer [6,7,8] and by Wise [9]. The process is pH limited to the neutral range with volume reduction of half and approximate gas production of 6000 cu. ft./ton (50% methane). While anaerobic digestion of sewage sludge has been commercially proven, the digestion of less biodegradable municipal solid waste is still not a proven technology at the commercial scale of operation.

The Energy Research and Development Administration (ERDA) awarded a contract to Waste Management Inc. (W.M.I.) "to evaluate and verify the technical and economical feasibility of the solid waste to methane fermentation process. Since anaerobic fermentation of solid waste materials has not been demonstrated on a large scale, there is a definite risk factor that the system will not perform as current research suggests". [10]

The proof of concept plant was built on an existing shredding and landfill site at Pompano Beach, Florida. Two digestors, were built with a total capacity of 100 ton/day of solid waste. Fig.1.1 shows a flow chart outlining the process. The plant was officially inaugurated in August 1978. Waste Management Inc. is conducting evaluation of the economic and operating characteristics of the plant.

1.3 Objectives of the Present Investigations

Municipal solid wastes contain numerous substances of potential

environmental concern. While some understanding of the composition of raw municipal waste and its leachate products is available, no information regarding characteristics of solid, liquid and gaseous outputs from anaerobic digestion exists. If centralized anaerobic digestion plants are to be environmentally viable, the characteristics and environmental effects of effluents from these plants must be acceptable. The environmental concerns are particularly acute where ground water supplies are precariously low and the water table is high, South Florida is such a location.

A characterization and environmental study was initiated by the Resource Recovery Group on August, 1978. The specific objectives are:

- a) Systematic characterization of solid, liquid and gaseous inputs and outputs.
- b) Investigations of leaching characteristic of output solid and liquid effluents, and the transport of pollutants to and through ground water systems.
- c) Analysis of environmental and process parameters to obtain causal relationships.

1.4 Summary of Technical Approach

The environmental impacts of front end processing equipment have been of secondary interest compared to the process itself. This priority was established since the front end facilities are generic to other municipal waste processing technologies and because of the existence of an already existing shredding and landfilling operation at Pompano.

A detailed description of the technical approach has been presented by Sengupta et al [11] in the first year's annual report. The approach

consists of physical, chemical, and biological characterization of all inputs and outputs at the plant. Analyses for major, minor and trace compounds of potential environmental concern, are being conducted. Relevant regulatory standards are being recognized and search for compounds on EPA priority pollutant list and carcinogen list are being conducted. The ultimate aim is to quantitatively relate pollution potential with plant operating parameters. Some mutagenic studies were conducted but had [11] inconclusive results. These studies are to be continued elsewhere. A significant part of the technical approach relates to development of predictive criterion for pollutant migration by leaching and modelling studies. Fig.1.2 shows a schematic drawing of the plant and the sampling locations.

During the first year, progress was reported through a semi-annual report and annual report by Sengupta et al [12]. During the second year quarterly reports by Sengupta et al [13,14,15] have summarized progress. This report presents a summary of tasks performed during August 1, 1979 through July 31, 1980 and as such contains repetitions of items in the quarterly reports. Reports on plant operation are available from WMI on a monthly basis.

1.5 Status Report

1.5.1 Plant Operation

- (1) Plant operation started in August 1978. Digester number 2 was filled till December 1978 when output filter cake and filtrate was available. The plant was initially seeded with sewage sludge.
- (2) The plant operated intermittently until November 1979 when it was shutdown for repair, modifications and cleaning.

- (3) The digester number 2 was filled again during April-May 1980.

Sewage sludge was added for the first time since start-up during 1978. It operated for approximately two months till June 1980.

Monthly reports from Waste Management Inc. to U. S. DOE summarize process parameters, plant inputs and description of operation and repair. Walter [16] summarized the operational history of the plant.

1.5.1.1 Accomplishments

- (1) The digestors have produced gas on an intermittent basis since start-up in August 1978.
- (2) Plant operation in the mesophilic range of $37\pm 2^{\circ}\text{C}$ has been conducted with pH successfully maintained in the 6.8-7.0 range by addition of lime.
- (3) The feed rate has reached 3.1 tons/day. This low feed rate has resulted in only 3% total solids in digester slurry and gas production of 5000-8000 cu.ft./day.

1.5.1.2 Problems

- (1) Numerous mechanical and operational problems have prevented the plant from stable operations. Thus both the process and environmental data reflect the transient behavior of plant including start-up and shutdown. Breakdown of conveyor systems and digester water seals have been relatively frequent.
- (2) Two explosions, one in the primary shredder and another in Digester No.1 have caused serious damage to the facilities though no injuries have been reported.
- (3) "Stringers" formed by textile and plastics have caused inefficient operation of agitators in the pre-mix tanks and the digestors.

Modifications in design have been implemented to avoid some of the problems mentioned.

1.5.2 Gas Characterization

- (1) Tests on reliability of saran, plastic, tedlar and glass containers were conducted. Glass bulbs proved to be suitable for syringe injections and tedlar bags for loop injection to GC.
- (2) The composition of the gas has not varied significantly over the last year. The ratio of CH_4/CO_2 (the major constituents) has varied between 1.42 to 1.19 with values around 1.15 being most frequent. A total of 21 samples were analyzed. Plant operation parameters such as pH, temperature, alkalinity, volatile acids and volatile solids have remained near constant. The highest value of volatile acids (1674 mg/l) produces the highest value of CH_4/CO_2 (1.42).
- (3) Ammonia which was identified at trace levels was found to increase to significant levels (1557 ppm - 1821 ppm). This was during plant restart in May 1980. The addition of sewage sludge at restart is one plausible source of this increase.
- (4) Apart from the major constituents, several other contaminants have also been observed. Of these, Vinyl chloride, Trichloroethylene and Tetrachloroethylene are in the EPA "Recommended list of Priority Pollutants". These compounds are in very low ppb levels.
- (5) The mechanical arrangements for installation and operation of the stack sampler has been complete. As soon as the plant is operational at near steady state again, stack sampling to determine particulate levels in output gas will begin. Gas traps will be added to the EPA-5 sampling train to obtain samples for ultra trace organic

analysis at the Ames laboratory.

1.5.3 Ambient Particulates and Airborne Bacteria

- (1) The extensive periods of down time for the plant provided an opportunity to utilize gas analysis personnel in initiating ambient particulate level monitoring. Particulate levels at three locations in the classification building were measured by a 4-stage hi-volume sampling system. The EPA 24-hour ambient standard was exceeded even without plant operation. However, the levels were below OSHA 8-hour standard. A total of 16 field experiments were conducted.
- (2) Significant concentration of particulates was found in the less than 1.1 μ size with and without plant operation. Particulates in this range can penetrate the alveoli of the lungs.
- (3) Total and fecal coliform levels have been measured for particulates collected in a nutrient broth in one of the impingers in the EPA-5 sampling train. Wide variations in levels have been observed. More data have to be collected before meaningful trends can be assessed.
- (4) An effort has been initiated to analyse whether there are significant differences in bacteria numbers with particulate size.

1.5.4 Solid and Liquid Phases

- (1) Seventeen field missions to collect samples were conducted. Some of these missions resulted in collection of complete sample sets others represent partial sample sets. Since November 1979, 3 missions have been conducted. The non-availability of weekly samples during the second half of the contract year provided a

a convenient period for a set of spiking studies to evaluate analytical methods that are commonly used in solid waste research.

- (2) Tables 4.3 to 4.8 summarize compounds identified in various input and output streams. Major environmental parameters for which significant number of samples have been collected are listed with mean, low and high values shown. Remarks regarding environmental significance in relation to regulatory standards and EPA priority pollutant lists are included. Trace compounds are identified and levels are indicated where available. It should be noted that only order of magnitude values are meaningful for trace organic analyses. Meaningful mass balances and correlations can be obtained when data for stable operation of plant is obtained.
- (3) Four forms of nitrogen, $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and total organic nitrogen has been monitored in the air-classified light fraction, the digester slurry, the filter cake and the filtrate. In the filter cake TON has been near constant though nitrate and nitrite nitrogen has shown significant variation. In the filtrate TON is near constant but the other forms of nitrogen has shown variation. These data suggest that except for TON all other nitrogen forms in the process are sensitive to input and operating parameters.
- (4) Total phosphate-phosphorus has been measured for the light fraction input, digester slurry, filter cake and wash water input and output. A significant decrease in phosphorus concentration in the input light fraction has been observed during July 1979 to August 1980 compared to the previous year. A significant decrease in phosphorus appear as significantly in the filter cake but is seen in the filtrate,

because phosphorus present in the slurry is primarily in the dissolved state. The phosphorus levels in wash water increases before and after washing.

- (5) Chloride levels have been monitored in the light fraction, digester slurry, filter cake, filtrate and wash water input and output. Though chloride levels of input light fraction has remained at near constant levels, increases have been observed in filtrate, filter cake and digester slurry, possibly owing to recirculation of filtrate. Chloride levels in wash water output has decreased primarily owing to decrease in chloride levels in the input wash water.
- (6) Sulfide concentrations have been measured in digester slurry, filtrate, wash water input and output. Significant variation in levels have been observed between samples. No trend was identified.
- (7) The BOD, COD and TOC levels have been monitored in light fraction, digester slurry, filtrate, filter cake and wash water input and output. The highest BOD level in the digester slurry (2345 mg/l) was one third of the highest values observed during the period prior January through June 1979 (7150 mg/l). The levels in the filtrate have varied significantly from a low of 312 to a high of 2981 mg/l. Similar variation were observed during the previous year. The BOD levels in filter cake and wash water are low.

The COD level in the light fraction varied in the approximately same range as the previous year. An increasing trend has been identified in the digester slurry and filtrate possibly caused by recycling of filtrate.

TOC levels have shown smaller variation compared to the previous

year.

The highest levels of BOD, COD and TOC observed are about 10 to 40 percent of reported values for leachate from sanitary landfills.

- (8) Fifteen samples of light fraction collected during July 1979 through June 1980 and a sample of filter cake were analyzed for C,H,N. content. The percentage of each element are very close to theoretical levels for cellulose, the minor differences probably caused by plastics and substances absorbed in the paper in the light fraciton.
- (9) The total and fecal coliform levels in digester slurry, filter cake and filtrate was monitored. The levels (except in wash water) dropped during July to mid September 1979 by one order of magnitude but reached the previous levels by November 1979. Bacterial levels were near "normal" for the short sampling period of May-June 1980 when the plant operated again. Attempmts were made at quantifying bacterial levels in the air-classified light fraction. This part of the investigation is being considerably strengthened by pursuing identification of specific pathogens though environmental standards are usually for total and fecal coliforms. This has necessitated a program for development of identification schemes. The work is being done during August 1980.
- (10) Heavy metal levels in light fraction, digester slurry, filter cake and filtrate have been conducted. There is considerable fluctuation in levels though most levels except for calcium are low. Some differences in values measured at Ames Laboratory and the University of Miami have been observed. Sample deterioration studies will be initiated after September 1980.

- (11) Spiking studies were conducted using simple and multiple compound spikes. Comparison of theoretical recovery with actual recovery rates from synthetic samples made from distilled water and spiked samples of filtrate showed significant variations. The analytical procedures followed 14th Edition of Standard Methods. The largest negative recovery rate was for NH_3 (-33%) and the largest positive recovery was for TON (805%); both were for the filtrate samples. The highest recovery rates were for the metals. The results indicate the magnitudes of analytical errors possible when using Standard Methods. However, these errors are comparable to errors that have been measured 'round robin blind tests' by various laboratories. (9)

1.5.5 Trace Analysis

- (1) The trace analysis reported have been conducted at Ames Laboratory. The analysis have been conducted on light fraction digester slurry, filter cake and filtrate. The approach has been to work with few samples with concentrated effort on development of analytical methods for identification of trace compounds.
- (2) A summary of compounds identified at Ames Laboratory is included in tables presented in Chapter 4. To date metals, PCB, pthalates, pesticides, numerous organic acids and phenols have been identified. During the process, methods for extraction have been developed.
- (3) At present methods for extraction of organic compounds from organics are being developed using particulate samples from the Ames RDF plant. These procedures will be used for gas stream particulates at the Pompano Beach plant.

1.5.6 Leaching Experiments

- (1) The studies have been directed towards obtaining experimental values for distribution coefficients for heavy metals and several anions in representative soils from the Pompano Beach site. The general objective however, has been to develop methods of general use in developing predictive information regarding pollutant transport.
- (2) Hallandale fine sand and Plantation muck are the principal soils in the Pompano area. The Plantation muck has three layers, top, middle and bottom layers. The soils were characterized for organic content, pH, initial concentration of cations and anions, and cation exchange capacity. Batch studies were conducted and Langmuir and Lapidus distribution coefficients for 8 metals and seven anions were determined. These coefficients can be used in transport models for predictive purposes. It has been found that the Langmuir model is capable of describing some of the complicated batch data behavior whereas the Lapidus-Amundsen model can only describe adsorption adequately. The procedure for conducting the studies is at present being evaluated for inclusion in standard procedures by an ASTM Committee.
- (3) In order to simulate flow through soil layers the traditional approach has been column studies. These studies are extremely time consuming and expensive. A method of using several extraction or batch column studies is being developed. The results of these studies will be compared with column studies. If the results are found satisfactory, batch-column studies will replace column simulation.

At present the batch column studies for cations and Hallandale fine sand has been completed. Comparisons with prediction obtained from numerical transport models using distribution coefficients determined by batch studies are promising.

1.5.7 Model Development

- (1) The only method of obtaining prior information regarding the possible impact of effluent disposal on ground water quality is by predictive models. Multi dimensional time dependent models are being developed; coefficients for these methods are obtained from the batch studies. The models will be verified comparing results with experimental values obtained by batch-column and column studies.
- (2) At present the one-dimensional model has been developed in two versions one using the linear Lapidus-Amundsen distribution coefficient and the other using Langmuir coefficients. The Lapidus-Amundsen model has been used to conduct a parametric study using non-dimensional numbers obtained from the governing equations. The parametric study has provided ranges of values for time periods and concentration in one-dimensional transport. Similar parametric studies were conducted using the Langmuir Model.
- (3) Preliminary comparisons of one-dimensional model results and batch column experiment data have been made. The results are encouraging.
- (4) The computer code for the two dimensional and three dimensional models are ready. When verified coefficients are obtained, these models can be used to predict transport of pollutants for which distribution coefficients have been determined.

1.5.8 Future Plans

- (1) All phases of work described here will continue.
- (2) Analysis of particulates in gas stream will be initiated.
- (3) Several duplicate sample analyses at Miami and Ames will be conducted and compared to determine sample deterioration and reliability of analytical methods. The compounds of interest will be especially those in trace quantities.
- (4) Analysis of selected trace organics will be done on a routine basis at Miami to study variability with plant input and operating conditions.
- (5) The investigation on bacteriological characterization will expand to identify specific pathogen.
- (6) A method for analyzing total plastic matter in solid waste will be attempted to be developed and tested. The fate of plastics will be studied in both the Pompano Beach pilot plant and in the University of Miami laboratory prototypes.

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PROCESS FLOW CHART

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

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

II. GAS QUALITY

During the first contractual year, a framework was established for determining the possible environmental impact of producing methane-rich gas from the large-scale anaerobic digestion of municipal solid waste. Critical attention was given to approach methodology, analytical instrumentation, sampling procedure, quality control, digester gas characterization, major process parameters, and a tentative procedure was defined for making the environmental assessment. The reader is referred to the first annual report, Sengupta et al [1], for a more detailed description of those areas. A summary of the gas composition observed during that period is presented in Table 2.1. It was noted that while the gas quality was similar to that in small-scale tests, De Renzo [2], and in landfills, Lockman et al [3], the H_2S levels were higher in the digester gas. It must be recognized, however, that the digester temperatures throughout the period were generally less than $30^{\circ}C$, which is significantly below the optimum mesophilic temperature of $40^{\circ}C$, and that the design operating capacity was not achieved.

During the second contractual year, digester gas was available essentially for five months (August, September, October, and November 1979; and May 1980). As a result of the extensive plant down-time, the research process was modified to include studies of ambient particulates and airborne bacteria levels during those periods. The results of that work will be described in the next section of this report.

The digester temperatures during the second year approached and extended into the lower mesophilic range ($35^{\circ}C$ - $40^{\circ}C$). Only in October 1979 was the optimum mesophilic temperature of $40^{\circ}C$ reached and

thermophilic conditions (50°C-60°C) have yet to be studied. Thus at best the results to date, while informative, must be interpreted in terms of unstable lower mesophilic conditions.

The following material represents a summary of the second year efforts. The reader is referred to the semi-annual report, Sengupta et al. [4], and the quarterly report, Sengupta et al. [5], for a more detailed discussion of the various areas.

2.1 Quality Control

Quality control continues to be of utmost concern in this type of field exercise. The most critical areas are in transporting representative samples from Pompano to Miami and in preserving them until an analysis can be made. To minimize liquid/gas reactions, the water is removed from the gas at the site using condensers. The tedlar bag samples are protected from direct solar radiation and maintained slightly higher than ambient temperature so that any leakage would be out of, not into, the container. Glass bulbs were initially submerged in ice water while in transit but the current procedure is to keep them warm also. Where possible, the analysis is at least initiated on the date of sample collection. The procedure is to intersperse periodic mass spectrometric analysis using a Finnigan GC/El-CI Mass Spectrometer with gas chromatographic analysis using a Hewlett-Packard Model 5834A, dual FID, dual TCD Gas Chromatograph. (See the first annual report for column configuration, valving, etc.) The work of Cushing et al. [6] and Lentzen et al. [7] serve as resources for our effort.

2.2 Analytical Results

The gas quality observed on individual dates during August to

November 1979 is summarized in Table 2.2. Those data were obtained using the HP GC, and the H₂S Ecolyzer. A comparative analysis of the major constituents is presented at the bottom of the table. GC, MS, and H₂S results for individual dates in May 1980 are listed in Table 2.3. It is of interest to note that both CO and vinyl chloride were observed the first year but not the second. While the observed H₂S levels the second year are not representative because of digester air seal problems, the levels do appear to be somewhat lower than during the first year. Relatively high levels of ammonia were detected this year along with several other constituents which have not been positively identified. The presence of ammonia was confirmed using NDIR instrumentation and the GC response factor was determined using 1400 ppm calibration gas. The presence of ammonia was previously noted during the first year of plant operation but not during the fall of 1979. The relatively high levels in May 1980 were probably related to the recent addition of sewage sludge to digester. Ammonia has been observed in landfills at a concentration of 0.71 mg/m³ which is about 1 ppm, Lockman et al. [3]. Attempts to identify the unknown constituents will begin as soon as gas becomes available.

2.3 Relationships With Major Process Parameters

A comparison of CH₄/CO₂ ratios with major process parameters during this contractual year is shown in Table 2.4. Observation of those data reveals no significant trends which is an indication that the system was unstable during the analysis period. Theoretical relationships to be expected for this technology are shown in Figure 2.1.

WMI records show that 305 tons input were processed during the period August to November 1979, 181 tons in May 1980, and 179 tons the first 15 days of June 1980. Unfortunately, the incomplete gas production records make it impossible to relate that parameter to input processed. According to De Renzo [2], the technology should produce about 6000 ft³ of gas per ton of processed input.

2.4 Conclusions

The first two years of plant operation have experienced major periods of down-time. The resulting instabilities have made it virtually impossible to evaluate the stable conditions that must be attained for the anaerobic digestion technology to be viable. The plant has not yet processed near its design capacity of 100 tons per day.

The gas quality resulting from unstable lower mesophilic conditions does not appear to pose serious environmental consequences for the input amounts currently being processed. However, the odorous characteristics of H₂S and its corrosive action in the presence of water may require it to be removed from the processed gas. The presence of ammonia at concentrations of 1500 ppm implies that specific emphasis should be given to that significant pollutant in future work. While there are no ambient air quality standards for ammonia, EPA [8], the OSHA 8-hr standard is 50 ppm, OSHA [9], and the odor threshold is 40.0 ppm. Much more data are needed to properly evaluate a full-scale operation at both mesophilic and thermophilic temperature conditions.

2.5 Future Work

Gas quality analysis will continue during the next contractual period with specific emphasis being given to the identification of trace constituents.

Hopefully it will be possible to obtain comprehensive gas quality data sets for both stable mesophilic and stable thermophilic conditions while the plant is operating near its design capacity.

With the completion of the new sampling ports, an explosion-proof power outlet, and the recent installation of a field laboratory at the site, we can now begin evaluating the particulates in the digester gas stream using stack sampling instrumentation and EPA Method 5 procedures. Considerable testing will be required, however, to define the proper analysis interval with the low flow rates and anticipated low particulate levels in the digester gas. Figure 2.2 illustrates the EPA Method 5 sampling train, EPA [10]. The sampling probe will be inserted into a 3-inch port located about 7.5 ft above ground level on a vertical section of 8-inch gas pipe, immediately upstream from where the gas is flared. That location should permit representative results.

With the collection of the above data, it will be possible to make assessments of the impact of the anaerobic digestion technology on the atmospheric environment.

References

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TABLE 2.1 Composite Summary of Digester Gas Quality
Observed 1 August 1978 - 31 July 1979,
Pompano Anaerobic Digester

Constituent	Concentration	Constituent	Concentration
O ₂	0-3%	1-Butene, 2-Butene	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
Propane	GC/MS Peak	NH ₃	GC/MS Peak
Water	GC/MS Peak		
Butane	GC/MS Peak		

TABLE 2.2 Digester Gas Composition, August to November 1979.

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.		

TABLE 2.3 Digester Gas Composition, May 1980

CONSTITUENT	COLLECTION DATE		
	5/7/80	5/14/80	5/28/80
Air (%)	0.6	1.3	2.1
CH ₄ (%)	52.3	49.2	52.3
CO ₂ (%)	47.1	49.5	45.6
C ₆ ⁺ (ppm)	9	44	77
H ₂ S (ppm)	46	3	1
CO (ppm)	0	0	0
N ₂ /O ₂	3.97	4.02	3.72
SO ₂	None	None	-
NO ₂	None	None	-
Mol Wt. 48	None	Trace	-
C1-C3 Mercaptans	None	None	-
Vinyl Chloride	None	None	-
HCl	None	None	-
NH ₃ (ppm)	1821	1619	1557
Benzene	None	None	-
Ethylene	None	None	-
Trichloroethylene	-	None	-
Tetrachloroethylene	-	None	-
Mol Wt 42	None	Trace	-

TABLE 2.4 Comparison of CH₄/CO₂ Ratios With Major Process Parameters

Date	CH ₄ /CO ₂	Temp (°C)	pH	Alkalinity mg/l Ca CO ₃	Volatile Acids mg/l CH ₃ COOH	Volatile Solids (%)
8/7/79	1.17	36.5	6.95	-	165	1.7
8/8/79	1.10	37.0	7.10	-	-	-
8/15/79	1.09	36.0	6.88	1869	228	1.6
8/31/79	1.42	35.8	7.01	1845	1674	-
9/14/79	1.08	35.0	7.06	2115	104	-
9/19/79	1.16	33.2	6.94	2148	91	1.6
9/20/79*	1.31	33.2	6.94	2142	81	1.6
9/28/79	1.21	33.9	6.98	2080	38	1.7
10/1/79	1.18	35.8	6.95	1964	102	1.8
10/5/79*	1.10	36.1	6.91	1962	75	1.9
10/18 to 11/15/79	1.19	37.0	6.90	2000	300	-
5/7/80*	1.11	31.1	7.08	2160	64	-
5/28/80*	1.15	32.2	6.91	-	-	2.1
5/30/80	1.14	32.2	6.79	2059	-	-

* Actual process data not available on these dates.
Estimates based on data for adjacent dates.

Source: De Renzo (2)

FIG. 2.1 The Relationship Between Gas Composition, Temperature, pH, and Alkalinity.

FIG. 2.2 EPA Method 5 Particulate Sample Apparatus

III. AMBIENT PARTICULATES AND AIRBORNE BACTERIA

A comprehensive state-of-the-art assessment of bacteria and virus levels at a refuse derived fuel (RDF) plant and other waste handling facilities has been prepared for EPA by Fiscus et al [1]. The facilities tested were a municipal incinerator, the St. Louis Refuse Processing Plant, a wastewater treatment plant, a refuse transfer station, and a sanitary landfill. Hi-Vol ambient air filters and Andersen agar plate impactors were used to collect the particulates and bacteria. Supplemental tests were performed at the RDF plant to evaluate particulate trace metals and asbestos. It was noted that all virus assays; and almost all Salmonella sp., Staphylococcus aureus, and Klebsiella sp. bacteria tests were negative. The highest total bacteria counts, total coliform, fecal coliform, and fecal Streptococci bacteria levels were found to be downwind from the RDF plant --- the lowest at the landfill. The same relative ranking applied for in-plant conditions. The number of bacteria containing particles did not decrease with decreasing size. In fact, as high as several thousand total bacteria counts per cubic meter were observed for particle sizes less than 1 μm . Bacteria colonies in air may range up to 700,000/ m^3 in a sewage treatment plant. Lead and zinc were the trace elements having the highest concentrations. Asbestos fibers were also present but all were below the threshold limit values (TLV's).

The extensive plant down-time during this contractual year provided the opportunity to begin study of ambient particulates and airborne bacteria at the WMI site in Pompano. To date, ambient particulate sampling has been performed at three locations within the Classification Building ,

see Figure 3.1, which is open on all sides, and at one location within the Storage Building. The locations within the Classification Building were as follows:

- 1) center of building, opposite control room
- 2) adjacent to the secondary shredder
- 3) adjacent to the trommel

The bacteria samples were all collected at the center of the Classification Building.

3.1 Ambient Particulates

A 4-stage Hi-Volume particulate sampling system with flow controller and an Andersen particle sizing head were used to sample the ambient particulates. The filters were desiccated, weighed, and handled in accordance with EPA [2] procedures. The results of the particulate sampling with the plant down is summarized in Table 3.1. Two runs were also made with the plant operating for comparison with the ambient levels.

It is readily seen in Table 3.1 that the EPA 24-hr ambient standard was exceeded at every location with the plant not operating. However, the levels were always below the OSHA 8-hr standard. The concentrations were independent of wind direction. Particulate concentrations were almost an order of magnitude higher with the plant operating but the OSHA standard was not exceeded. (On those dates only 14 or less tons input were processed).

The most significant finding was the relatively large concentration of particulates less than $1.1 \mu\text{m}$ in size whether or not the plant was operating. Particles that small penetrate the deepest part of the lung -

the alveoli. As a result, specific emphasis will be focused on those particulates during the coming year.

3.2 Airborne Bacteria

Airborne bacteria were collected using the stack sampling pump and impinger train. The procedure was to place 25 ml of either lactose broth or half-strength nutrient broth into each of the first two impingers. The third impinger contained drierite. Air in the Classification Building was pumped through the train at the rate of 1 cfm for 30 minutes. The broth was then returned to Miami where it was brought up to 100 ml with sterile buffered dilution water. Standard membrane filtration techniques were used and the filters were incubated on m-Endo agar LES, m-FC agar, or standard plate count agar at the appropriate temperature ($35\pm0.5^{\circ}\text{C}$ or $44.5\pm0.2^{\circ}\text{C}$) for 24 or 48 hours. Attempts to use the Hi-Vol to collect samples have been largely unsatisfactory because of the considerable bacteria die-off. We will explore that further and possibly will try agar plate impactors.

The bacteria levels observed when the plant was not operating are summarized in Table 3.2. The large differences in the WMI bacteria levels throughout the period agreed with the findings of Fiscus et al (1). Fassel [3] reported more consistent levels at the Ames Solid Waste Recovery Ssystem. Project work is just underway in this area and much more data will be needed to make definitive conclusions.

3.3 Particulate/Bacteria Relationships

Since a relatively high percentage of particulates were found to be less than $1\text{ }\mu\text{m}$ in size at the Pompano facility, it is of health interest to determine if they contain bacteria. On July 31, 1980, an investigation

of that relationship was made using the 4-stage hi-volume particulate sampler. The filters were sterilized but not desiccated or weighed prior to placing them in the sampler. Air was then drawn through the filters at the rate of 20 cfm for 9 minutes. The filters were placed in trays containing m-Endo agar LES at the site and transported to Miami for incubation. The results of that experiment with the plant not operating were as follows:

<u>Particulate Size</u>	<u>Total Coliforms</u>
>7 μ	0
3.3-7 μ	0
2.0-3.3 μ	0
1.1-2.0 μ	0
<1.1 μ	8 CFU

While the results are consistent with the findings of Fiscus et al (1), additional tests are needed.

3.4 Future Work

Investigations of ambient particulates and airborne bacteria will continue during the next contractual period. The data base will be enlarged to include conditions with the plant operating. Comparative analyses will be made with non-operating conditions and the question of inhalable particles containing bacteria will be studied. EPA has not yet regulated airborne bacteria because of their localized nature. It may, however, be significant for personnel at refuse disposal facilities.

References

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- 1 Power Station
- 2 Power Station
- 3 Control Room
- 4 Air Classifier
- 5 Trommel
- 6 Shredder

Hi Volume Sampler Location. (X)

FIG. 3.1 Classification Building

TABLE 3.1 Particulate Concentration ($\mu\text{g}/\text{m}^3$)

1980 Date	Sampling Location	No. Hrs.	>7 μ	3.3-7 μ	2.0-3.3 μ	1.1-2.0 μ	0-1.1 μ	Σ All Sizes	Wind Dir/ Speed (mph)
Plant Not Operating:									
Jan18-19	1	24	-	-	-	-	-	153.4	ENE/3
Jan23-24	1	24	-	-	-	-	-	181.5	WNW/7
Feb5-7	1	24	-	-	-	-	-	320.0	NW/6
Feb14-15	1	24	-	-	-	-	-	188.0	NNW/3
Feb21	1	8	-	-	-	-	-	316.0	ESE/8
Feb28-29	1	24	234.3	146.9	90.8	49.1	18.4	539.5	SW/3
Mar6-7	1	24	200.0	70.0	20.0	40.0	50.0	380.0	NE/3
Mar11-12	1	24	278.0	59.0	44.0	6.0	393.0	780.0	ENE/5
Mar25-26	1	24	83.0	53.0	23.0	25.0	20.0	204.0	SSW/5
Apr1-2	1	24	99.0	58.5	37.8	136.0	106.7	438.0	NNE/8
Jun3-4	2	24	648.0	159.0	75.0	65.0	789.0	1737.0	-
*Jun10-11	2	24	346.0	77.0	7.0	7.0	152.0	589.0	-
Jun17-18	3	24	108.0	32.0	31.0	21.0	112.0	304.0	-
Jul23	4	3	18.5	12.8	5.2	4.3	23.3	64.1	-
Plant Operating:									
May13-14	2	24	684.3	226.4	137.0	65.7	1009.6	2123.0	-
May27-28	2	24	1769.9	180.9	121.0	76.0	1211.0	3358.8	-
EPA 24-Hr. Ambient Standard								150 $\mu\text{g}/\text{m}^3$	
OSHA 8-Hr. Inert Dust Standard								15 mg/m^3	
1. Classification Bldg, Center									
2. Classification Bldg, Adjacent to Secondary Shredder									
3. Classification Bldg, Adjacent to Trommel									
4. Inside Empty Storage Bldg.									
* Plant Operated 4 Hrs. Only.									

TABLE 3.2 Airborne Bacteria Levels

	U.M. 2/27/80	Sampling 3/19/80	Date			Ames Solid Waste Recovery System *	
			4/28/80	7/16/80	7/23/80	Avg.	Max
Total Coliform CFU/ft ³	0.26	110	0.86	1.3x10 ⁴	0	5.9	10.8
Fecal Coliform CFU/ft ³	1.9	140	-	1.0x10 ⁴	0	3.1	3.1
Total Plate Count CFU/ft ³	78	1200	2000	3.0x10 ⁴	1.3	-	-
Wind Conditions (mph)	NNE/4	E/9	-	-	-	N/A	N/A
* Inside processing area of SWPP before dust collectors were installed, plant not operating.							

IV. SOLID AND LIQUID PHASES

4.1 Introduction

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. The various sampling sites are indicated in the flow diagram (Figure 4.1). Samples have not been collected from sites Number 3 (sewage sludge) and Number 10 (tipping floor wash) due to their unavailability.

During this past year, 17 sampling trips have been conducted; their dates and the samples collected are listed in Table 4.1. Samples were preserved as specified in last year's Annual Report [1].

Regular sampling has not been conducted since mid-November 1979 because of the extensive repairs and modifications to the RefCOM. Two attempts to resume sampling (in March and in May) were aborted due to further repairs and modifications to the plant.

During this time, a spiking study was conducted to explore the reliability of the analytical methods. A copy of the final manuscript of the resulting paper was included in the last quarterly report [3]. A synopsis is included in Section 4.4, below.

In addition, a paper entitled "Characterization and Environmental Effect of Waste Streams from Anaerobic Digestion of Municipal Solid Waste" has been prepared. The entire manuscript has been included with the last quarterly report [2]; it is not reprinted here, since a major portion of this report is an expanded version of that paper.

4.2 Methods of Analysis

All physical, chemical and biological procedures used in the analysis of samples were taken from Standard Methods [3]. In some cases, however, modifications were made to accommodate the physical characteristics of the samples [1].

4.3 Results and Discussion

A summary of all analyses of samples collected since January 1979 has been prepared for each sampling site. The data for air classified heavies, air classified lights, digester slurry, filter cake, filtrate, wash water input, and wash water effluent are listed in Table 4.2 through 4.8, respectively. These tables include the data obtained by Ames as well as that obtained by the Miami team. The data are reported as means and ranges with samples from each of the two project years listed separately.

4.3.1 Nitrogen

Four forms of nitrogen i.e. $\text{NH}_3\text{-N}$, $\text{NO}_2^-\text{-N}$, $\text{NO}_3^-\text{-N}$ and total organic nitrogen have been measured in the various input and output streams of the plant during the period July 1979 through June 1980.

In the air-classified light fraction, which constitutes the shredded municipal solid waste feed to the digester, the concentrations of total organic nitrogen and ammonia nitrogen have remained fairly uniform during the above-mentioned period, the mean values being 0.63 mg/g and 0.23 mg/g respectively (Fig. 4.2). However, during the previous six months i.e. January 1979 through June 1979, the mean values of these parameters were 0.45 mg/g and 0.25 mg/g respectively (Table 4.3).

In the digester slurry, the mean concentration of ammonia nitrogen was 126.03 mg/l (Fig. 4.3) which is lower than that found in the previous six-month period, January 1979 through June 1979, when the mean value was 191.56 mg/l (Table 4.4). However, on the contrary, the mean nitrite and nitrate concentrations indicate a noticeable increase in the values of 1.35 μ g/l and 11.82 mg/l (Fig. 4.3) than that found in the earlier six-month period (0.027 μ g/l and 2.77 mg/l). Although variation in trends has been noticed in levels of ammonia nitrogen, nitrite and nitrate, the mean concentration of total organic nitrogen has remained almost constant during both the periods January 1979 through June 1979 and July 1979 through June 1980. The mean values found were 63.83 mg/l and 63.38 mg/l respectively. One possible explanation for this constant trend in the organic nitrogen content of the digester slurry is the relatively stable contribution of the microbial bio-mass in the digester.

The total organic nitrogen concentration in the filter cake remained relatively unchanged, the mean levels being 0.41 mg/g (Fig. 4.4) formerly and 0.49 mg/g (Table 4.5) in the last six months. The mean level of nitrite nitrogen indicates a major increase in concentration during this period (July 1979 through June 1980) from that found in the previous period (January 1979 through June 1979). The concentration increased from 0.0014 μ g/g to 0.37 μ g/g. The concentration of nitrate nitrogen, however, has dropped significantly to 0.07 mg/g from 0.85 mg/g, found in the previous period.

In the filtrate, the mean concentrations of organic nitrogen, ammonia nitrogen, nitrite and nitrate during July 1979 through June 1980 were 46.16 mg/l, 113.04 mg/l, 2.75 μ g/l and 5.04 mg/l (Fig. 4.5). During

the earlier six-month period, January 1979 through June 1979, the corresponding mean values of concentrations were 44.42 mg/l, 183.87 mg/l, 18.00 µg/l and 2.55 mg/l (Table 4.6).

4.3.2 Total Phosphate Phosphorus

In the air-classified light fraction, the total phosphorus concentration varied over a more narrow range (0.26 - 1.16 mg/g), with mean at 0.52 mg/g (Fig. 4.8), than that in the previous period (January 1979 through June 1979) when the variation was from 0.1-4.0 mg/g and the mean value was 1.10 mg/g (Table 4.3). This indicates a lowering concentration of phosphorus in the raw waste input to the digester during the latter period.

There is a marked decrease in the phosphorus concentration in the digester slurry during this period (168 mg/l - Fig. 4.9) compared to that found in the earlier period (250 mg/l - Table 4.4). This reduction is due in part to the apparent lower phosphorus input with the air classified lights and to reduced nutrient addition of diammonium phosphate to the digester. This lowering of phosphorus concentration is also observed somewhat in the filter cake (0.85 mg/g to 0.70 mg/g - Fig. 4.10 and Table 4.5). This is due to the fact that the phosphorus present in the digester slurry is mainly in the dissolved state; in which case it is carried through with the filtrate and not retained with the solids in the filter cake. Consequently, the lowering trend of phosphorus concentration is observed better in the levels found in the filtrate in which the mean concentration dropped from 69.16 mg/l (January 1979 through June 1979) to 60.52 mg/l (July 1979 through June 1980 - Fig. 4.11).

In the wash water input, the mean phosphorus concentration is

very low (0.09 mg/l - Fig. 4.12) which increased to 0.44 mg/l (Fig. 4.13) in the wash water output due to contribution from washing of the vacuum filter cloth.

4.3.3 Chloride

The mean chloride concentration of the air classified light fraction (1.24 mg/g, Fig. 4.8) has not altered significantly this year from that which was found last year (1.34 mg/g, Table 4.3).

However, a general increasing trend in the mean chloride level is noticeable this year in the digester slurry (from 165.33 mg/l to 229.74 mg/l, Table 4.4), filter cake (from 0.31 mg/g to 0.62 mg/g, Table 4.5) and filtrate (from 148.11 mg/l to 238.46 mg/l, Table 4.6). This build-up of chloride concentration in the digester may be due to the recirculation of the filtrate back to the digester. The mean chloride content (48.37 mg/l, Table 4.7) of the wash water input has dropped considerably this year from that found last year (76.91 mg/l, Table 4.7). Consequently, there has also been a lowering of chloride levels this year in the wash water effluent from 91.96 mg/l to 53.02 mg/l (Table 4.8).

4.3.4 Sulfide

The sulfide concentration has been monitored in the digester slurry, filtrate, wash water input and effluent. During this year, the sulfide concentration in the digester slurry varied from 0.0 to 6.53 mg/l (Fig. 4.9) which was lower than that found last year when it varied from 1.87 to 9.06 mg/l (Table 4.4). The sulfide level in filtrate was slightly lower than that in the digester slurry and varied from 0.0 to 4.94 mg/l (Fig. 4.11) between July 1979 through June 1980. During the earlier period, January 1979 through June 1979, sulfide level in the

filtrate varied from 1.52 to 5.33 mg/l which shows a fairly similar range of values to that of this year. Wash water input showed a sulfide concentration varying from 0.0 to 2.4 mg/l (Fig.4.12) between July 1979 through June 1980. The sulfide level slightly increased in the wash water effluent due to contribution from impurities left over in the cloth of vacuum filter. The levels varied between 0.97 to 7.95 mg/l (Fig.4.13); the corresponding levels found between January 1979 through June 1979 were between 1.19 to 6.13 mg/l.

4.3.5 BOD, COD, TOC

From July 1979 through June, 1980, BOD of the digester slurry varied between 224 to 2345 mg/l (Fig.4.15), with the levels found in November 1979 lying close to the upper value found during this period. During the earlier period (January through June 1979) the BOD of the digester slurry varied between 1272 to 7150 mg/l (Table 4.4). The BOD of the filtrate varied from 312 to 2981 mg/l (Fig.4.17) during July 1979 through June 1980 with the levels found earlier between January 1979 through June 1979 ranging between 390 to 2429 mg/l (Table 4.6). 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 Chian & De Walle [4]. 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 in the above study. One of the reasons for this is that the

raw waste may be more completely metabolized by the microorganisms under the controlled conditions in the digester 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 affect 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 [4].

The COD level of the air classified light fraction varied between 179 mg/g and 1620 mg/g (Fig. 4.14) during July 1979 through June 1980 which shows a slightly higher range of concentration compared to that obtained in the previous period, January 1979 through June 1979 (286 mg/g to 1226 mg/g, Table 4.3). The COD of the digester slurry varied between 7500 mg/l to 32,515 mg/l (Fig. 4.15) from July 1979 through June 1980 which indicates an increasing trend compared to that found in the period January through June 1979 when the level varied between 12880 to 26640 mg/l (Table 4.4). This increase may be attributed to the continuous recycling of the filtrate over a long period which may be causing a gradual build up of the non-biodegradable organic matter. The filtrate also shows an increasing trend in COD ranging from 2514 mg/l to 9950 mg/l (Fig. 4.17) compared to the values during the earlier six month period, January through June 1978, when it varied between 1700 to 8500 mg/l (Table 4.6).

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. COD values of leachate from sanitary landfill reported in a study by Chian and De Walle [4] showed COD levels ranging from 40 to 89,520 mg/l which indicate a large variation and much higher levels than that found in the filtrate of the digester under study. Another study by Chian and De Walle [5] 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 fairly uniform during July 1979 through June 1980, the values ranging from 1365 mg/l to 2719 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 (Table 4.6). Chian and De Walle [5] 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 shows a considerable variation on a day-to-day basis, which has also been noted in other research studies by Chian and De Walle [4]. It may also be meaningful to study the ratio of different parameters as well as their absolute values. In the digester slurry the BOD/COD ratio varied between 0.03 to 0.07 during this year (July 1979 through June 1980), which indicates a fairly uniform quality of the slurry as compared to that found during January through June 1979 when it varied between 0.10 to 0.27.

In the case of the filtrate, however, the BOD/COD ratio varied from 0.12 to 0.30 during this year but was uniform at a value of 0.29 during the earlier period, January through June 1979. Miller et al [6] 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 Chian and De Walle [4] 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, indicating also a buildup of non-biodegradable organic matter in landfills as well as in digestors. However, similar field studies on actual soil samples with the filtrate from the digester would have to be performed to determine the lowering of BOD/COD ratio over given periods of time. The COD/TOC ratio of the filtrate varied between 1.9 to 3.7 during this year and from 2.4 to 4.3 during last year, which indicates a similar range of values during both the periods. Chian and De Walle [4] 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 [7] 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 270 to 1560 mg/l (Table 4.4) and that in the filtrate varied from 18400 to 36600 mg/l (Table 4.6) during July 1979 through June 1980. Corresponding values observed during January through June 1979 were 2000 to 9500 mg/l (Table 4.4) and 500 to 4200 mg/l (Table 4.6) respectively.

The suspended solids in digester slurry varied from 10700 to 21200 mg/l during July 1979 through June 1980 and that in the filtrate varied between 11600 to 16300 mg/l. Corresponding levels of suspended solids observed during January through June 1979 in digester slurry and filtrate were between 14000 to 27000 mg/l and 1800 to 5100 mg/l respectively.

4.3.7 Elemental Analysis

Fifteen samples of air classified light fraction, collected from July 1979 through June 1980, and one sample of filter cake were analyzed for carbon, hydrogen and nitrogen contents, on a percent-by-weight basis. These results, along with the theoretical levels for cellulose, are summarized in Table 4.9. 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 the paper or to compounds present in the plastics. 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 one 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 [10]). Bacterial samples were also collected in May and June, 1980. These samples also showed normal levels (6.3×10^6 total, 6.1×10^6 fecal; 1.1×10^7 total, 5.7×10^6 fecal; 4.6×10^6 total, 4.4×10^6 fecal; for digester slurry (CFU/100 ml), filter cake (CFU/100 g) and filtrate (CFU/100 ml), respectively. Owing to the spotty nature of plant operations such as feed, nutrient additions and mixing, it is felt that these data may be inaccurate and hence they are not plotted in the figures. The fluctuating levels may be related to changing rates of nutrient addition, or to changing quality of the refuse input. When the bacterial population became 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 measurements were 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. Once the plant begins operations and sampling resumes, another run of air classified light fraction is planned as part of the increase in emphasis on bacterial analysis.

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 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 between July, 1979 and June, 1980 are summarized in Tables 4.2 through 4.8. Data are reported as means and ranges. Results from the last year (January to June 1979) are included for comparative purposes.

The data indicate that levels of most metals have stabilized in the various digester streams. The notable exception to this is manganese. Throughout this year, manganese levels have been approximately twice as high as previously observed. Fluctuations are relatively large however, and there is much overlap within the ranges of the two years' results. More data will be needed to determine if there is an increasing trend.

A comparison of heavy metal concentrations in the filtrate as performed by the Miami team, with one performed by the Ames team (Sengupta et al [11]), revealed major differences in levels of cadmium, chromium, cobalt, copper, iron, manganese and zinc. The levels reported by Ames was 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 [10]). 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, they may be misleading due possibly to adsorption of the metal ions onto the glass walls

of the sample container. Therefore, samples sent to Ames for heavy metal analyses are being sent in plastic bottles; samples for organic analyses continue to be sent in glass.

Air classified light and air classified heavy samples fluctuate quite widely in the levels of the heavy metals. If the value of one sample is very high, the mean level for that metal at that sampling site will be affected. Therefore, a direct comparison of the means will provide little insight into possible changes. More samples will allow for better understanding of the yearly changes in solid waste composition.

4.4 Spiking Study

4.4.1 Introduction

Analytical procedures can be affected by sample constituents other than the one of interest. Chemical interactions between the various constituents present in a sample can result in raised or lowered values of the parameter being measured. Such interferences may be referred to as "matrix effects". Measurement of dissolved oxygen by the Winkler technique, for example, is subject to positive interferences from oxidizing agents, and to negative interferences from reducing agents [3]. These types of interferences also apply to other parameters of interest. The objective of this study was to determine the effectiveness of standard analytical techniques, such as those described in Standard Methods [3], in analyzing anaerobically digested refuse samples of unique characteristics as compared to the domestic wastewaters and sludges for which these techniques are accepted.

Two different types of studies are normally performed by analytical chemists in order to determine how much a given technique is susceptible to matrix effects in the samples. The first uses 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 is not possible with refuse samples, at present, since the composition is not completely known to enable the preparation of a synthetic sample.

The second type of study, which was used in this work, requires the addition of known amounts of the parameter of interest (called "spikes") to actual samples. The resulting mixture was then analyzed and the amount of spike added was determined.

De Walle et al [8] described a "round-robin" series of analyses on landfill leachate and ground water samples. In that study, no synthetic samples were prepared; however, one sample was spiked with 29 parameters of interest and distributed to 32 laboratories in the United States and Canada for analysis. Overall mean relative recoveries ranged from -138% to 328%.

Edwards et al [9] discussed a study of five certified water analysis laboratories in California. Synthetic samples were prepared and analyzed in a "double-blind experiment". The analysts did not know that these test samples were being used to evaluate their performances. Four types of samples were used: Nutrients in deionized water; minerals in synthetic ground water, both spiked and unspiked; trace elements in deionized water; and trace elements in seawater, both spiked and unspiked. Relative errors in the analysis of synthetic groundwater samples ranged from -75% to +827%.

Recoveries in the spiked mineral sample ranged between -14% and +230% with 100% being the exact amount added.

4.4.2 Method

In our study, process filtrate was spiked in appropriate amounts so that the final concentration varied from 1 to approximately 2.5 times the amount of that constituent normally present in an actual sample. Furthermore, an appropriate amount of distilled water was added to keep the final volume constant. All additions were performed prior to any pretreatment steps.

In all cases, the analyses were performed in the usual manner, as described in Section 4.1, above. In most cases, the spiked samples were analyzed in duplicate.

In addition, analysis was performed on a composite spike. In this case, each of the constituent was added to a single solution. Two different levels of spike were used, along with two blinds, one in distilled water and one in filtrate.

4.4.3 Data Analysis

Data generated by these analyses can be evaluated in a number of ways. The slope, intercept, and correlation coefficient of the least squares straight line can be calculated for the concentration found in the mixture versus the concentration of spike added. The intercept value represents the most probable value of the constituent present in the original unspiked sample. The correlation coefficient indicates whether the least squares line is a statistically proper description of the data. The slope indicates the relative recovery of the method. The results of these calculations for the ammonia nitrogen spike are presented in Figure 4.25. The graph

depicts a plot of the concentration of ammonia-nitrogen found in the mixture of filtrate, spike and water, on the ordinate, versus the concentration of ammonia nitrogen from the spike in that mixture on the abscissa. The relative recoveries for the other parameters examined in this study are listed in Table 4.10, along with those values found by De Walle et al [8] and Edwards et al [9].

In all cases except for silver, the correlation coefficient indicates that the least squares line yields a reasonable value of the constituent and is a statistically valid description of the data. In the case of silver (Figure 4.26), however, the concentration found reaches an asymptote at 0.11 mg/l. This is probably due to precipitation of silver by chloride. This precipitation, however, is not likely to affect results at the normally encountered levels of 0.05-0.06 mg/l found in filtrate.

In order to determine if recoveries for other metals were affected at levels higher than those normally encountered, geometrically increasing spikes were conducted for four selected metals. Copper, cadmium, iron and zinc were added at levels of 5, 50 and 100 times the amounts normally present in filtrate. In all four cases, the recoveries were constant up to 100 times the level of metal normally present in filtrate.

Relative recoveries were also determined for six different composite spikes, and are listed in Table 4.11. Negative recoveries were found here for some of the non-metal parameters. In general, the non-metal parameters showed poorer reliability than did the metals. In many cases, however, the recovery found in filtrate samples is nearly identical to that found in the distilled water samples. These "distilled-water-matrix-controlled recoveries" are listed in the last column in Table 4.11.

These recoveries only provide limited information. Figure 4.27 shows the recovery graph for nitrite. Note that the distilled water matrix yields a straight line (6.7% theoretical) while the filtrate matrix curve is more complex. The least squares line for these data is nearly a horizontal line (recovery = 1.6%). The recovery on the first leg (between points A and B), however, is -3.2%.

While the above data analysis can be used to determine the accuracy of the test, another method of analyzing the data can indicate the precision. If it is assumed that the spike is measured in the proportion indicated by the relative recovery, then subtracting that amount from the quantity found in the mixture results in an estimate of the concentration of the original unspiked sample. The mean, standard deviation and standard error for these values for all parameters are listed in Table 4.12. The standard deviations and standard errors are listed as both absolute and relative values. Relative values are expressed as a percentage of the mean.

4.4.4 Discussion of Results and Conclusion

There appears to be few similarities between the relative recoveries found in this study and those reported by De Walle et al. [8] for landfill leachate and by Edward et al. (9) for synthetic samples (Table 4.10). Relative recoveries found in this study ranged from 44% for nitrate nitrogen to 174% for calcium. De Walle et al. [8] reported values (means of many laboratories) between 0138% (lead) and +328% (potassium); Edwards et al. reported recoveries ranging from -350% (lead) to +230% (nitrate). Negative recoveries were found in our study only with "mixed spike" samples. It is very likely that interferences between spiking solutions resulted

in the negative recoveries found. This points out the importance of conducting spiking experiments with single spikes, or at least with an appropriate control: one in which all the spikes are added to distilled water. This, then, must be analyzed by identical methods so as to separate matrix effects from the sample itself and those from self-interference within the spikes. Most cases of interferences found in composite spikes in this study were mainly due to interactions between the constituents of the spiking solution itself.

For individual spikes, the mean of the recoveries is 98%, and nearly two thirds (11 out of 18 parameters) lie within the range of 80% to 120%.

The results show good precision. The relative standard deviations (or coefficients of variation) are on the order of 10% for most of the parameters analyzed. Only the COD parameter had a relative standard deviation greater than 21% (78%). This is quite reasonable and in good agreement with those values found in Standard Methods [3]. De Walle et al. [8] reported coefficients of variation between 32% (COD) to 210% for cadmium. The much lower levels found validate that differences between laboratories are greater than differences within a laboratory.

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TABLE 4.1 Summary of Samples Collected

Date	Sample Collection Sites
<u>1979</u>	
7/25	7
7/30	5, 8, 11
8/8	1, 2, 5, 7, 8, 11, 12
8/15	5 8, 11
8/23	2, 5, 7, 8, 11, 12
9/7	1, 2, 5, 7, 8, 11, 12
9/14	2, 5, 7, 8, 11, 12
9/20	2, 5, 7, 8, 11, 12
9/28	2, 5, 7, 8, 11, 12
10/11	1, 2, 5, 7, 8, 11, 12
10/19	2, 5, 11
11/1	1, 2, 5, 11
11/8	2, 5, 7, 8, 11, 12
11/15	2, 5, 7, 8, 11, 12
<u>1980</u>	
5/14	1, 2, 5, 7, 8
5/28	2, 5, 7, 8, 11, 12
6/11	2, 5, 7, 8, 11, 12
<u>Sites</u>	<u>Sample Description</u>
1	Air Classified Heavy
2	Air Classified Light
5	Digester Slurry
7	Filter Cake
8	Filtrate
11	Vacuum Filter Wash Water Input
12	Wash Water Effluent

TABLE 4.2 Summary of Air Classified Heavy Fraction Analyses

Parameter	Jan. 1979-June 1979			July 1979-June 1980			Units	Remarks
	Mean	Low	High	Mean	Low	High		
*Cadmium	12	.880	25	3.51	0.92	10.3	mg/L	3
Calcium	6200	750	16800	7810	831	12500	"	
*Chromium	4.80	5.85	11.70	5.50	4.02	9.62	"	1,2,3
Cobalt	0.66	0.2	2.1	0.97	0.41	1.92	"	
*Copper	5400	9.710	26700	13.6	8.9	21.3	"	1,2,3
Iron	860	390	1420	620	488	1210	"	1,2
*Lead	200	38.2	376.0	Not Available			"	1,2,3
Manganese	80	17.5	204	94.2	42.7	179	"	
*Nickel	23	3.30	90	5.62	3.85	7.21	"	
*Silver	0.49	.300	.840	0.61	0.27	0.93	"	3
*Zinc	230	33.2	758	270	41.3	783	"	1,2

Remarks: 1) Discharge Standards exist for this parameter
 2) Ground Water Standards exist for this parameter
 3) EPA Drinking Water Standards exist for this parameter
 * Priority Pollutant specified by EPA.

TABLE 4.3 Summary of Air Classified Light Fraction Analyses

Parameter	Jan. 1979-June 1979			July 1979-June 1980			Units	Remarks
	Mean	Low	High	Mean	Low	High		
Organic Nitrogen	0.45	0.14	0.87	0.63	0.17	1.79	mg/g	4
Ammonia Nitrogen	0.26	0.00	0.73	0.23	0.00	0.54	"	2,4
Chloride	1.34	0.46	3.14	1.24	0.05	1.65	"	1,2,3
Total Phosphate								
Phosphorus	1.09	0.10	4.00	0.52	0.26	1.16	"	
COD	851	286	1226	796	179	1620	"	
*Cadmium	1.60	0.41	3.46	1.77	0.57	3.91	"	3
Calcium	5500	440	10700	6560	3210	8760	"	
*Chromium	14.0	3.64	36.50	13.0	4.8	35.1	"	1,2,3
Cobalt	2.30	0.70	4.20	2.19	0.93	3.71	"	
*Copper	2000	3.93	1230	25.6	3.62	54.4	"	1,2,3
Iron	930	400	1546	504	384	624	"	1,2
*Lead	81.0	16.82	201	75.1	29.3	168	"	1,2,3
Manganese	120	25.90	533	56.7	27.1	83.7	"	
*Nickel	4.00	0.91	10.30	3.12	1.15	7.32	"	
*Silver	0.58	0.22	1.23	0.61	0.19	1.27	"	3
*Zinc	340	59	1260	359	157	821	"	1,2
Carbon	43.9	41.9	45.9	45.8	42.8	51.9	g/100g dry wt.	
Hydrogen	5.87	5.64	6.40	6.36	5.92	7.80	"	
Nitrogen	0.51	0.26	1.01	0.41	0.17	0.77	"	
Oxygen	49.7	46.9	52.1	47.4	40.1	50.9	"	
Digester Input per day	2.60	0.0	10.47	7.26	0.0	19.28	Tons	5
*Arochlor 1248	1560	820	2300	-	-	-	ppb	6,7,8
*Diethylhexylphthalate								6,8,9
*Dimethylphthalate								6,8,9

- Remarks:
- 1) Discharge Standards exist for this parameter
 - 2) Ground Water Standards exist for this parameter
 - 3) EPA Drinking Water Standards exist for this parameter
 - 4) This Parameter will be oxidized to Nitrate for which EPA Drinking Water Standards exist.
 - 5) Data compiled from WMI "Technical Status Reports," March 1978-June 1980
 - 6) Analyses conducted at Ames Laboratory. Data compiled from Sengupta et al [1,10].
 - 7) Arochlor is a PCB
 - 8) One sample only (June 1980). Different isolation procedures were used; only the higher value reported here. See Chapter V.
 - 9) Detected, but concentration unspecified
- * Priority Pollutant specified by EPA.

TABLE 4.4 Summary of Digester Slurry Analyses

Parameter	Jan. 1979-June 1979			July 1979-June 1980			Units	Remarks
	Mean	Low	High	Mean	Low	High		
Organic Nitrogen	63.82	49.28	112.31	63.38	36.29	79.52	mg/L	4
Ammonia Nitrogen	196.66	117.33	294.00	126.03	74.30	158.48	"	2,4
Nitrite Nitrogen	18.43	0.84	53.32	1.35	0.01	11.10	µg/L	4
Nitrate Nitrogen	2.77	1.11	9.18	11.82	1.08	73.08	mg/L	3,4
Chloride	165.33	31.92	247.02	229.74	205.21	267.93	"	1,2,3
Total Phosphate								
Phosphorus	249.70	25.00	447.30	168.43	102.75	303.57	"	
Sulfide	4.68	1.87	9.06	4.35	0.00	6.53	"	
BOD ₅	3085.0	1272.0	7150.0	1379	224.00	2345.0	"	
COD	19323	12880	26640	17636	7500	32515	"	
* Cadmium	0.13	0.03	0.30	0.15	0.04	0.19	"	3
Calcium	520	290	688	543	360	708	"	
* Chromium	1.20	0.44	5.40	0.82	0.50	1.51	"	1,2,3
Cobalt	0.16	0.11	0.21	0.14	0.1	0.4	"	
* Copper	3.6	1.19	14.00	2.56	1.47	4.27	"	1,2,3
Iron	91	60	132	96	75	120	"	1,2
* Lead	7.50	0.30	50	Not Available			"	1,2,3
Manganese	5.60	3.60	10	11.1	7.1	14.7	"	
* Nickel	0.45	0.27	0.96	0.48	0.31	0.70	"	
* Silver	0.063	0.02	0.10	0.06	0.03	0.07	"	3
* Zinc	18	4.80	29	20	13	29	"	1,2
Barium	----	----	----	5.1	3.0	7.2	"	
Suspended Solids	19.4	14.0	27.0	13.6	10.7	21.2	g/L	
Dissolved Solids	6.7	2.0	9.5	0.94	0.27	1.56	"	
Temperature	26.04	23.38	31.13	34.31	32.10	36.01	°C	5,6
pH	6.87	6.80	6.93	6.97	6.68	7.24	-	5,6
Alkalinity	1964.08	1636.21	2035.03	2005.7	1610.63	2171.53	mg/L CaCO ₃	5,6
Volatile Acids	166.51	32.53	281.79	467.74	108.9	1685.46	mg/L	5,6

- Remarks:
- 1) Discharge Standards exist for this parameter
 - 2) Ground Water Standards exist for this parameter
 - 3) EPA Drinking Water Standards exist for this parameter
 - 4) This Parameter will be oxidized to Nitrate for which EPA Drinking Water Standards exist.
 - 5) Data compiled from WMI "Technical Status Reports," March 1978-June 1980
 - 6) Process control parameter
- * Priority Pollutant specified by EPA

TABLE 4.5 Summary of Filter Cake Analyses

Parameter	Jan. 1979-June 1979			July 1979-June 1980			Units	Remarks
	Mean	Low	High	Mean	Low	High		
Organic Nitrogen	0.49	0.32	0.68	0.41	0.07	1.01	mg/g	4
Ammonia Nitrogen	0.22	0.13	0.32	0.17	0.01	0.75	"	2,4
Nitrite Nitrogen	1.39	0.01	16.95	0.37	0.09	2.00	µg/g	4
Nitrate Nitrogen	0.85	0.00	13.97	0.07	0.02	0.34	mg/g	3,4
Chloride	0.31	0.09	0.68	0.62	0.34	1.10	"	1,2,3
Total Phosphate								
Phosphorus	0.70	0.17	1.27	0.85	0.09	3.16	"	
BOD ₅	37.98	11.2	62.00	5.90	0.23	21.38	"	
COD ₅	258	3.0	448	427	167	764	"	
* Cadmium	1.10	0.41	2.37				"	3
Calcium	2600	500	4930	3692	521	8110	"	
* Chromium	7.00	2.92	19.20	6.10	2.24	9.96	"	1,2,3
Cobalt	1.00	0.58	1.70	1.00	0.60	1.31	"	
* Copper	71.0	2.30	420	21.0	5.61	33.4	"	1,2,3
Iron	600	220	834	680	273	2290	"	1,2
* Lead	80	37.70	264	Not Available			"	1,2,3
Manganese	50	24	120	46	26.1	63.2	"	
* Nickel	3.20	1.60	4.01	2.0	1.6	3.5	"	
* Silver	0.48	0.21	1.15	0.61	0.41	1.03	"	3
* Zinc	150	117	264	163	123	317	"	1,2
* Arochlor 1248	3.3	(One Sample)		----	----	----	ppb	5,6
* Diethylhexylphthalate	10 ⁶	(One Sample)		----	----	----	"	5
* Dimethylphthalate	10 ⁶	(One Sample)		----	----	----	"	5

- Remarks:
- 1) Discharge Standards exist for this parameter
 - 2) Ground Water Standards exist for this parameter
 - 3) EPA Drinking Water Standards exist for this parameter
 - 4) This Parameter will be Oxidized to Nitrate for which EPA Drinking Water Standards exist.
 - 5) Analyses Conducted at Ames Laboratory. Data compiled from Sengupta et al, [10].
 - 6) Arochlor is a PCB

* Priority Pollutant specified by EPA.

TABLE 4.6 Summary of Filtrate Analyses

PARAMETER	JANUARY 1979-JUNE 1979			JULY 1979-JUNE 1980			UNITS	REMARKS
	MEAN	LOW	HIGH	MEAN	LOW	HIGH		
ORGANIC NITROGEN	44.42	17.25	101.92	46.46	27.2	66.53	mg/L	4
AMMONIA NITROGEN	183.87	106.85	235.2	113.04	77.90	146.36	"	2,4
NITRITE NITROGEN	18.00	1.59	50.82	2.75	0.01	22.1	µg/L	4
NITRATE NITROGEN	2.55	0.00	8.80	5.04	0.15	11.7	mg/L	3,4
CHLORIDE	148.11	31.92	260.32	238.46	13.7	353.42	"	1,2,3
TOTAL PHOSPHATE	69.16	24.00	143.12	60.52	0.49	213.10	"	
SULFIDE	3.66	1.52	5.33	3.45	0.00	4.94	"	
B.O.D. ₅	1343.00	490.00	2429.00	817.00	312.00	2981.00	"	
C.O.D.	4599	1700	8500	6741.00	2514.00	9950.00	"	
*CADMIUM	0.057	0.02	0.12	0.12	0.05	0.18	"	3
CALCIUM	300	207	447	296	201	424	"	
*CHROMIUM	0.34	0.12	0.72	0.47	0.27	0.83	"	1,2,3
COBALT	0.12	0.06	0.18	0.17	<.05	0.40	"	
*COPPER	0.74	0.17	1.50	1.32	0.90	1.69	"	1,2,3
IRON	29	14.20	60	32	26	38	"	1,2
*LEAD	1.30	0.50	3.88	Not Available			"	1,2,3
MANGANESE	2.40	0.31	3.25	6.98	4.60	8.56	"	
*NICKEL	0.25	0.11	0.38	0.34	0.20	0.71	"	
*SILVER	0.37	0.01	0.06	0.03	<0.01	0.06	"	3
*ZINC	8.50	2.40	44	10	3.9	27	"	1,2
BARIUM	-	-	-	2.8	1.5	4.2	"	
C.C.E.	221	2.00	950	-	-	-	"	
SUSPENDED SOLIDS	2.4	1.8	5.1	12.7	11.6	16.3	g/L	
DISSOLVED SOLIDS	2.6	0.5	4.2	24.9	18.4	36.6	"	
T.O.C.	1740	700	2000	1862	1365	2719	mg/L	

TABLE 4.6 CONTINUED

PARAMETER	JANUARY 1979-JUNE 1979			JULY 1979-JUNE 1980			UNITS	REMARKS
	MEAN	LOW	HIGH	MEAN	LOW	HIGH		
ACETIC ACID	2300			-	-	-	ppm	5,7
*DIELDRIN	0.015			0.13			ppb	5,7,
*AROCHLOR 1248	3.6	3.3	4.0	22			ppb	5,6,7
*DIETHYL PHTHALATE	255	10	500	-	-	-	ppb	5
*DIBUTYL PHTHALATE	30	30	30	-	-	-	ppb	5
*DIETHYL HEXYL PHTHALATE	255	10	500	-	-	-	ppb	5
*DIISOBUTYL PHTHALATE	10	10	10	-	-	-	ppb	5
*BUTYLBENZYL PHTHALATE	1	1	1	-	-	-	ppb	5
*FLUORAN THANE	.006			-	-	-	ppb	5,7
*NAPHTHALENE	2	2	2	-	-	-	ppb	5,7
*PYRENE	.009			-	-	-	ppb	5,7
*DDD	-	-	-	0.16			ppb	7
*DDT	-	-	-	0.16			ppb	7
2,4-D				32			ppb	7
HYDROLYZED DCPA				0.05			ppb	7
PROPIONIC ACID								8
DIMETHYL BUTANOIC ACID								8
4-METHYL OCTANOIC ACID								8
OCTANOIC ACID								8
7-METHYL NONANOIC ACID								8

TABLE 4.6 CONTINUED

PARAMETER	JANUARY 1979-JUNE 1979			JULY 1979-JUNE 1980			UNITS	REMARKS
	MEAN	LOW	HIGH	MEAN	LOW	HIGH		
BENZENE ACETIC ACID								8
BENZENE PROPIONIC ACID								8
BENZENE BUTANOIC ACID								8
TOLYACETIC ACID								8
(DIMETHYL BENZENE) ACETIC ACID								8
3-METHYL BENZOIC ACID								8
TETRAMETHYL PENTANOIC ACID								8
3,6-DIMETHYL OCTANOIC ACID								8
2-ETHYL BUTANOIC ACID								8
2-2 DIMETHYL BUTANOIC ACID								8
HEXADECANOIC ACID								8
3-OCTENOIC ACID								8
TRIMETHYL-2- PENTENOIC ACID								8

TABLE 4.6 CONTINUED

PARAMETER	JANUARY 1979-JUNE 1979			JULY 1979-JUNE 1980			UNITS	REMARKS
	MEAN	LOW	HIGH	MEAN	LOW	HIGH		
4-METHYL CYCLOHEXANOIC ACID								8
4-(1,5-DIMETHYL- 3-OXOHXYL) CYCLOHEXANOIC ACID								8
4-METHYL BENZOIC ACID								8
3,5-DIMETHYL BENZOIC ACID								8
2-HYDROXY-3- METHYL BENZOIC ACID								8
2-METHYL-3,4- DIHYDROXY BENZOIC ACID								8
BUTANEDIOIC ACID								8
α -1,4-DICARBOXYLIC ACID								8
4-METHYL PHTHALIC ACID								8
ABIATIC ACID								8
DIBUTYL PHOSPHORIC OR DIISOBUTYL PHOSPHORIC ACID								8
2-(4-CHLOROPHENOXY)- 2-METHYL PROPANOIC ACID								8, 9
2-METHOXY-2- PENTENDIOIC ACID								8

-
- Remarks:
- 1) Discharge Standards exist for this parameter.
 - 2) Ground Water Standards exist for this parameter.
 - 3) EPA Drinking Water Standards exist for this parameter.
 - 4) This parameter will be oxidized to Nitrate for which EPA Drinking Water Standards exist.
 - 5) Analysis conducted at Ames Laboratory, Data compiled from Sengupta et al [1,10].
 - 6) Arochlor is a PCB.
 - 7) One sample only. Different isolation procedures were used. Only the higher value reported here. See Chapter V.
 - 8) Detected, but concentration unspecified.
 - 9) Herbicide decomposition product

* Priority Pollutant specified by EPA.

TABLE 4.7 Summary of Wash Water Input Analyses

Parameter	Jan. 1979-June 1979			July 1979-June 1980			Units	Remarks
	Mean	Low	High	Mean	Low	High		
Organic Nitrogen	1.10	0.00	3.53	0.83	0.00	5.10	mg/L	4
Ammonia Nitrogen	0.41	0.00	2.35	0.47	0.00	1.51	"	2,4
Nitrite Nitrogen	2.67	0.32	8.59	0.06	0.00	0.39	µg/L	4
Nitrate Nitrogen	0.63	0.37	1.69	0.69	0.00	2.55	mg/L	3
Chloride	76.91	0.00	182.41	48.37	5.00	71.44	"	1,2,3
Total Phosphate								
Phosphorus	0.31	0.00	0.78	0.09	0.01	0.23	"	
Sulfide	0.93	0.00	3.73	1.40	0.00	2.40	"	
BOD ₅	0.33	0.00	1.00	2.73	0.33	8.90	"	
COD	70.00	0.00	194.0	48.0	0.00	98.00	"	
*Cadmium	0.06	0.03	0.08	0.06	0.01	0.10	"	3
Calcium	190.0	108.0	260.0	183	160	219	"	
*Chromium	0.046	0.01	0.32	0.15	0.03	0.46	"	1,2,3
Cobalt	0.060	0.04	0.11	0.07	<0.05	0.20	"	
*Copper	0.11	0.02	0.37	0.45	0.06	0.96	"	1,2,3
Iron	1.40	1.02	1.71	1.6	0.99	2.7	"	1,2
*Lead	ND	----	<0.15	Not Available			"	1,2,3
Manganese	0.038	0.01	0.10	0.06	0.01	0.12	"	
*Nickel	0.088	0.03	0.16	0.13	0.05	0.24	"	
*Silver	ND	----	<0.01	ND	----	<0.01	"	3
*Zinc	4.80	0.06	44.00	0.55	0.40	0.81	"	1,2
Barium	----	----	----	0.2	0.1	0.3	"	
TOC	----	----	----	0.0	0.0	0.0	"	

- Remarks:
- 1) Discharge Standards exist for this parameter.
 - 2) Ground Water Standards exist for this parameter.
 - 3) EPA Drinking Water Standards exist for this parameter.
 - 4) This Parameter will be oxidized to Nitrate for which EPA Drinking Water Standards exist.
- * Priority Pollutant specified by EPA.

TABLE 4.8 Summary of Wash Water Effluent Analyses

Parameter	Jan. 1979-June 1979			July 1979-June 1980			Units	Remarks
	Mean	Low	High	Mean	Low	High		
Organic Nitrogen	10.50	0.00	34.69	2.72	0.00	11.38	mg/L	4
Ammonia Nitrogen	3.68	0.00	11.49	1.09	0.00	3.02	"	2,4
Nitrite Nitrogen	11.15	2.26	28.42	1.99	0.00	15.80	µg/L	4
Nitrate Nitrogen	1.59	0.45	2.13	0.96	0.00	2.44	mg/L	3,4
Chloride	91.96	6.08	202.17	53.02	5.00	71.44	"	1,2,3
Total Phosphate								
Phosphorus	1.53	0.46	3.28	0.44	0.04	1.14	"	
Sulfide	3.06	1.19	6.13	2.54	0.97	7.95	"	
BOD ₅	61.65	35.43	87.88	16.85	5.75	45.47	"	
COD	221.0	59.00	588.0	343.0	13.0	889.0	"	
*Cadmium	0.058	0.04	0.07	0.10	0.01	0.17	"	3
Calcium	160.0	148.0	196.0	175	160	205	"	
*Chromium	0.073	0.50	0.11	0.23	0.02	0.81	"	1,2,3
Cobalt	0.073	0.40	0.90	0.14	<0.05	0.30	"	
*Copper	0.25	0.10	0.77	0.60	0.10	1.31	"	1,2,3
Iron	1.70	1.07	2.59	2.7	1.6	10.1	"	1,2
*Lead	0.20	0.10	0.30	Not Available			"	1,2,3
Manganese	0.14	0.02	0.30	0.40	0.10	15.1	"	
*Nickel	0.09	0.05	0.12	0.17	0.05	0.29	"	
*Silver	0.012	0.01	0.02	0.01	<0.01	0.03	"	3
*Zinc	0.64	0.26	2.00	0.95	0.56	2.15	"	1,2
Barium	----	----	----	0.3	0.1	1.2	"	
TOC	----	----	----	5.4	0.0	7.9	"	

- Remarks:
- 1) Discharge Standards exist for this parameter
 - 2) Ground Water Standards exist for this parameter
 - 3) EPA Drinking Water Standards exist for this parameter
 - 4) This Parameter will be oxidized to Nitrate for which EPA Drinking Water Standards exist.
- * Priority Pollutant specified by EPA.

TABLE 4.9 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	45.82	42.82-51.92	48.41	44.45
HYDROGEN	6.36	5.92-7.80	6.30	6.22
NITROGEN	0.41	0.17-0.77	0.86	0
OXYGEN**	47.40	40.11-50.94	44.43	49.34

* All data reported as g/100 g dry weight

** Calculated by difference:
Per cent Oxygen = $100 - (\% \text{ Carbon} + \% \text{ Hydrogen} + \% \text{ Nitrogen})$

*** 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%

TABLE 4.10 Results of Relative Recoveries

PARAMETER	FOUND IN THIS STUDY ON FILTRATE (%)	FOUND BY DE WALLE ET AL. (1979) ON LEACHATE	FOUND BY EDWARDS ET AL. (1977) ON SYNTHETIC GROUND WATER % (LOWEST, HIGHEST)
Total Organic Nitrogen	93	-	-
Ammonia Nitrogen	84.1	245	-
Nitrite Nitrogen	119	-	-
Nitrate Nitrogen	44	-126	10,230
Total Phosphorus	157	-31.5	-
Chloride	104	172	66,222
COD	70	32.9	-
TOC	65	137	-
Sulfide	80	-	-
Zinc	86.1	11.7	3,80
Calcium	174	8.7	-
Iron	86	-8.4	-
Manganese	85.1	-	-
Nickel	88.5	96.7	-
Cobalt	154	-	-
Cadmium	56.7	31.4	<0, <96
Copper	111	14.3	-92,150
Chromium	101	25.5	0,24

TABLE 4.11 Recoveries in Composite Spike

PARAMETER	DIST. WATER MATRIX		FILTRATE MATRIX		REC. OF FILT/REL.REC. OF D.W.
	REL.REC.	CORR.COEF.	REL.REC.	CORR.COEF.	
NH ₃	0.00%	1.00	-33.3%	-.866	-
TON	602%	.9995	805%	.998	1.34
NO ₂	6.66%	.999	1.59%	.501	0.239
NO ₃	2.28%	.948	1.86%	.968	.815
P	37.4%	.871	37.2%	.811	.994
Cl	-0.11%	-.866	6.03%	.999	-55.00
S	10.2%	.878	1.45%	.277	.142
COD	53.3%	.999	53.2%	.972	.997
TOC	346%	.988	370%	.995	1.07
Ca	96.8%	.9996	97.9	.9991	1.01
Co	150%	1.000	175%	.86	1.17
Cr	87.2%	1.000	91.7%	.985	1.05
Mn	79.7%	.994	88.9%	.998	1.12
Zn	85.8%	.998	58.0%	.9998	0.676
Cu	101.9%	.985	94.2%	.988	.925
Fe	92.7%	.997	93.3%	.971	1.01
TKN	174%	.9995	209%	1.00	1.20

Correlations are significant if the correlation coefficient is greater than 0.950 (p=.05).

TABLE 4.12 Concentration in Unspiked Sample

TEST	FOUND DIRECTLY*	INTERCEPT OF STRAIGHT LINE*	CALCULATED BY SUBTRACTION OF SPIKE			
			STANDARD DEVIATION		STANDARD ERROR	
			ABSOLUTE*	RELATIVE	ABSOLUTE*	RELATIVE
Total Organic Nitrogen	43.35	39.6	7.7	19.3%	3.8	9.7%
Ammonia	149.2	143.3	9.1	6.4%	3.2	2.2%
Total Phosphorus	89.8	97.9	8.7	8.9%	4.4	4.5%
Chloride	239	252	12.7	5.0%	4.5	1.8%
COE	224	200	157	78%	55.6	27.7%
Nitrite	0.0190	0.0211	0.0025	12%	0.0009	4%
Nitrate	3.11	2.95	0.25	8.4%	0.10	3.4%
TOC	1243	1132	134	12%	47	4.2%
Zn	6.8	6.6	0.48	7.3%	0.17	2.6%
Ca	402	392	28	7.1%	10	2.5%
Fe	19.4	19.9	1.3	6.3%	0.45	2.2%
Mn	1.76	1.79	0.06	3.3%	0.02	1.2%
Ni	0.30	0.29	6.2	21%	2.2	7.6%
Co	0.14	0.15	0.014	9.1%	0.005	3.2%
Cd	0.15	0.14	0.03	21%	0.01	7.7%
Cr	0.29	0.30	0.04	12%	0.01	4%
S ⁻²	0.64	0.602	0.05	8.3%	0.03	5%

* All data as mg/l.

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

FIG. 4.2 $\text{NH}_3\text{-N}$ and ORG.-N in Air Classified Light Fraction

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

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

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

FIG. 4.6 ORG.-N, $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$ in Wash Water Input

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

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

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

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

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

* Values x 100

** Values x 10

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

* Values x 10

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

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 and COD in Wash Water Input

FIG. 4.19 Concentration of BOD and COD in Wash Water Effluent

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.

FIG. 4.25 Ammonia Spike in Filtrate, Relative Recovery = 0.841, Correlation Coefficient = 0.9899

FIG. 4.26 Silver Spike in Filtrate

FIG. 4.27 Phosphate Composite Spike in Filtrate and Distilled Water

FIG. 4.28 Nitrite Composite Spike in Filtrate and Distilled Water

V. TRACE ANALYSIS

The following section is a summary of tasks performed during the last quarter. This is excerpted substantially from a quarterly report by Dr. Chriswell.

5.1 Progress

The digester at the RefCOM Facility at Pompano Beach resumed intermittent operation late in this report period. The one set of sample that has been obtained since resumption of operations is still being characterized. Pesticide determinations have been completed on the process filtrate sample taken during June, 1980. During the extended period when the Pompano Beach facility was not in operation emphasis was placed on the improvement of analytical methods for characterizing effluent constituents.

5.1.1 Pesticide Determinations in Process Filtrate

PCB's, Dieldrin, DDD, DDT, 2,4-D acid, and hydrolyzed DCPA were detected in the process filtrate sample taken during June, 1980. The levels of these contaminants were very low (see Table 5), but it is considered significant that with the exception of PCB's none of these species has previously been detected in process filtrate. The detection of 2,4-D acid and hydrolyzed DCPA reflects the development of a new, more effective XAD-4 anion exchange procedure for their isolation from aqueous samples such as process filtrate. The detection of DDT, DDE and Dieldrin may reflect a change in digester feedstock composition or a change in digester operation.

The limiting factor in the determination of pesticides in process filtrate is the isolation step. Thus, the higher value for each pesticide is considered more accurate.

5.1.2 Isolation of Pesticides from Water

As previously reported, a technique has been developed at the Ames Laboratory for isolating acidic organic impurities from aqueous solutions. Part of this procedure involves passing an aqueous sample through an ion exchange resin which retains acidic materials. The substrate for this ion exchange resin is Amberlite XAD-4 resin which is an excellent adsorbent for neutral organic species. Simultaneously with the accumulation of acidic materials, some neutral species are retained on the XAD-4 substrate. These neutral species are diluted with a solvent such as methanol before dilution of the acidic materials with an acidified solvent. It has been discovered that this step, which was originally intended as a clean-up step, leads to greater recovery of some organic neutral species than does the use of conventional adsorption or solvent extraction techniques. This enhanced recovery efficiency has been documented in laboratory studies, with samples from the anaerobic digester (see the previous section) and with samples from the Des Moines River at several locations in Iowa (see Table 5.2).

5.1.3 Isolation of Organic Species from Particulates

Particulates formed during the combustion of organic fuels such as digester gas contain adsorbed organic species. Isolation and characterization of these adsorbed compounds is required to assess the potential environmental effect of the use of digester gas. Conventional techniques for isolation of materials from particulates are ineffective or marginally effective for some species. This is primarily because particulate matter contains silica, alumina

and activated carbon, all of which are excellent adsorbents.

A new isolation technique based on partial dissolution of particulates with hydrofluoric acid (HF) has been developed. The HF serves to dissolve the silica and deactivate the alumina and, thus, make it more feasible to recover some organic species from the residual solids and liquids. The basic techniques were described in the previous quarterly report and will be described in detail in a paper being prepared for submission to Analytical Chemistry.

Because no digester gas particulates are available, the technique has been tested using electroprecipitator ash from the Iowa State University power plant. Constituents were isolated from this ash using the HF treatment, a similar technique in which hydrochloric acid (HCl) was substituted for HF and a conventional ultrasonic solvent extraction procedure.

Treatment of the ash with either HCl or HF led to the isolation of greater amounts of most organic species than did ultrasonic extraction. Because the goal of this work was to evaluate the technique rather than determine ash constituents no serious attempt was made to identify isolated materials. However, major constituents were tentatively identified as phenols, phthalate esters, and polyaromatic hydrocarbons.

One marked difference in the use of HF and HCl was in the recovery of phenol. HF treatment led to the isolation of large amounts of phenol while HCl treatment and conventional extraction yielded none.

A summary of the findings is included in Table 5.3.

5.2 Status

One objective of this study has been to characterize constituents present in potential effluents from the anaerobic digester. A great deal of progress has been made towards this objective. The intermittent operation of the digester at the RefCOM Facility at Pompano Beach has allowed time to be devoted to intensive study of individual samples and has allowed adequate time for the development of analytical methodologies.

A second objective of this study is to determine the levels of contaminants present in potential plant effluents. These data are required to assess the potential environmental impact of the facility at Pompano Beach. Because of the sporadic operation of the digester, no sample of plant effluents obtained to date can be considered as representative of typical operation. Until stable operation of the digester is obtained, accomplishing the objective of determining the levels of contaminants in plant effluents will not be possible.

TABLE 5.1 Pesticides in Process Filtrate - June, 1980

Isolation Procedure	Concentration of Listed Species (ng/g)					
	PCB's (Arochlor 1248)	Dieldrin	DDD	DDT	2,4-D Hydrolyzed Acid	DCPA
XAD-4 Anion Exchange	12.2	0.04	0.12	0.11	32.0	0.05
MeCl ₂ Extraction	22.0	0.13	0.16	0.05	ND*	ND*

* ND = Not Detected

TABLE 5.2 Pesticides Determined in Water Samples from the Des Moines River in Iowa, (ng/g)

<u>Pesticide</u>	<u>Location</u>			
	<u>Boone</u>	<u>Saylorville</u>	<u>Des Moines</u>	<u>Red Rock</u>
<u>Isolation Technique</u>				
<u>Atrazine</u>				
XAD-2 Adsorption	0.73	0.71	0.45	2.28
XAD-4 Anion Exchange	0.74	0.82	--	1.50
<u>Propachlor</u>				
XAD-2 Adsorption	0.29	0.31	0.20	0.99
XAD-4 Anion Exchange	0.30	0.30	--	0.72
<u>Matribuzin</u>				
XAD-2 Adsorption	0.23	0.22	0.08	0.09
XAD-4 Anion Exchange	0.23	0.23	--	0.09
<u>2,4-D Acid</u>				
XAD-2 Adsorption	N.D.	N.D.	N.D.	0.86
XAD-4 Anion Exchange	1.31	N.D.	0.04	0.73
<u>DCPA</u>				
XAD-2 Adsorption	0.008	0.006	0.003	0.004
XAD-4 Anion Exchange	0.007	0.007	0.012	0.004
<u>DCPA Hydrolyzed</u>				
XAD-2 Adsorption	N.D.	N.D.	N.D.	N.D.
XAD-4 Anion Exchange	0.03	N.D.	0.04	0.03
<u>Dieldrin</u>				
XAD-2 Adsorption	0.004	0.002	0.001	0.002
XAD-4 Anion Exchange	0.006	0.003	0.005	0.003
<u>Alachlor</u>				
XAD-2 Adsorption	1.28	1.32	0.55	0.86
XAD-4 Anion Exchange	1.41	1.41	0.77	0.77
<u>Cyanazine</u>				
XAD-2 Adsorption	0.86	1.02	--	2.44
XAD-4 Anion Exchange	0.95	1.23	0.43	2.28
-- = not determined				
N.D. = not detected				

TABLE 5.3 Extraction of Organic Species from Electroprecipitator Ash

<u>Isolation Technique</u>	<u>Total Organic Material (mg/Kg)</u>	<u>Phenol (mg/Kg)</u>
HF Treatment	14.0	13.0
HCl Treatment	1.0	0.0
Ultrasonic	0.2	0.0

VI. LEACHING EXPERIMENTS

6.1 Introduction

The work in this Chapter was done largely by Dipankar Dasgupta in conjunction with his thesis work, [17]. Except for Sections 6.4 and 6.6.5, the material is essentially the same as that presented in Reference [17].

There are various factors influencing metal migration through soil. Research identifying some of these factors has been published by Fuller, et al [1]. Korte, et al [2] report metal movement as influenced by soil physical and chemical properties. Leachate of varying properties affect the movement of certain metal ions through a clay mineral system, Griffin, et al [3].

In order to develop confident guidelines for predicting pollutant migration through soil, the soil must be uniquely characterized. A literature survey indicates that the principal factors which can be used in the characterization of the pollutant and porous medium are;

- (a) organic content of the soil
- (b) pH of the soil paste
- (c) density of the soil
- (d) initial concentration of different cations of interest in the soil
- (e) the soil cation exchange capacity
- (f) pH of pollutant medium
- (g) initial concentration of the different cations in the pollutant medium

The key mechanisms which govern interaction within a soil leachate system are convection, diffusion, biological transformation, chemical adsorption or desorption, precipitation and transformation. There are other secondary effects, eg. plant uptake. These mechanisms are dependent on the characteristics of the soil and the leachate. It is

these physical, chemical and biological phenomena. Instead these mechanisms may be approximated by certain mathematical expressions. The effect of diffusion can be lumped within a single term, the hydrodynamic dispersion coefficient, Cherry [4]. This coefficient lumps the effect of molecular and turbulent diffusion. The biological transformation can be expressed in terms of a decay term. According to this assumption, the rate of change of pollutant concentration due to biological organisms is directly proportional to the concentration in the liquid phase, Metry [5].

Chemistry adsorption is modelled by an equation describing the dependency of the sorbed concentration on the solution concentration. This is done by using an appropriate adsorption isotherm, Genuchten [6].

The hydrodynamic dispersion coefficient and the biological rate constant are dependent on certain characteristic properties of the soil. These properties are the porosity of the soil, clay, sand & silt content of the soil, organic content of the soil, etc.

The chemical rate constant is dependent on the above mentioned characteristic properties of the soil, certain characteristic properties of the leachate and also on interactions that exist within the soil leachate system. As such these coefficients have to be determined by direct experimentation with the particular soil leachate system.

To achieve this objective, the following steps were taken in this phase of the work.

- (i) Characterization of the pollutant transport media/matrix media
- (ii) Batch experiments for the four Pompano Beach soils at pH 6.8
- (iii) Batch column experiments

6.2 Soil Characterisation

In a soil survey, U.S.D.A. [12], of the area around the Pompano Beach area the principal types of soil were recognised as:

- (a) Hallandale fine sand
- (b) Plantation muck

Hallandale fine sand consists of a single type of soil between the ground surface and bedrock. The soil profile of Plantation muck shows three distinct layers--the top, the middle and the bottom. The soils were characterized by determining their--

- (i) organic content
- (ii) pH of paste
- (iii) initial concentration of the eight cations; copper, zinc, iron, manganese, cadmium, chromium, calcium
- (iv) cation exchange capacity

6.2.1 Organic Content

The organic content of the soils was determined by loss of ignition method. A known weight of sundried soil was ashed to constant weight at 1000 F in a muffle furnace. The difference in weight gave the organic content of the soil.

6.2.2 pH Determination

The soil was saturated with carbon dioxide-free distilled water. After half an hour, the pH of the paste was measured with a digital pH meter. The experiment was repeated for each soil. The average of the two experimental results are shown in Table 6.2.

6.2.3 Initial Concentration Of Cations

The initial concentration of the eight cations; copper, zinc, manganese

iron, nickel, cadmium, chromium and calcium were determined by sequential batch extraction process. The soils were extracted several times until the extract showed negligible amounts of all the cations. The procedure adopted was:

- (1) 10 g. of soil was shaken with 100 ml. of 7.5N nitric acid for 24 hrs.
- (2) the bottles containing the soil acid mixture were allowed to sit for 30 mins. and the supernatant poured out.
- (3) the supernatant was dried on a steam table heated in an oven at 150 C for 3 to 4 hrs.
- (4) the residue obtained after ashing was dissolved in 15N nitric acid diluted with distilled water and filtered through Wattman 100 filter paper.
- (5) the filtrate was brought up to 100 ml. in volumetric flask and then analysed on an atomic absorption spectrometer.
- (6) the remains in the bottle after step (2) was reshaken for 24 hrs. with 50 ml. of 7.5N nitric acid.
- (7) steps (1) through (4) were repeated until the level of all the cations of interest in the extract became negligible.

The results for all four soils are shown in Table 6.3.

6.2.4 Cation Exchange capacity

The cation exchange capacities of the soils were determined according to the procedure in reference, Mario [13].

4-5 g. of the soil was saturated with four successive 33 ml. increments of pH 8.2, 60% ethanol solution of 0.1N NaOAc- 0.1N NaCl. Equilibrium was achieved by shaking the soil solution mixture for 5 mins. The exhausted solutions were decanted after centrifugation. If the soil was initially high in salts ($EC_e > 2 \mu\text{mhos/cm.}$) it was washed with one 33 ml. increment of water before saturation. Excessive washing was prevented

to avoid loss of soil particle during decantation.

The saturated samples were extracted with three 33 ml. increment of 1.0N pH 7.0 solution of MgNO_3 . Both sodium (Na_t) and chloride (Cl_t) were subsequently determined in solution. Chloride was determined so that the soluble sodium (Na_{sol}) from the excess saturating solution carried over from the saturating step to the extraction step may be deducted from the total sodium to obtain exchangeable sodium (Na_{exch}).

Thus

$$\text{C.E.C} = (\text{Na}_t - \text{Na}_{\text{sol}})$$
$$= \text{Na}_t - [\text{Cl}_t (\text{Na}/\text{Cl})_{\text{sat. sol.}}]$$

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

The results are tabulated in Table 6.4.

6.2.5 Equilibrium Studies

One of the major assumptions made in the development of the mathematical model, for predicting pollutant attenuation by soil, is that the soil and the infiltrating leachate are always in equilibrium. This is substantiated by the fact that the downward movement of the leachate is extremely slow. To simulate this in the laboratory, the time needed for a soil leachate system to come to equilibrium has been experimentally determined. The equilibrium experiment was designed to determine this time for all the four soils. The experimental procedure adopted was:

- (i) 10.0 g. of soil was mixed with 100.0 ml. of leachate in a 250.0 ml. polystyrene bottle.
- (ii) several such mixtures were made and the bottles were attached to a shaker at the same time.
- (iii) the bottles were removed from the shaker after time intervals

of 24, 48, 72 and 96 hrs. from the start.

(iv) the contents of each bottle were filtered under pressure in an ultra-filtration unit through 2 micron filter paper.

(v) the filtrate was evaporated on a steam table, heated at 150° C. in an oven and then ashed at 550° C in a muffle furnace.

(vi) the residue was dissolved in 15N nitric acid diluted with distilled water and filtered through Wattman 3 filter paper.

(vii) the filtrate was brought up to 100.0 ml. in a volumetric flask and analysed for the eight cations of interest on an Atomic Absorption Spectrometer.

(viii) the length of time beyond which the heavy metal concentration did not change appreciably was defined as the equilibrium time.

6.3. Batch Experiment on Cations

This experiment was designed to understand the nature of chemical interaction existing within a particular soil leachate system. In order to quantify this chemical behavior, two independent adsorption isotherms, the linear Lapidus & Amundson [7] and the nonlinear Langmuir, Tanji [8] were assumed. The experimental results were used to determine the chemical rate constants appearing in the mathematical expressions representing the respective isotherms. The procedure adopted was:

(i) 0.2, 1.0, 2.0, 5.0, 10.0 g. of soil were mixed with 100.0 ml. of leachate in five separate bottles.

(ii) the bottles were shaken for the length of equilibrium time as determined in the previous experiment.

(iii) the contents of the bottle were filtered under pressure in an ultra-filtration unit through 2 micron filter paper.

(iv) the filtrate was dried on a steam table, heated in an oven at 150°C. and ashed in a muffle furnace at 550°C.

(v) the residue was dissolved in 15N nitric acid and diluted with distilled water and filtered through Whatman 3 filter paper. The filtrate was brought up to 100.0 ml. in a volumetric flask.

(vi) the solution was analysed on an Atomic Absorption Spectrometer for the eight cations of interest.

6.4 Batch Experiment On Anions

The experiment was designed to determine the chemical interaction between the soil and the leachate with regards the anions, i.e., (i) total organic carbon (TOC), (ii) phosphate-phosphorus, (iii) total organic nitrogen (TON), (iv) ammonia-nitrogen, (v) nitrite-nitrogen, (vi) nitrate-nitrogen, (vii) total nitrogen. The procedure adopted was as outlined below.

- (i) 0.3, 1.5, 3.0, 7.5, 15.0 g of soil were mixed with 150.0 ml of leachate in five separate bottles.
- (ii) the bottles were shaken for the length of equilibrium time as determined by the method described in the previous section.
- (iii) the contents of the bottle were filtered under pressure in an ultra-filtration unit through 2 micron filter paper.
- (iv) the anions were analysed according to standard methods, (14).

6.5 Batch Column Experiment

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 attenuate different chemical species. However, an important limitation of

this method is the time and effort required to analyse a sufficient number of samples to make predictions of migration rates. This usually takes months and may even take years. However, sequential batch extraction of soil with leachate can provide much the same information, Houle & Lang (9). 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 extraction can be the basis for an accelerated testing of flow of leachate through soil.

In the present work the sequential batch experiment (from now on being referred to as batch experiment) was performed to provide the following information:

(i) variation in concentration of the eight cations (Cu, Zn, Fe, Mn, Ni, Cd, Cr, Ca) in the liquid phase, as the leachate travels through the different layers of soil.

(ii) variation with time in the concentration of the eight cations at a particular depth.

The experimental procedure adopted was:

(i) 100.0 g of soil was mixed with 1000.0 ml. of leachate in a bottle.

(ii) the bottle was shaken for the length of equilibrium time.

(iii) the contents of the bottle were filtered under pressure in an ultra-filtration unit through a 2 micron filter paper.

(iv) 100.0 ml. of the filtrate was separated for analysis.

(v) the remaining portion of the filtrate was mixed with new soil such that the ratio of the volume of the filtrate to the weight of the soil was 10:1.

(vi) the soil obtained as residue from the filtration process was mixed with new filtrate in the same ratio.

(vii) steps (i) to (iv) were repeated for each bottle.

(viii) this process was continued till twenty four different samples were obtained.

(ix) all the samples were stored at pH below 2.0 and analysed as per steps (iv) to (vi) of the batch experiment.

The flow chart for the experiment is shown in Fig.6.29. The notations used are:

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

A_{IJ} = 100.0 ml. of aliquot for analysis obtained on filtration of the contents of bottle B_{IJ} .

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

6.5.1 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 particular volume

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

Let

X = weight of soil.

V = volume of filtrate

A = area of the column

L = length of the column

ρ = bulk density of soil

W = pore water velocity

The time taken by the leachate to travel length L of the column is L/W . The time needed to collect volume V of the leachate at the first sampling port is V/WA . Length L of the column to contain weight X of soil of bulk density ρ_b is $X/\rho_b A$.

Thus if volume V of leachate is mixed with weight W of soil the composition of the leachate after it has been shaken is equivalent to the composition of leachate collected at the ports of a continuous column over a period of time equal to V/WA , where the ports are separate by a distance of $X/\rho_b A$.

6.6 Results And Discussions

The results for organic content of the soil are tabulated in Table 6.1.

Hallandale fine sand has the least amount of organic matter. This soil is totally sandy in nature. Plantation muck bottom layer is also sandy but since it is the bottommost layer of an otherwise clayey soil, it has some amounts of organics. Plantation muck middle and top layer have more than 50% by weight of organic matter. These two soils are very rich in grass, roots and other types of vegetations. The top layer has about 5% more organics than the middle layer.

6.6.1 pH of Soil

These results are tabulated in Table 6.2.. All the soils are basic in nature. This is expected since Florida soils contain a high percentage of limestone.

6.6.2 Initial Concentration Of Metallic Species On Soil

The results for the initial concentration of the various cations in the four soils are tabulated in Table 6.3. Fig. 6.1-6.8 show the concentration of the cation in various extracts.

For all the four soils, the concentration of calcium is highest. Presence of limestone and other calcium bearing rocks accounts for this. Besides calcium, the level of iron is also very high. Since the soils are basic in nature 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 the alkaline pH decreases the mobility of the element, Allaway (15). This attributes to the high concentration levels of the metal.

Concentration of all cations in Plantation muck middle and top layer are much higher than that in Plantation muck bottom layer and Hallandale fine sand. Both these layers have high clay contents. Clayey

soils are known to have higher cation concentrations, U.S. Army Engg. (16).

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, zinc, iron and calcium have been desorbed 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 both these soils. These metals are extracted after the sites containing the more mobile cations copper, iron and calcium have been replaced by hydrogen ion.

Plantation muck middle and top layers behave very similarly. It can be seen from Figs. 6.1-6.8 that none of the cations show selective desorption. This may be because of high concentration levels of all the cations.

6.6.3 Cation Exchange Capacity

The cation exchange capacity for all the four soils is tabulated in Table 6.4.

It can be seen that the C.E.C. for Hallandale fine sand is about the same as that for Plantation muck bottom layer, which is mainly sand. The C.E.C's for the Plantation muck top and middle layer are very similar since both are clayey in nature.

As is expected the C.E.C's for Plantation muck top and middle layers are about 3 times that for Hallandale fine sand and Plantation muck bottom layer. Clayey soils compared to sandy soils are known to

have higher cation concentration and therefore more exchangeable sites.

The C.E.C's for all the four soils are less than the respective cation concentration expressed in micro eq/g. This is because hydrogen ion is more active than sodium, hydrogen being above sodium in the electrochemical series.

6.6.4 Batch Experiment On Cations

The adsorption isotherms for the batch experiment on cations are shown in Fig.6.9 - 6.16. As has been discussed two independent isotherms have been used to model the chemical adsorption and ion exchange. Let us first consider the Langmuir nonlinear isotherm.

The mathematical equation which describes this isotherm is,

$$S = \frac{K_1 K_2 C}{1 + K_1 C} \quad (6.6.4-1)$$

where

S = amount of cation adsorbed per unit mass of the soil

C = concentration of the cation in the liquid phase at equilibrium

K_1, K_2 = experimentally determined chemical rate constants

As discussed by Veith, et al [10], and Harter, et al [11], unless adsorption is proven to be the only phenomenon present by an independent experiment, the constants K_1 and K_2 may not have much physical significance. However, the form of the equation makes it a reasonable tool to fit the experimental data obtained in the present work. The constants K_1 and K_2 have been obtained by least squares fit from the plot of $1/S$ Vs $1/C$. Equation (6.6.4-1) may be written as

$$\frac{1}{S} = \frac{1}{K_1 K_2} \frac{1}{C} + \frac{1}{K_2} \quad (6.6.4-2)$$

So the constants K_1 and K_2 are obtained from the intercept and the gradient of the straight line plots. These values are listed in Table 6.6.

It should be noted that the experimental values of nickel and cadmium were in general not very good. This is because the concentration of these metals were close to or below the detection limit on an Atomic Absorption Spectrometer.

From the experimental results, the following features stand out. In general the shape of the adsorption isotherm tend to follow one of the two forms shown in Table 6.7. In Table 6.7(a), the adsorption isotherm tend to a maximum value of $S = K_2$. This value of S is the maximum amount of cation that can be adsorbed by the soil under the environment studied. From equation (6.6.4-1) for $S = \frac{1}{2}S_{\max}$, $C = 1/K_1$. Therefore K_2 is an equilibrium constant while K_1 gives the rate at which the equilibrium is reached or it is an equilibrium rate constant. If adsorption is not the only phenomenon present, the coefficients K_1 and K_2 can take negative values. Such a case is indicated in Table 6.7(b). In this figure there appears to be a value of the equilibrium concentration $C = 1/K_1$ beyond which there can be no experimental points. This probably indicates that precipitation of the cation has taken place. With the experimental technique used there was no way of distinguishing between adsorption and precipitation.

From the Figs. 6.9 - 6.16 it can be seen that for all the cations Plantation muck middle and top layer exhibit better adsorption capabilities than the other two soils. This is expected since clayey soils absorb more than sandy ones.

Most of the cations, except iron and chromium, for Plantation muck top layer, and calcium and nickel for Hallandale fine sand follow the trend shown in Table 6.7(b). There is a maximum value of the concentration in the solution phase. If the concentration level goes beyond this, the cation is precipitated. This may be because of very high levels of calcium in the leachate.

A close look at equation (6.6.4-1) indicates that the two constants must be of the same sign. Opposite signs on K_1 and K_2 will give rise to a negative slope for the straight plot between $1/S$ and $1/C$. A negative slope implies that the concentration in the sorbed phase should fall with the rise in the solution concentration. This is physically not possible. The results tabulated in Table 6.5 show that all the constants are negative which is expected.

The Lapidus and Amundson linear constants are listed in Table 6.6. They were found by fitting a straight line through the data points. All the constants are positive which is expected.

6.6.5 Batch Experiment on Anions

The adsorption isotherms for the batch experiment on anions are shown in Figs. 6.17 - 6.28. The results are clearly more scattered than those for the cations.

Considering the results for total organic carbon (TOC), Fig. 6.17, it appears that the experimental data sit on two or three characteristics instead of one for each of the three Plantation muck layers. This could be explained by soil inhomogeneity. The T.O.C. for Hallandale fine sand was not done.

The experimental results for phosphate-phosphorus are presented

in Fig.6.18. There appears to be two characteristics for each of the soils.

The results for the total organic nitrogen (T.O.N.) are shown in Figs.6.19, 6.20. There appears to be more than one characteristic for Plantation muck top layer. The isotherms for Plantation muck middle and bottom layers are vertical straight lines. This means that the equilibrium concentration of the anion does not change with different ratios of soil/leachate. The T.O.N. results for Hallandale fine sand is scattered.

Figures 6.21, 6.22 are the results for nitrite-nitrogen. The adsorption constants for nitrite-nitrogen in the three layers of Plantation muck are given in Table 6.8. The results for Hallandale fine sand display at least three characteristics.

Figures 6.23, 6.24 are the results for nitrate-nitrogen. All four isotherms for the four types of soil have vertical straight line portions. This means that the nitrate anion concentration in the liquid is unchanged at equilibrium over a range of soil/leachate ratios.

The results for ammonia-nitrogen are presented in Figs.6.25, 6.26, and those for total nitrogen are presented in Figs.6.27, 6.28. The two sets of curves are very similar because total nitrogen is made up principally of ammonia-nitrogen. The results for Hallandale fine sand, Figs. 6.26 and 6.28, are well-behaved. The characteristics are vertical straight lines, which means that the ammonia anion concentration and the total nitrogen concentration remain essentially unchanged for different soil/leachate ratios. The results for the three layers of Plantation muck, however, display inhomogeneity. There are more than one branch

in the ammonia-nitrogen and the total nitrogen characteristics for each of the top layer, the middle and the bottom layers.

Besides inhomogeneity of the soil, inhomogeneity of the leachate has contributed to the widely scattered results. The fact that the different forms of nitrogen, for instance, are constantly changing their oxidation states with the shaking process, have also enhanced the inherent inhomogeneity in the liquid phase.

6.6.6 Batch Column Experiment

Figs. 6.30 - 6.37 show the variation of the cation concentration with depth for two instances of time. The concentrations have been nondimensionalised with respect to the initial concentration of the cation. The depth has been nondimensionalised with respect to the simulated length of the column.

Referring to section 6.5.1 the length of the simulated column between the consecutive sampling ports is $X/\rho_b A$. Since for this particular experiment the same leachate was shaken with six new batches of soil, the total length of the simulated column is $\Sigma X/\rho_b A$. The summation is for the six different weights of the soil for the six different batches. Thus the nondimensional distance between each sampling port is $X/\Sigma X$. The time needed to collect volume V of the leachate at a particular sampling port was calculated as V/WA . This time is nondimensionalised with respect to the time taken by the leachate to travel the whole length of the simulated column. Thus the nondimensional time over which a sample of leachate of volume V is collected is $V\rho_b/\Sigma X$.

From the plots in Figs. 6.30 - 6.37 it can be seen that all the cations follow a similar trend. Concentration of the cations decrease

with depth. This is the case when there is no desorption or precipitation present.

Copper in Fig. 6. 30 behaves abnormally. Although it is expected that the absorptive capacity of the soil should decrease with time, the opposite is found to happen. The concentration of copper in the liquid phase is found to decrease with time upto the nondimensional depth of 0. 8. This could be an experimental error.

For zinc, copper, iron and manganese the experimental results have been compared with the predictions made with the model. These four cations were chosen since their initial concentration in the leachate is well above the detection level on an Atomic Absorption Spectrometer. The predictions made with the Lapidus Amundson model were found to be considerably different from the experimental results. As such the profiles obtained with this model have not been plotted.

The Langmuir model was run for two different types of boundary conditions at the bottom of the soil layer, i.e. at $Z=L$. The boundary conditions chosen were;

$$\text{at } Z=L \quad -D \frac{\partial C}{\partial Z} + WC = VC \quad (6.6.6-1)$$

$$\text{at } Z=L \quad \frac{\partial C}{\partial Z} = 0 \quad (6.6.6-2)$$

The model was run for $D'=0.0068$, $K'=0.0$ and R' as obtained from the batch experiment.

Figs. 6. 38 - 6. 41 show the concentration profiles obtained with the model for the two different kinds of boundary conditions. It is seen from the plots that the predictions made by the Langmuir model, run with the second (6.6.6-2) boundary condition does not compare

well with experimental results below the nondimensional depth of 0.5.

Predictions made by using the first (6.6.6-1) boundary condition compares well with the experimental results.

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SOIL	ORGANIC CONTENT g/Kg
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 Organic Content of Soil

SOIL	AVERAGE pH
HALLANDALE FINE SAND	8.20
PLANTATION MUCK BOTTOM LAYER	7.30
PLANTATION MUCK MIDDLE LAYER	7.30
PLANTATION MUCK TOP LAYER	7.10

TABLE 6.2 pH of Soil

SOIL	Cu	Zn	(mg/g)		Cd	Cr	Ca	
			Fe	Mn				
HALLANDALE FINE SAND	.0010	.0063	.1028	.0051	.0041	.0032	.0047	.0944
PLANTATION MUCK BOTTOM LAYER	.0018	.0058	.3102	.0057	.0060	.0031	.0052	.9330
PLANTATION MUCK MIDDLE LAYER	.0055	.0107	19.004	.0375	.0124	.0050	.0207	23.71
PLANTATION MUCK TOP LAYER	.0055	.0096	4.163	.0123	.0084	.0033	.0142	17.87

TABLE 6.3 Initial Concentration of Cations in Soil

SOIL	CATION EXCHANGE CAPACITY meq/gm
HALLANDALE FINE SAND	1.13
PLANTATION MUCK TOP LAYER	4.53
PLANTATION MUCK MIDDLE LAYER	4.09
PLANTATION MUCK BOTTOM LAYER	1.58

TABLE 6.4 Cation Exchange Capacity

	COPPER	ZINC	MANGANESE	IRON	NICKEL	CADMIUM	CHROMIUM	CALCIUM
	HALLANDALE FINE SAND							
K ₁	.206	.870	.616	.071	.604	.072	1.729	1.117
	PLANTATION MUCK TOP LAYER							
K ₁	.248	.448	.521	.226	.892	.506	2.905	.751
	PLANTATION MUCK MIDDLE LAYER							
K ₁	.076	.375	1.127	.036	1.090	.193	.865	2.784
	PLANTATION MUCK BOTTOM LAYER							
K ₁	.266	.413	.159	.186	2.328	.323	.346	2.164

TABLE 6.5 Linear Constants

	COPPER	ZINC	IRON	MANGANESE	NICKEL	CADMIUM	CHROMIUM	CALCIUM
K ₁	-1.4620	-.4850	-.0800	-.5540	-4.336	-17.9760	-10.8240	-.0030
K ₂	-0.0001	-.0001	-.0010	-.0004	-0.0020	-0.0020	-0.0010	-.4580
HALLANDALE FINE SAND								
K ₁	-1.6820	-.5090	-.0630	-.5860	-5.360	-6.6570	-3.1760	-.0030
K ₂	-0.0004	-.0010	-.0120	-.0010	-0.0005	-0.0030	-0.0010	-.168
PLANTATION MUCK TOP LAYER								
K ₁	-1.5070	-.5020	-.0980	-1.0500	-5.1070	-4.9620	-7.3600	-.0030
K ₂	-0.0003	-.0010	-.0060	-.0410	-0.0010	-0.0040	-0.0010	-.2150
PLANTATION MUCK MIDDLE LAYER								
K ₁	-1.6820	-.4870	-.0840	-.5810	-4.9670	-4.7140	-12.3400	-.0020
K ₂	-0.0010	-.0003	-.0030	-.0003	-.0010	-0.0060	-0.0010	-.3600
PLANTATION MUCK BOTTOM LAYER								

TABLE 6.6 Langmuir Coefficients

TABLE 6.7 Adsorption Isotherm

TABLE 6.8 Adsorption Coefficients for the Anions

Parameter	Curve	$K_1 =$	$K_2 =$	(Vertical Line) $C =$
TOC	T1	-	-	1.00
	T2	-0.650	0.0004	-
	M1	-	-	1.15
	M2	-	-	1.42
	M3	-0.168	0.015	-
	B1	-	-	0.708
	B2	-	-	1.35
	B3	0.148	-0.033	-
P04-P	T1	-	-	1.64
	T2	-0.085	0.095	-
	M1	-0.287	-0.308	-
	M2	-0.171	0.062	-
	B1	-0.321	-0.008	-
TON	T1	-	-	8.2
	M1	-	-	3.52
	B1	-	-	6.73
NO ₂ -N	T1	-0.163	0.067	-
	M1	-0.034	0.096	-
	B1	-	-	10.8
	B2	-10.7	0.0004	-
NO ₃ -N	T1	-	-	1.07
	M1	-	-	1.08
	B1	0.641	0.014	-
NH ₃ -N	T1	-	-	167
	T2	-0.005	0.005	-
	M1	-0.005	-0.065	-
	B1	-0.005	-0.064	-
	B2	-0.005	-0.066	-
TOT.N	T1	-	-	194
	T2	-0.004	0.041	-
	M1	-0.004	-0.271	-
	B1	-0.005	-0.079	-

FIG.6.1 Initial Concentration of Copper in Soil

FIG.6.2 Initial Concentration of Zinc in Soil

FIG.6.3 Initial Concentration of Iron in Soil

FIG. 6.4 Initial Concentration of Manganese in Soil

FIG.6.5 Initial Concentration of Nickel in Soil

FIG.6.6 Initial Concentration of Chromium in Soil

FIG.6.7 Initial Concentration of Cadmium in Soil

FIG.6.8 Initial Concentration of Calcium in Soil

ADSORPTION ISOTHERM FOR COPPER

(1) PLANTATION MUCK TOP LAYER □

(2) PLANTATION MUCK MIDDLE LAYER ☆

(3) PLANTATION MUCK BOTTOM LAYER ▲

(4) HALLANDALE FINE SAND *

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

FIG.6.9 Adsorption Isotherms for Copper.

FIG.6.10 Adsorption Isotherms for Zinc

ADSORPTION ISOTHERM FOR IRON

FIG. 6.11 Adsorption Isotherms for Iron

FIG.6.12 Adsorption Isotherms for Manganese

ADSORPTION ISOTHERM FOR NICKEL

(1) PLANTATION MUCK TOP LAYER $\square$

(2) PLANTATION MUCK MIDDLE LAYER $\star$

(3) PLANTATION MUCK BOTTOM LAYER $\triangle$

(4) HALLANDALE FINE SAND $\ast$

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

FILTRATE P.H=6.9

FIG.6.13 Adsorption Isotherms for Nickel

FIG.6.14 Adsorption Isotherms for Cadmium

ADSORPTION ISOTHERM FOR CHROMIUM

(1) PLANTATION MUCK TOP LAYER $\square$

(2) PLANTATION MUCK MIDDLE LAYER $\star$

(3) PLANTATION MUCK BOTTOM LAYER $\triangle$

(4) HALLANDALE FINE SAND $\ast$

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

FIG.6.15 Adsorption Isotherms for Chromium

FIG.6.16 Adsorption Isotherms for Calcium

FIG.6.17 Adsorption Isotherm for TOC in Plantation Muck; (●) Top Layer, (■) Middle Layer, (□) Bottom Layer.

FIG.6.18 Adsorption Isotherm for Phosphate Phosphorus in Plantation Muck; (●) Top Layer, (■) Middle Layer, (□) Bottom Layer.

FIG.6.19 Adsorption Isotherm for Organic Nitrogen in Plantation Muck; (●) Top Layer, (■) Middle Layer, (□) Bottom Layer.

FIG. 6.20

FIG. 6.21 Adsorption Isotherm for Nitrite-Nitrogen In Plantation Muck;
 (•) Top Layer, (■) Middle Layer, (□) Bottom Layer.

FIG. 6. 22

FIG. 6.23 Adsorption Isotherm for Nitrate-Nitrogen in Plantation Muck;
 (•) Top Layer, (■) Middle Layer, (□) Bottom Layer.

FIG. 6.24

FIG. 6.25 Adsorption Isotherm for Ammonia-Nitrogen in Plantation Muck;
 (•) Top Layer, (■) Middle Layer, (□) Bottom Layer.

FIG . 6. 26

FIG. 6.27 Adsorption Isotherm for Total-Nitrogen in Plantation Muck;
(●) Top Layer, (■) Middle Layer, (□) Bottom Layer.

FIG 6.28

FIG.6.29 Flow Chart for Batch Column Experiment

FIG.6.30 Batch Column Experimental Results

FIG.6.31 Batch Column Experimental Results

FIG. 6.32 Batch Column Experimental Results

FIG.6.33 Batch Column Experimental Results

FIG.6.34 Batch Column Experimental Results

FIG. 6.35 Batch Column Experimental Results

FIG.6.36 Batch Column Experimental Results

FIG.6.37 Batch Column Experimental Results

FIG 6.38 Comparison of Batch Column results with Model predictions

— B.C at $Z=L$
 $-D \frac{\delta C}{\delta Z} + WC = VC$
 Langmuir Model

- - - B.C at $Z=L$
 $\frac{\delta C}{\delta Z} = 0$
 Langmuir Model

+ + + Lapidus Model
 $t/t_{ref} = 2.25$

- · - · - Lapidus Model
 $t/t_{ref} = 5.75$

⊙ Experimental
 Result $t/t_{ref} = 2.25$

× Experimental
 Result $t/t_{ref} = 5.75$

FIG 6.39 Comparison of Batch Column results with Model predictions

FIG 6.40 Comparison of Batch Column results with Model Predictions

FIG 6.41 Comparison of Batch Column results with Model Predictions

VII. MODELLING

7.1 Introduction

The types of mathematical models that have been developed for use in ground water contamination problems can be classified into four distinct groups: Saturated-unsaturated transport models Reference [1] thru [8], saturated-only transport models [9] thru [15], unsaturated-only transport models [16] thru [22], and analytical transport models [23][24].

Saturated-only transport models ignore the dynamics of the unsaturated zone between the waste disposal site and the ground water table. The change in properties of the leachate as it moves through the unsaturated zone cannot be accounted for in these models. To use these models it is necessary to have a method of quantifying the amount and quality of leachate reaching the groundwater table.

Unsaturated-only models cannot be used to describe contaminant migration in groundwater systems. However, the different models in this group are very useful tools for studying the mechanisms of contaminant transport in the unsaturated zone.

The saturated-unsaturated transport models are versatile as they are a combination of the saturated only and the unsaturated only models.

7.2 Approach

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, [25, 26]. 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, [27].

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

$$\phi \frac{\partial \gamma}{\partial t} + \text{div}(\overline{C_a \vec{v}}) - D \phi \text{div}(\nabla \gamma) + (1-\phi) \frac{K_1 K_2 \rho_s}{(1+K_1 \gamma)^2} \frac{\partial \gamma}{\partial t} = 0 \quad (7.3.1)$$

where C_a = mass concentration of component 'a'

ϕ = porosity

$\vec{v}$ = velocity vector

D = diffusivity

K_1, K_2 = Langmuir constants

ρ_s = 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, (27). 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

This section discusses the parametric studies with the Langmuir model.

The parametric studies with the Lapidus Amundson model has been presented in Reference [31] and published in Reference [32]. Reference [32] is appended.

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_o = 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 $K_1' = K_1 \gamma_o$

and $K_2' = (\frac{1-\phi}{\phi}) K_1 K_2 \rho_s$ 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 $t = 0$.

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 interface is taken to be that whatever diffuses out of the bottom of the top-soil layer is convected 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 species through the soil, the non-dimensionalized form of the finite difference model representing the one dimensional pollutant equation was computed under twenty-three different combinations of the three nondimensional groups. The combinations were chosen to cover the domain of interest. The highest value of the non-dimensional group was taken as 100.0 and the lowest value as -10.

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 twenty-three 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 eight of the twenty-three cases investigated are also attached. Figures 7.1-8 correspond to case (1) - (8) 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. 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 165.14 dimensionless units for case (19) in Table 7.1. This corresponds to the case of least mobility. The shortest steady state time is 0.0282 dimensionless unit for case (23) 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 high affinity of the pollutant to the solid phase. Case (23) corresponds to a condition of diffusion dominating over convection and the pollutant has no affinity to the solid phase.

7.5 Relative Mobility Studies with the One Dimensional Model

The models used were (i) the Lapidus-Amundson model and (ii) the Langmuir model. The one-dimensional Lapidus Amundson model transport equation is

$$\phi \frac{\partial C}{\partial t} + W \phi \frac{\partial C}{\partial Z} - D \phi \frac{\partial^2 C}{\partial Z^2} + (1-\phi) K_d \rho_s \frac{\partial C}{\partial t} = 0 \quad (7.5.1)$$

where C = intrinsic average ion 'a' concentration in the liquid

ϕ = porosity

D = diffusivity

W = average porewater velocity

ρ_s = density of the soil

Z = spatial dimension

t = time

The one dimensional Langmuir model transport equation is

$$\frac{\partial C}{\partial t} + W \frac{\partial C}{\partial Z} - D \frac{\partial^2 C}{\partial Z^2} + (1-\phi) \frac{K_1 K_2 \rho_s}{(1+K_1 C)^2} \frac{\partial C}{\partial t} = 0 \quad (7.5.2)$$

The initial and boundary conditions used are:

$$C = C_0 \quad \text{at} \quad Z=0 \quad \text{for} \quad t > 0 \quad (7.5.3a)$$

$$D \frac{\partial C}{\partial Z} + (V-W)C = 0 \quad \text{at} \quad Z=L \quad \text{for} \quad t < 0 \quad (7.5.3b)$$

$$C = 0 \quad \text{for} \quad 0 \leq Z \leq L \quad \text{for} \quad t = 0 \quad (7.5.3c)$$

where W = ground water velocity or in the aquifer

L = total depth of the soil column

It is assumed that an aquifer lies below the soil layer. The boundary condition at $Z = L$ means that whatever diffuses out of the bottom of the soil layer is carried away by the aquifer.

The pollutant transport models using the Lapidus-Amundson isotherm and (ii) the Langmuir isotherm, were solved numerically using experimental values for the distribution coefficients K_d , K_1 and K_2 . A literature survey was conducted to choose the representative values for the hydrodynamic dispersion coefficient D , the average pore water velocity W , and the ground water velocity V . The factors taken into

consideration for choosing these values are the characteristics of the soil, the characteristics of the liquid, the location of the site to which the model is applied, the hydrological characteristics of the aquifer and the average rainfall on the site. The values chosen are tabulated in Table 7.2.

Both the models were solved numerically for the four soils and the eight cations. It was assumed that only one type of soil lay between the bottom of the landfill and the top of the aquifer. The total depth of the soil was taken to be three meters. The concentration of a cation was nondimensionalized with its initial value, i.e. before reaction with the soil. The reference time for the numerical work was $L/W=3.45$ years.

The variation in the concentration of the eight cations, in a particular soil with depth, as predicted by both the models have been found. The change in the concentration profiles with time have also been determined. The steady state time is taken to be a measure of the relative mobility of the various cations. The steady state time is the length of time required for a particular ion to reach the steady state profile (which was determined numerically). A short steady state time indicates mobility, whereas a long steady state time indicates lack of mobility.

The criterion used for convergence is that the concentration profile does not change in the second decimal place in a time-step Δt . The time-step used for the Lapidus-Amundson model is 5×10^{-5} dimensionless unit, and that for the Langmuir model is 9×10^{-4} dimensionless unit.

7.5.1 Results

The variation in the concentration of a particular cation, manganese,

with depth is shown in Figure 7.9. These are typical of the curves obtained for all the eight cations with the four types of soils. Each curve is for a particular instant of time. The time corresponding to each curve is expressed in terms of dimensionless units (reference time = $L/W = 3.45$ years). In Fig.7.9, the plot is for the Lapidus-Amundson transport model prediction of manganese migration in Hallandale fine sand.

The values of the dispersion coefficient, the pore water velocity, the ground water velocity, the porosity and the depth are stipulated to be identical for both the models. Since the distribution coefficients only affect the transient terms in the models, it is expected that the steady state profiles are the same for both models. Moreover, since the initial conditions used for both models are the same, and the steady state profiles are the same, it is expected that the transient profiles are similar. However, the times to reach steady state for a particular cation and soil are predicted to be different by the two models.

The steady state times in dimensionless units for the migration of the eight cations in the four soils studied are tabulated in Tables 7.3 and 7.4. The results for the Lapidus-Amundson model are listed in Table 7.3, and those for the Langmuir model are listed in Table 7.4. The Langmuir model predictions are believed to be more accurate since the distribution of the ion between the solid and liquid phases is better modelled by the Langmuir isotherm. This can easily be seen from the experimental results of Chapter 6.

From Table 7.3, the most mobile cation is iron for Plantation muck top layer, and manganese for the other three soils. The least mobile

cation is chromium for Hallandale fine sand and Plantation muck bottom layer, nickel for Plantation muck top layer and calcium for Plantation muck middle layer.

From Table 7.4, the most mobile cation is manganese for Hallandale fine sand and Plantation muck bottom layer, iron for Plantation muck middle layer and copper for Plantation muck bottom layer. The least mobile cation is nickel for Hallandale fine sand and Plantation muck bottom layer, cadmium for Plantation muck top layer, and manganese for Plantation muck middle layer.

It can be seen that the predictions made by the Lapidus-Amundson model are quite different from those made by the Langmuir model. This is because the Lapidus-Amundson model assumes a linear distribution of the cation exists, whereas the Langmuir model more closely describes the nonlinear distribution of the cation between the soil and the liquid.

7.6 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

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

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

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

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 7.5. 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.

7.6.1 Results

The boundary conditions used to solve eqn. (7.6.1) 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 7.10-14 and have been chosen as a test case.

Figures 7.10 and 7.11 are the results for case (A) in Table 7.5. 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 7.12 and 7.13 are the results for case (B) in Table 7.5. 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 7.14 gives the results for case (C) in Table 7.5. 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).

7.6.2 Experimentally Determined Coefficients

The 2-D model is also solved for boundary condition (C) shown in Table 7.5, 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. 7.15 are as follows:

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

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

$$K_1' = K_1 \gamma_0 = -1.31436 \times 10^{-1} \quad (K_1 = -3.651 \text{ } \mu\text{g/mg})$$

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

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 7.15 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 7.16 shows what happens to the plume in Fig. 7.15 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.

7.7 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

$$\begin{aligned} \left[1 + \frac{(1-\phi)}{\phi} \frac{K_2'}{(1+K_1'\gamma')} \right] \frac{\partial \gamma'}{\partial t} + (u' \frac{\partial \gamma'}{\partial x'} + v' \frac{\partial \gamma'}{\partial y'} + w' \frac{\partial \gamma'}{\partial z'}) \\ - D \left(\frac{\partial^2 \gamma'}{\partial x'^2} + \frac{\partial^2 \gamma'}{\partial y'^2} + \frac{\partial^2 \gamma'}{\partial z'^2} \right) = 0 \end{aligned} \quad (7.7.1)$$

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

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

If the diffusion coefficient in the longitudinal direction is different from that in the y- and z-direction, eqn. (7.7.1) may be written as:

$$\begin{aligned} & \left[1 + \frac{(1-\phi)}{\phi} \frac{K_2'}{1+K_1' \gamma'} \right] \frac{\partial \gamma'}{\partial t} + (u' \frac{\partial \gamma'}{\partial x'} + v' \frac{\partial \gamma'}{\partial y'} \sigma + w' \frac{\partial \gamma'}{\partial z'} \sigma) \\ & - (D_1' \frac{\partial^2 \gamma'}{\partial x'^2} + D_2' \frac{\partial^2 \gamma'}{\partial y'^2} + D_2' \frac{\partial^2 \gamma'}{\partial z'^2} \sigma) = 0 \end{aligned} \quad (7.7.2)$$

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 (7.7.1) and (7.7.2) is $\gamma'=0$, at $x'>0$, $y'>0$, $z'>0$, $t=0$ ie. there is no pollutant in the domain of interest initially.

7.7.1 Results

The domain investigated in Figs.7.17-7.19 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.7.17 and 7.18 are shown in Table 7.6. 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 longer significant changes in the concentration of the pollutant.

Figures 7.17 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 7.18 shows the pollutant plume at steady state after 9.503 years. Figure 7.19 shows what happens to the plume in Fig. 7.18 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 7.19 shows the condition after 15.5 years i.e. about 6 years after pollution is discontinued).

In Figs. 7.20 and 7.21, the 3-D domain is same as for Figs. 7.17-7.19, 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. 7.22, 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. 7.20 and 7.21. The figure shows the pollutant plume at steady state after 16.51 years.

Compared to the two dimensional model, the steady state time is shorter 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).

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TABLE 7.1 Parametric Studies with Langmuir Model

	D'	K ₁ '	K ₂ '	$\gamma'(Z^*=1)$ AT STEADY STATE	STEADY STATE TIME
(1)	100	100	100	0.99	0.033
(2)	100	100	0.15	0.99	0.028
(3)	100	0.15	100	0.99	0.98
(4)	100	0.15	0.15	0.99	0.03
(5)	0.15	100	100	0.50	2.72
(6)	0.15	0.15	100	0.50	115.55
(7)	0.15	100	0.15	0.50	1.03
(8)	0.15	0.15	0.15	0.50	1.93
(9)	0.1	-0.1	5	0.50	15.07
(10)	0.1	-1	5	0.50	55.81
(11)	0.1	-10	5	0.50	11.76
(12)	0.1	-0.1	50	0.50	90.06
(13)	0.1	-1	50	0.50	114.15
(14)	0.1	-10	50	0.50	12.12
(15)	0.01	-0.1	5	0.50	9.58
(16)	0.01	-1	5	0.50	17.37
(17)	0.01	-10	5	0.50	17.16
(18)	0.01	-0.1	50	0.50	84.69
(19)	0.01	-1	50	0.50	165.14
(20)	0.01	-10	50	0.50	152.55
(21)	0.01	0	0	0.50	1.36
(22)	0.1	0	0	0.50	1.38
(23)	100	0	0	0.99	0.028

INPUT PARAMETER	VALUE CHOSEN	REFERENCE
1. Hydrodynamic dispersion coefficient, D	63.0 m ² /Yr	Freeze and Cherry (28)
2. Pore water velocity, W	0.87 m/Yr	Metry (29)
3. Ground water velocity V	28.1/Yr	Travers (30)

TABLE 7.2

CATIONS	HALLANDALE FINE SAND	PLANTATION MUCH TOP LAYER	PLANTATION MUCK MIDDLE LAYER	PLANTATION MUCH BOTTOM LAYER
Cu	21	9	6	19
Zn	88	12	16	34
Fe	62	4	50	40
Mn	8	5	2	17
Ni	60	77	46	67
Cd	8	11	8	38
Cr	173	12	36	220
Ca	112	72	117	56

TABLE 7.3 Steady State Times of the Cations in the Four
Soils - Lapidus-Amundson Model.

$$\text{Criterion: } \left(\frac{C}{C_0} \right)_{t_s} - \left(\frac{C}{C_0} \right)_{t_s - \Delta t} \leq 1 \times 10^{-2}$$

Where t_s = steady state time

$$\Delta t = 5 \times 10^{-5}$$

CATIONS

HALLANDALE
FINE SANDP.M. TOP
LAYERP.M. MIDDLE
LAYERP.M. BOTTOM
LAYER

Cu	0.35	1.5	1.0	9.0
Zn	0.50	1.4	1.6	0.8
Fe	0.55	0.6	23.0	1.7
Mn	0.32	0.9	27.0	0.7
Ni	91.30	1.2	5.0	10.0
Cd	43.90	2.5	2.5	8.0
Cr	2.50	1.5	15.0	1.3
Ca	13.60	1.5	2.0	3.0

$$\text{Criterion: } \left(\frac{C}{C_0} \right)_{t_s} - \left(\frac{C}{C_0} \right)_{t_s - \Delta t} \leq 1 \times 10^{-2}$$

Where t_s = steady state time

$$\Delta t = 9 \times 10^{-4}$$

TABLE 7.4 Steady State Times of the Cations in the Four Soils - Langmuir Model...

TABLE 7.5 Boundary Conditions Used for the 2-D Model

<p>(A)</p>
<p>(B)</p>
<p>(C)</p>

TABLE 7.6 Boundary Conditions for the 3-D Model.

FIG.7.1 One Dimensional Model

FIG. 7.2 One Dimensional Model

FIG. 7.3 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 Migration of Manganese in Hallandale Fine Sand

FIG.7.10 Concentration Contours

FIG.7.11 Concentration Contours

FIG.7.12 Concentration Contours

FIG.7.13 Concentration Contours

FIG.7.14 Concentration Contours

FIG.7.15 Concentration Contours

FIG.7.16 Concentration Contours

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

FIG.7.18 Migration of Cadmium in Hallandale Fine Sand, Pompano Beach Plant Site

FIG.7.19 Clearing of Pollutant Plume (Cadmium in Hallandale Fine Sand)

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

FIG.7.21 Migration of Cadmium in Hallandale Fine Sand, Pompano Beach Plant Site

FIG. 7.22 Migration of Cadmium in Hallandale Fine Sand

APPENDIX

NUMERICAL SIMULATION OF CHEMICALLY REACTING FLOW THROUGH SOILS: A PARAMETRIC STUDY

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ABSTRACT

A one dimensional mathematical model has been developed to predict pollutant migration in soil-leachate systems. Adsorption and ion exchange has been modelled using the Lapidus Amundson linear steady state isotherm. The concept of dispersion as a lumped parameter has been used. The effect of biological organisms has been incorporated in a decay term. The equation and boundary conditions have been nondimensionalised. Three non-dimensional groups have been obtained. These groups relate rate of diffusion, rate of convection, rate of biological transformation and rate of chemical adsorption. Parametric studies have been done to determine the influence of these groups on the pollutant attenuation capability of the soil. Variation of concentration profiles with time have been found. Mass of pollutant diffusing and convecting into the soil layers and relative portions that are chemically adsorbed and biologically transformed have been found as functions of time.

Experiments have been carried out to determine the pollutant attenuation capability of the soil beneath a specific landfill. Migration patterns of eight different cations (Cu, Zn, Mn, Fe, Cr, Ca, Cd, Co) have been predicted using the mathematical model developed.

Parametric studies indicate that the soil-leachate system in which a cation is least mobile corresponds to the case where the rate of convection is more than ten times the rate of diffusion, the rate of biological transformation is hundred times or more than the rate of convection and the concentration in the sorbed phase is hundred times more than that in the solution phase.

NOMENCLATURE

A = An arbitrary surface area under consideration (m^2)
C = Concentration of a particular pollutant species in the liquid phase (mg/l)
C₀ = Initial concentration of the pollutant species in the liquid phase (mg/l)
C' = Concentration/Initial concentration
D = Hydrodynamic dispersion coefficient (m^2/yr)
D' = Rate of diffusion/rate of convection (reference velocity = W)
 ϵ = Void ratio of the soil = $\frac{\text{Void Volume}}{\text{Total Effective Volume}}$
E' = Rate of diffusion/rate of convection (reference velocity = V)
K = Biological transformation rate constant (1/yr)
K_t = Distribution Coefficient (lt/gms)
K' = Rate of biological transformation/rate of convection
L = Total length of the soil layer (m)
P_{Din} = Mass of pollutant diffusing into the soil layer in time Δt
P_{Cin} = Mass of pollutant convecting into the soil layer in time Δt
P_{Out} = Mass of pollutant discharging into the aquifer in time Δt
P_{Chem} = Mass of pollutant chemically adsorbed by the soil in time Δt

P_{Bio} = Mass of pollutant biologically transformed in time Δt
R' = Mass of pollutant in sorbed phase/mass of pollutant in solution
S = Concentration of the pollutant species in the solid phase (mg/gms)
t = Time (yr)
t' = Time/reference time
V = Aquifer velocity (m/yr)
W = Pore water velocity (m/yr)
Z' = Depth/total length of soil layer

INTRODUCTION

The types of mathematical models that have been developed for use in ground water contamination problems can be classified into four distinct groups: Saturated-unsaturated transport models Reference [1] thru [8], saturated-only transport models [9] thru [15], unsaturated-only transport models [16] thru [22], and analytical transport models [23] [24].

Saturated-only transport models ignore the dynamics of the unsaturated zone between the waste disposal site and the ground water table. The change in properties of the leachate as it moves through the unsaturated zone cannot be accounted for in these models. To use these models it is necessary to have a method of quantifying the amount and quality of leachate reaching the ground-water table.

Unsaturated-only models cannot be used to describe contaminant migration in groundwater systems. However, the different models in this group are very useful tools for studying the mechanisms of contaminant transport in the unsaturated zone.

The saturated-unsaturated transport models are versatile as they are a combination of the saturated only and the unsaturated only models. In the present work a one dimensional mathematical model has been developed by considering mass conservation for a particular pollutant species in the liquid phase. The interaction between the solid and liquid phase has been expressed as a chemical transformation term. The effective rate law assumed, describes a linear dependency of the sorbed concentration on the solution concentration, Fuller [25]. A separate biological transformation term has been introduced to account for biological effects.

This paper deals with a numerical study to determine the effects of the different parameters responsible for the interactions within a soil leachate system. Three non-dimensional groups have been derived comparing rate of convection against rate of diffusion, rate of convection against rate of biological transformation and mass of sorbed pollutant against mass of pollutant in solution. The effect of each of these nondimensional groups on the concentration profile has been studied. The amount of pollutant mass stored in the soil by chemical adsorption and that transformed by biological mechanisms has been identified as a fraction of the net mass diffusing and convecting into the soil. The rate of pollutant accumulation within the soil-leachate system has also been studied. Batch experiments have been conducted to obtain distribution coefficients and simulation results have been compared to results from the parametric study.

FORMULATION

Assumptions and Approximation

In the development of the model for predicting pollutant migration in the soil beneath a landfill, certain simplifying assumptions have been made and these are discussed below.

- The pore water velocity is in the vertically downward direction. This is because the major driving force causing the pore water flow is gravity.
- The rate of diffusion in the horizontal direction is

negligible compared to that in the vertical direction. According to Cherry [26] the coefficient of hydrodynamic dispersion which governs the rate of diffusion can be expressed in terms of two components,

$$D = \alpha W + D^*$$

where α is a characteristic property of the porous medium known as the dynamic dispersivity for the solute in the porous medium, W is the pore water velocity in the direction in which the dispersion is considered and D^* is the coefficient of molecular diffusion. Consistent with the assumption that the pore water velocity is in the vertical direction only, the dispersion coefficient in the horizontal direction is much lower than that in the vertical direction.

- c) The rate of flow of the leachate through the soil is such that at every instant the pollutant species in the liquid and the solid phases are in equilibrium. This equilibrium is expressed mathematically by assuming that the concentration of the pollutant in the liquid phase is directly proportional to that in the solid phase.
- d) The soil underneath the landfill is bounded by an aquifer. The aquifer has a constant horizontal velocity.
- e) The concentration of a particular pollutant species is a constant when it reaches the top of the soil layer beneath the landfill. This assumption is made to simplify the model.

Analysis

This model has been developed by considering the mass balance for a particular species of the pollutant within the liquid phase. The interaction between the solid and liquid interface is included in the chemical and biological transformation terms. The chemical equilibrium between the pollutant species in the liquid and solid phase has been assumed linear following Lapidus and Amundson [24] and Lindstrom et al. [27].

The nondimensional form of the pollutant transport equation is derived in Appendix 1.

$$D' \frac{\partial^2 C'}{\partial Z'^2} - \frac{\partial C'}{\partial Z'} - K' C' = \frac{\partial C'}{\partial t'} (R' + 1)$$

The three nondimensional groups may be physically interpreted as discussed below.

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

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.

$$K' = \frac{L/W}{1/K}$$

Thus K' is the ratio of the time taken by the pollutant to convect through a particular distance to the time taken by the pollutant to be biologically transformed.

$$R' = \frac{K_t \left(\frac{dc}{dt} \right)_0}{\left(\frac{\epsilon}{1-\epsilon} \right) \left(\frac{dc}{dt} \right)} = \frac{(1-\epsilon) \frac{ds}{dt}}{\epsilon \frac{dc}{dt}}$$

Thus R' is the ratio of the rate at which pollutant is being chemically transformed to the total rate of change the pollutant concentration in the liquid phase.

The boundary condition at the top of the soil layer ($Z=0$) is $C=C_0$ for $t>0$. In the nondimensional form $C'=1$ at $Z'=0$ for all $t'>0$. The other boundary condition at the soil aquifer interface is

$$-D' \frac{\partial C'}{\partial Z'} + CW = CV$$

Defining a nondimensional group, $E' = \left(\frac{D}{VL} \right)$, the boundary condition is

$$- \frac{\partial C'}{\partial Z'} + \frac{C'}{D'} = \frac{C'}{E'}$$

Estimate of Pollutant Mass Stored in the Soil

The physical phenomena governing the movement of the pollutant species through the soil are diffusion and convection. Adsorption of the pollutant species by the soil is due to the presence of exchangeable sites within the soil, whereas transformation of one pollutant species to another form is by biological changes caused by certain organisms.

At every instant of time some amount of pollutant enters the soil layer through the soil landfill interface by diffusion and convection. A portion of it is chemically adsorbed by the soil and a portion is biologically transformed to some other form. The remaining leaves through the soil aquifer interface again by convection and diffusion.

- a) The total amount of pollutant mass diffusing into the soil layer through the soil landfill interface in an infinitesimal interval of time ΔT is given by

$$P_{Din} = -D \frac{\partial C}{\partial Z} \cdot \epsilon \cdot A (\Delta T)$$

where P_{Din} = mass of pollutant diffusing into the soil layer in time Δt . If we assume that at any instant the concentration of the interstitial fluid is a constant equal to " C_0 " then at that instant the total amount of pollutant mass stored within the soil layer is " $C_0 A L \epsilon$ ". We denote this quantity by " P_{Ref} " and use it to non-dimensionalise the pollutant mass stored.

Nondimensionalise P_{Din} with respect to P_{Ref}

$$P'_{Din} = -D' \left(\frac{\partial C'}{\partial Z'} \right) \Delta T'$$

- b) The total amount of pollutant mass convecting into the soil layer through the soil landfill interface in an infinitesimal interval of time Δt is given by

$$P_{Cin} = CW \epsilon A (\Delta T)$$

Nondimensionalising P_{Cin} with respect to P_{Ref} ,

$$P'_{Cin} = C' \cdot \Delta T'$$

- c) The total amount of pollutant discharging into the aquifer is equal to the sum total of the pollutant diffusing and convecting out through the soil aquifer interface. According to the boundary condition, this quantity is equal to the amount of pollutant carried away by the aquifer. Hence the total amount of pollutant discharging into the aquifer in an infinitesimal interval of time ΔT is

$$P_{Out} = C \cdot V \cdot \epsilon \cdot A \cdot \Delta T$$

Nondimensionalising this quantity with respect to P_{Ref} ,

$$P'_{Out} = C' \Delta T' \frac{D'}{E'}$$

- d) Total amount of pollutant chemically adsorbed by the soil in an infinitesimal interval of time " ΔT " is given

$$\int_0^L \int_0^T K_t (1-\epsilon) \rho A \frac{\partial C}{\partial t} dt dz$$

Nondimensionalising P_{Chem} with respect to P_{Ref} ,

$$232 \quad P'_{Chem} = \int_0^1 \int_0^{T'} R' \frac{\partial C'}{\partial t'} \Delta T' dz'$$

- e) Total amount of pollutant biologically transformed into some other form of species by organisms present in the soil in the infinitesimal interval of time ΔT is given by

$$\int_0^L \int_0^{\Delta T} K C_e A dt dz$$

Nondimensionalising P_{Bio} with respect to P_{Ref} ,

$$P'_{Bio} = \int_0^1 \int_0^{\Delta T'} K' C' A' dt' dz'$$

Parametric Study

To get an understanding of the different physical parameters, the nondimensionalised form of the one dimensional pollutant equation was numerically solved with nine different combinations of the three nondimensional groups. To cover the domain of interest, the highest value of the nondimensional grouping was taken as 100.0 and the lowest value as 0.15. The nine different cases computed for the model are tabulated in Table 1. The forward time central space scheme was used to solve the governing equation.

CASE	D'	K'	R'
1	100.0	100.0	100.0
2	100.0	100.0	0.15
3	100.0	0.15	100.0
4	100.0	100.0	0.15
5	0.15	0.15	0.15
6	0.15	100.0	100.0
7	0.15	0.15	100.0
8	0.15	100.0	0.15
9	1.0	1.0	1.0

Table 1

To justify the choice of these two values, a literature survey was conducted to determine the range within which the different parameters of interest could fall. The maximum and minimum values for the different input parameters as found from literature are shown in Table 2. The upper limit for none of the non-dimensional groups exceed 100.0, the lower limit in some cases may be below 0.15. Since none of the input parameters take negative values the lowest possible figure any of the nondimensional groups can take is zero. The computer model was run under two cases with K' and R' replaced by 0.0 instead of 0.15. It was found that the transient concentrations at any depth differed by a maximum of 7% while the steady state profiles showed no change. Thus, the choice of 0.15 instead of 0.0 did not give rise to a substantial difference in the results.

INPUT PARAMETER	MAXIMUM VALUE	MINIMUM VALUE
D	.34 m ² /yr. Metry[28]	.03 m ² /yr. Genuchten[31]
K	.876 yr ⁻¹ . Metry[28]	.00876 yr ⁻¹ . Metry[28]
W	1.75 m/yr. Metry[28]	.088 m/yr. Metry[28]
K _t	2.9 t/g. Sengupta[29]	.03 t/g. Sengupta[29]
ρ	2.5 g/c.c. Holland[30]	1.4 g/c.c. Mahaloch[32]
c	.64. Sengupta[29]	.36

Table 2

For all nine cases the variation of pollutant concentration with depth and time were found and plotted till the steady state profile was attained. Steady State has been defined as the situation after which the variation of the pollutant concentration, at any grid point, with time is less than or equal to 10^{-6} . At any instant of time, the total amount of pollutant diffusing and convecting into the soil layer was found. Fractions of this chemically adsorbed by the soil and biologically transformed into some other species was determined as a function of time.

After steady state was reached, the model was run with no net inflow of pollutant through the landfill soil interface. This defined a situation when the landfill has been completely depleted of a particular species of pollutant.

Results

The steady state time and the steady state pollutant concentration at the soil aquifer interface for the nine cases investigated are listed in Table 3. After the landfill has been depleted of a particular pollutant (ie. $C_0=0$); the time after which the concentration of that pollutant at the soil aquifer interface becomes negligible is also listed. Concentration below 10^{-6} are taken as negligible.

An analytical check was carried out to verify the steady state concentration profiles. The steady state concentration at the aquifer determined analytically is tabulated. Compared to this solution the numerical solution has a variation of $\pm 5\%$.

CASE	D'	K'	R'	STEADY STATE TIME FOR POLLUTION	CONC(Z'=1) AT STEADY STATE (NUMERICAL IC')	CONC(Z'=1) AT STEADY STATE (ANALYTICAL IC')	STEADY STATE TIME FOR CLEANSING
1	100.0	100.0	100.0	5.120	0.59	0.57	5.120
2	100.0	100.0	0.15	0.2048	0.59	0.57	0.2048
3	100.0	0.15	0.15	0.2048	0.84	0.84	0.2048
4	100.0	0.15	100.0	5.120	0.84	0.84	5.120
5	0.15	0.15	0.15	10.240	0.04	0.045	10.24
6	0.15	0.15	100.0	40.96	0.04	0.045	40.96
7	0.15	100.0	0.15	0.320	0.0	0.14×10^{-9}	0.32
8	0.15	100.0	100.0	40.96	0.0	0.14×10^{-9}	40.96
9	1.0	1.0	1.0	5.12	0.006	0.0055	5.12

Table 3

The steady state pollutant mass stored in the soil through the various mechanisms is listed in Table 4. The values have been nondimensionalised with respect to the reference mass $CoLA_e$. Plots of concentration of a cation C' , with the depth Z' are shown in Fig.1-9. The transient profiles are concentration profiles at different instants of time. The time increment is the numerical value of the time for the preceding plot. Case I ($D'=100.0$, $K'=100.0$, $R'=100.0$) and Case II ($D'=100.0$, $K'=100.0$, $R'=0.15$) show identical steady state profiles. The trend of concentration variation with depth is very similar. The steady state times are different. For Case I it is 5.12 while that for Case II is .2048. This indicates that soils with identical diffusion, convection and biological characteristics but with different chemical properties will have similar concentration profiles, but their rate of change with time is different. The soil with poor chemical adsorption allows the aquifer to be polluted at an earlier stage.

Case III ($D'=100.0$, $K'=0.15$, $R'=0.15$) and IV ($D'=100.0$, $K'=0.15$, $D'=100.0$) behave very similarly. They have similar trends and the same steady state profile. Case III with a very low value of $R'=0.15$, ie. a poor chemical adsorption characteristic, comes to steady state much earlier than Case IV.

From the above mentioned four cases, Case I for which diffusion and biological transformation rates are 100 times convection rate and a high chemical adsorption property, is best suited for pollutant attenuation. For this soil the pollutant reaches the aquifer after

time=0.03 t_{ref} . This time is 200 times higher than that for Case II and Case III and 1½ times higher than Case IV. The concentration of the pollutant at the aquifer soil interface at steady is also the lowest (0.59).

From Fig. 5 & 6 it can be seen that the profiles for Case V and VI look identical. They have similar trends and the same steady state profiles. The steady state time for Case VI is 40.96 while that for Case V is 10.24. The same value for the groups D' and K' attributes the similar steady state profile. The difference in the non-dimensional group R' explains the difference in steady state times. Case VI with a high value for R', ie. a very good chemical adsorption property, attenuates the pollutant effectively.

Case VII and VIII are particularly interesting. For these soils the pollutant never reaches the aquifer. The high value of K' ie. a biological transformation rate 100 times higher than convection rate attributes to a very slow concentration change in the liquid phase. For Case VIII steady state is reached after time=40.96 where as for Case VII it is reached after time=0.32. This difference is because of the difference in the value of the group R'.

The concentration profiles for Case IX (D'=1.0, K'=1.0, R'=1.0) are similar to Case V and Case VI. The steady state profile is some what different. The steady state time is half that for Case V. This indicates that lower the values for each of the three nondimensional groups, the faster it takes to reach steady state. The steady state concentration at Z'=1 is same as that for Case IV and Case V.

Of all the eight cases representing eight extreme situations, Case VIII corresponds to the case of least mobility and Case III corresponds to the highest.

Fig.10-18 shows the variation with time in the net amount of pollutant diffusing and convecting into the soil layer, and the fraction of it chemically adsorbed and biologically transformed.

Case I and Case IV have identical values for D' and R', but the difference in K' accounts for the difference in the amount of pollutant biologically transformed and chemically adsorbed. For Case IV most of the pollutant is chemically adsorbed while for Case I the major portion is biologically transformed. For Case II with very low values for K' and R', most of the pollutant remains in the liquid phase without being adsorbed or transformed. In such a case, the aquifer is polluted very quickly. For Case III chemical adsorption is negligible compared to biological transformation, while for Case IV the opposite holds true. This is because for Case III K'=100.0 and R'=0.15 while for Case IV K'=0.15 and R'=100.0.

For Case I the pollutant convecting into the soil layer and that retained in the interstitial fluid is negligible and so these are not shown in Fig.10. For Case II the biologically transformed pollutant and that retained in the interstitial fluid are negligible and overlap each other on the time axis in Fig.11. Case IV has negligible amounts of pollutant being convected, biologically transformed and retained in the interstitial fluid. This is shown in Fig.12.

Case V is interesting. For this case the amount of pollutant diffusing out after time=10. t_{ref} is more than that diffusing in. After this time the net amount of pollutant diffusing into the soil is negative. Fig.14 shows this. Case V and Case VI are the only two cases which the net amount of pollutant convected in till steady state is higher than that diffused in. Case IX behaves similar to Case V. The net amount of pollutant diffused into the soil at steady state is negative. For this case the amount of pollutant chemically adsorbed and biologically transformed are nearly equal.

Fig.19 shows the variation in concentration with

depth for an actual run conducted with soil from undisturbed ground near an anaerobic digestion facility at Pompano Beach. Filtrate from the plant was used as leachate or the pollutant media. Batch experiments were carried out to determine the chemical transformation rate coefficients K_t for 8 different cations namely, copper,

zinc, manganese, iron, chromium, cadmium, cobalt and calcium. Chemical adsorption and ion exchange reactions was modelled using Lapidus Amundson linear isotherms. The model assumes linearity between the concentration in the adsorbed phase and that in the solution phase. Hydrodynamic dispersion coefficient for similar type of soil was found from literature and used in the model. Representative values were chosen for the pore water and ground water velocities. The concentration profiles for all the eight different cations are identical in nature. This is because the two nondimensional groups D' and K' are the same for all the cases. Table 5 lists the distribution coefficient (K_t) for the eight cations investigated.

Table 6 lists the different coefficients used in the model for the actual run.

CASE	D'	K'	R'	NET POLLUTANT MASS DIFFUSED IN TILL STEADY STATE	NET POLLUTANT MASS CONVECTED IN TILL STEADY STATE	NET POLLUTANT MASS BIOLOGICALLY TRANSFORMED TILL STEADY STATE	NET POLLUTANT MASS CHEMICALLY ADSORBED TILL STEADY STATE
1	100.0	100.0	100.0	230.51	2.56	172.17	70.40
2	100.0	0.15	0.15	0.99	0.10	0.01	0.13
3	100.0	100.0	0.15	7.64	0.10	7.30	0.10
4	100.0	0.15	100.0	87.32	2.56	0.31	89.48
5	0.15	0.15	0.15	-2.92	5.12	0.57	0.12
6	0.15	100.0	100.0	41.28	21.63	104.26	3.68
7	0.15	0.15	100.0	10.25	20.63	19.28	0.13
8	0.15	100.0	0.15	0.32	0.16	0.80	0.003
9	1.0	1.0	1.0	2.94	2.86	2.92	2.68

Table 4

Cations	Cu	Zn	Fe	Mn	Ni	Cd	Cr	Ca
Distribution Coefficient K_t	.206	.870	.616	.071	.604	.072	1.729	1.117

Table 5 Distribution Coefficient for Hallandale Fine Sand.

D	K	W	V	L	D'	K'
.06m ² /yr	.08/yr	.87m/yr	26.1m/yr	1m	0.89	.09

Table 6

Conclusion

- The case of least attenuation is where the aquifer is polluted with 82% of the incoming concentration in only 0.2048 t_{ref} . This case is a soil-leachate system for which the diffusion rate is 100 times more than the convection rate, the convection rate is 100 times more than the biological transformation rate and the chemical rate constant is of the order of 0.1.
- The case of best attenuation is where the pollutant "never" reaches the aquifer. This case is a soil-

leachate system for which the convection rate is 100 times the diffusion rate, the biological transformation rate is 100 times the convection rate and the chemical rate constant is high with a value around 100.

- (c) The model is very sensitive to changes in the value of the nondimensional group D' . From Fig. 1-9 it can be seen that for the same values of R' and K' but for different values of D' the concentration profiles change drastically.
- (d) Changes in nondimensional group R' involving the chemical rate constant K_t shifts the concentration profile with respect to time. For such cases the steady state profiles are the same but the steady state is reached after different times.
- (e) For large values of all the three nondimensional groups D' , K' and R' the net amount of pollutant diffusing into the soil at every instant of time is at least six times more than that for all the other cases.

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Appendix 1

The mass balance for a single species of pollutant within the liquid phase is

Net rate of mass inflow through diffusion + Net rate of mass inflow through convection - Rate of mass change due to chemical adsorption - Rate of mass change due to biological transformation = Net rate of mass change with time.

This balance gives the governing equation as:

$$D \frac{\partial^2 C}{\partial Z^2} - W \frac{\partial C}{\partial Z} - \frac{(1-\epsilon) \rho \partial S}{\epsilon \partial t} - KC = \frac{\partial C}{\partial t} \quad (1)$$

From assumption (C) in the previous section, $S = K_t C + K'_t$

or $\frac{\partial S}{\partial t} = K_t \frac{\partial C}{\partial t}$, substituting in equation (1) we get,

$$D \frac{\partial^2 C}{\partial Z^2} - W \frac{\partial C}{\partial Z} - KC = \left[\frac{1-\epsilon}{\epsilon} \rho K_t + 1 \right] \frac{\partial C}{\partial t} \quad (2)$$

This is the one dimensional pollutant transport equation.

The one dimensional pollutant transport equation is a second order linear partial differential equation. It requires one initial condition and two boundary conditions for solution. The choice of boundary conditions is governed by the physical situation for which the model will be used. Consistent with the assumptions stated in the previous section, the most appropriate condition at the top of the soil layer ($Z=0$) is $C=C_0$ and that at the bottom of the layer ($Z=L$) is $-D \frac{\partial C}{\partial Z} + CW = CV$

The initial condition is $C=0$ for $t=0$ $Z>0$

The three independent variables in the pollutant transport equation are concentration C , depth Z and time t . These three variables have been nondimensionalised with respect to three reference quantities:

C_0 = the initial concentration of the pollutant

$t_{ref} = L/W$ = the reference time

and L = the total depth of the soil layer.

Nondimensionalizing we get

$$D' \frac{\partial^2 C'}{\partial Z'^2} - \frac{\partial C'}{\partial Z'} - K' C' = \frac{\partial C'}{\partial t'} (R' + 1)$$

FIG.1 CASE I

FIG.2 CASE II

$D=100.00$ $K=0.15$ $R=0.15$

TIME (t/t_{ref}) FROM 0.0301 TO 0.2048

INCREMENT (t/t_{ref})

VARIATION OF CONCENTRATION WITH DEPTH

FIG. 3 CASE III

$D=100.00$ $K=0.15$ $R=100.00$

TIME (t/t_{ref}) FROM 0.0050 TO 5.1200

INCREMENT (t/t_{ref})

VARIATION OF CONCENTRATION WITH DEPTH

FIG. 4 CASE IV

$D=0.15$ $K=0.15$ $R=0.15$

TIME (t/t_{ref}) FROM 0.020 TO 10.2400

INCREMENT (t/t_{ref})

VARIATION OF CONCENTRATION WITH DEPTH

FIG. 5 CASE V

$D=0.15$ $K=0.15$ $R=100.00$

TIME (t/t_{ref}) FROM 0.80 TO 40.9600

INCREMENT (t/t_{ref})

VARIATION OF CONCENTRATION WITH DEPTH

FIG. 6 CASE VI

$D=0.15$ $K=100.00$ $R=0.15$

TIME (t/t_{ref}) FROM 0.040 TO 0.3200

INCREMENT (t/t_{ref})

VARIATION OF CONCENTRATION WITH DEPTH

FIG. 7 CASE VII

$D=0.15$ $K=100.00$ $R=100.00$

TIME (t/t_{ref}) FROM 5.12 TO 40.96

INCREMENT (t/t_{ref})

VARIATION OF CONCENTRATION WITH DEPTH

FIG. 8 CASE VIII