CHEMICAL MODELING OF A DAIRY WASTE/WATER MANAGEMENT, POLLUTION CONTROL SYSTEM FOR FARM MANAGEMENT IN PUERTO RICO

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SUMMARY

This project involved the establishment of a chemical model of a waste management system on a small dairy farm, with the intention that such a model could be used as a basis for evaluation and optimization of said system. The system used involved water flushing of dairy animal wastes into a temporary holding tank in which the diluted wastes are chopped and homogenized. The homogenized slurry is then pumped either to a large anaerobic lagoon, where microbial degradation of organic and inorganic components takes place or for the charging of an anaerobic digestion tank for the production of methane gas. The methane gas can then be used as a fuel for electricity production. Lagoon water is then used for field irrigation.

This particular project involved the measurement of the inorganic species nitrate, potassium, calcium, magnesium, and sodium at the influx to the holding tank, the holding tank, the influx to the lagoon and in the lagoon. Emphasis was placed on the development of the most appropriate analytical techniques for obtaining species data which would allow the evaluation of the system from the pollution abatement and cost recovery points of view.

Results demonstrate the utility of ion selective electrodes and atomic spectroscopy (flame emission and atomic absorption) for such analyses and indicate that in some cases the measurement of low levels of nitrogen species (nitrate, nitrite, ammonium) by automated colorimetric techniques is probably more suitable,

although this would require treatment of samples from the first two stages of the system to remove colored impurities.

Additionally, the anaerobic lagoon system shows great promise from the point of view of organic matter and nutrient degradation (i.e. pollution control), without those disadvantages encountered in more temperate climates. This is obtained, however, with the loss of most of the nitrogen fertilizer value of the wastes.

INTRODUCTION

Today it is known that the disposal of manure is a major problem for the farmer with concentrated or confined livestock. The land application of manure is part of almost every livestock facility. The benefits and harms from direct land application of animal waste are related to the major fertilizer nutrients, trace nutrients, and salinity of the wastes, respectively. Considerable effort is being expended at this time by the agricultural and agricultural engineering communities in studies involving the use (as opposed to direct disposal) of these animal wastes as fertilizers and/or sources of energy. One of the main incentives for these projects is citizen and government recognition of the dangers of ground water pollution caused by direct watershed disposal of large, concentrated amounts of animal wastes. Pollution occurs as a result of receiving waters oxygen depletion due to both the high concentration of organic matter and a high concentration of inorganic nutrients which promote rampant biological activity.

Studies of alternative uses for collected animal wastes are carried out to find ways of minimizing the chemical and biological impact of these materials on local water supplies and to determine ways of decreasing the costs involved. This is especially important in an area such as Puerto Rico, where the majority of animal operations involve small farms, whose profit margins are quite low and to whom the added costs of waste management may be the difference between profit and loss. In addition, much of the water supply (including domestic drinking water) comes directly from runoff and a history of waste management in order to protect the environment is all but non-existant. Public awareness of the affects of ground water pollution has become sensitized due to a large number of pollution problems involving contamination of municipal wells. These and other incidences have led to the emergence of an extremely vocal environment protection lobby on the local and Commonwealth levels.

The problems and phenomena addressed by animal waste control studies to date (most of which are carried out in temperate areas) can be quite different from those encountered in tropical climates such as that of Puerto Rico. For instance, in Puerto Rico the ground never freezes, there is no runoff from melting snow, and rain occurs frequently in large quantities (compared to say Kansas). These factors (and others) make it difficult to apply the results of most previous waste management studies to Puerto Rican animal farms.

An initial query to local Environmental Protection Agency officials has revealed that there are no data available on the presence or possible concentrations of chemical species generated by dairy farms (or any other type of animal husbandry operation) in Puerto Rico. A lack of such basic knowledge leaves local agriculture extension personnel in the position of being able to give only uninformed advice to local animal operations concerning waste disposal or utilization.

The Agricultural Experiment Station is presently operating an experimental Dairy Operation at the Lajas Substation in Lajas, Puerto Rico. An energy related project is being carried out at this dairy to set up a waste management system which will involve collection of solid and liquid animal wastes in the milking parlor and two adjacent feeding areas. The waste is flushed with water to a concrete collecting tank where it is stirred and the solid particles reduced to a homogeneous slurry. This slurry is then pumped to an earthen lagoon operated under anaerobic conditions or to a digestion tank where anaerobic digestion will produce methane gas. The methane gas produced will be used as an auxiliary source of energy for water heating or possibly generating electricity. The water in the earthen lagoon is to be used for the irrigation of nearby fields, thereby utilizing the bulk of the flushing water for irrigation and applying the biologically degraded waste components to the land evenly over a period of time.

This project was conceived for the purpose of obtaining the necessary information concerning the concentrations of pertinent chemical species in the original waste slurry and how the concentrations of these species are effected by the various stages in the waste management system. Samples were collected at the farm during the period of February to May 1986. During this time 12 sets of samples were collected on 12 different days. Each sample was analyzed for the presence or concentration of nitrate ion and potassium (ionic and total). In addition some or most of the samples were analyzed for the presence or concentration of sodium, calcium, magnesium, pH, salinity, lead, cadmium, iron, copper and zinc. To our knowledge these results are the only ones of this type existing for a dairy operation in Puerto Rico. In addition these analyses have led to knowledge and experience in the difficulties and limitations to the analytical procedures used for this particular type of study. This knowledge is being used to continue and expand this project leading within a year or so to a far more complete model of this particular type of system in the Puerto Rican setting.

THEORY AND PREVIOUS STUDIES

The practice of disposal of animal wastes by land application has been accepted and practiced for many decades in the mainland United States (1). Originally this practice was carried out as a means of disposal without causing serious pollution problems to the local watersheds. Although studies of the nature and content of the chemical make up of farm animal waste can be traced back to 1931 (2,3) only since around 1970 has the number of variables controlling the chemical content and fate of land applied manure become apparent. Research carried out since this time has made some gains in identifying the chemical content of various animal manures and the effects of these chemical species on the soil, runoffwaters, and crops of the land to which they are applied (4,5).

Studies have been carried out on such topics as: Nutrient recovery of digested swine manure on grain and pasture (6), nitrogen and phosphorus movement from surface applied manure, winter and spring runoff from manure application plots (7), transport of potential pollutants in runoff water from land areas receiving animal wastes (8). These studies tend to be limited in scope, particularly from the stand point of the quantitative chemical data reported. Even with the limited amount of data collected it becomes obvious from these studies that 1) a large number of variables are involved in determining the chemical content of manure from a particular source and 2) that these variables tend to be different for each farm system studied. For example; the nutrient, salt, micronutrient, metals content of animal waste is dependent on the 1) type of animal involved, 2) its diet, 3) its environment, etc.. The fates of the chemical species in an animal waste varies with 1) how it is collected, handled, and applied, 2) the type of soil to which it is applied, 3) the crops grown on the land, 4) weather conditions during and after application, etc..

For practical purposes, the application of manure must be done in a way that avoids degrading the soil, water and air or the pollution of these systems. Both direct solid and liquid application of manure has been practiced in the mainland United States for many decades. When the manure includes runoff or dilution water, it can supply irrigation water where needed.

To use this liquid manure, a lagoon is needed for collection. The size of the lagoon depends on the size of the herd, local regulations and topographical and environmental conditions. Basically there are two types of lagoons; aerobic and anaerobic. Anaerobic processes will occur in an anaerobic lagoon where the bacteria (normally present in solid animal waste) can degrade the solid material in the absence of oxygen. An aerobic lagoon requires a means of injecting air into the system on a continuous basis in order to supply the oxygen necessary to maintain the aerobic bacteria and their processes. In general (i.e. temperate climate) practice anaerobic lagoons are considered to have the following advantages over aerobic lagoons (9).

1- The anaerobic process will decompose more organic matter per unit volume.

2- In an anaerobic process the facultative bacteria will multiply rapidly and convert the organic solids to liquid and biogas.

3- Since no oxygen is required, and therefore no aeration system is needed this cost is saved.

4- Long storage times permit labor flexibility, while bacteria break down solids.

The usual disadvantages of anaerobic lagoons are considered to be:

1- In areas where winter water temperatures are close to or below freezing, lagoons experience spring and autumn water turnovers. This leads to a mixing of organic rich bottom waters with the surface. This combined with sudden increases while bacteria break down solids.

The usual disadvantages of anaerobic lagoons are considered to be:

1- In areas where winter water temperatures are close to or below freezing, lagoons experience spring and autumn water turnovers. This leads to a mixing of organic rich bottom waters with surface. This combined with sudden increases in microbial action, due to warmer temperatures, often leads to the emanation of foul odors.

2- In general low microbial activity during periods of low temperature followed by higher temperatures with the resultant higher microbial activity can make management of an anaerobic lagoon difficult.

3- Loss of nitrogen through reduction to volatile gases and phosphorous due to settling leads to a drastic loss of fertilizer value for anaerobic lagoons.

As can be seen a climate such as Puerto Rico's with almost constant high temperatures means that one can obtain all of the advantages of an anaerobic lagoon, without suffering any of the disadvantages (with the exception of fertilizer value loss). For these reasons the anaerobic lagoon would appear to be the ideal system of waste control/disposal in a tropical area such as Puerto Rico.

If one considers the primary function of a waste management system to be pollution control then fertilizer value and energy conversion become a means of recovering the cost of the pollution. In pollution tems animal wastes lead to: Oxygen consumption in local waters, due to organic matter oxidation by biological activity; Eutrophication, mainly from nitrogen and phosphorous species; Bacterial contamination of local waters, Increased salinity in local waters and soils by cationic species in the waste and any toxic substances (such as toxic metals) in the waste will also be transferred to local soils and waters.

If we concentrate on the chemical aspects of these phenomena (i.e. ignore bacterial contamination), the anaerobic lagoon should be capable of reducing most of the organic material in the animal waste, before disposal. In terms of eutrophication, the most important contribution from manure and urine will be large amounts of nitrogen species. At first these will be in the form of urea, ammonia, and organic nitrogen (amino acids, proteins, etc.). At a neutral to acid pH, with aerobic conditions, these species will be rapidly converted to nitrate. In the lagoon under anaerobic conditions the nitrate will be rapidly reduced to nitrite, within 24 hours. Within another 24 hours the nitrite is further reduced to volatile nitrogen oxides or nitrogen gas. These volatile gases then evaporate out of the system into the atmosphere (10). In addition phosphate species tend to settle out within the lagoon leading to very low phosphorous concentrations in the lagoon water. So from the eutrophication point of view anaerobic lagoon liquid should be quite innocuous. This can be verified by measurement primarily of nitrate, but also of nitrite and phosphates.

Irrigation water salinity is important, not only from the standpoint of total salt content and the tolerance of certain crops for cationic salts, but also from the point of view of soil conservation. In this respect the most important factor is the sodium absorption ratio (SAR) defined as:

$$SAR = \frac{[\,Na^{+}\,]}{\left(\frac{[Mg^{2+}] + [Ca^{2+}]}{2}\right)^{\frac{1}{2}}}$$

where the species concentrations are in units of milliequivalents/L. An excess of sodium over other cations can lead to a breakdown in soil structure leading to a loss of soil permeability. Therefore, the concentrations of sodium, calcium, and magnesium in the lagoon water are an important consideration as to its suitability for irrigation. In addition the total salinity in terms of water conductivity can be important in terms of water/crop compatibility.

With these considerations in mind it was decided to concentrate efforts on the measurement of nitrate, potassium, sodium, calcium, magnesium and those trace metals for which atomic absorption sources were available (zinc, iron, copper, lead and cadmium).

THE DAIRY FARM AND ITS WASTE MANAGEMENT SYSTEM

The Lajas Center of Research and Development Station (CIDA) is one of six that the College of Agricultural Sciences operates on the island. This station was founded in 1946 in an effort to conduct research toward the agricultural development of the Lajas Valley.

The station is located in the Lajas Valley in the South-West part of Puerto Rico about 100 ft above sea level. The total land area of the valley is about 160 square miles (about 100,000 acres). Around 1/6 of the valley area is under irrigation where sugar cane is planted. On the non-irrigated land livestock and livestock products are the most important. In 58 acres out of the main body, pastures grow naturally and dry cows and calves are taken there for feeding.

The Lajas Valley irrigation system is operated by the Electrical Energy Authority and the water comes from reservoirs where rain water is collected. There are three reservoirs in the station which are filled with water from the irrigation system. The type of soil in the station is basically heavy clay (Fraternidad Clay). It is a fertile soil with a pH ranging from 6 to 7. The average annual rain-fall is 42" which is not distributed evenly through-out the year. Rainy seasons extend from August to November and the months when it rains the most are August, September, and October. The driest months are January, February and March.

The average maximum temperature is 88 °F (32 °C) and the average minimim is 65 °F (18 °C).

The main areas of research conducted in the station include: animal science, agronomy, plant protection, and aquaculture.

The animal science area basically includes feeding and management, animal waste handling and utilization. The dairy farm of the station operates with Brown Swiss and Holsteins. There is a total of 89 cows out of which 74 are milking and 15 are dry cows. There are also 23 female and 25 male calves. There are 18 heifers and two bulls.

WASTE HANDLING SYSTEM:

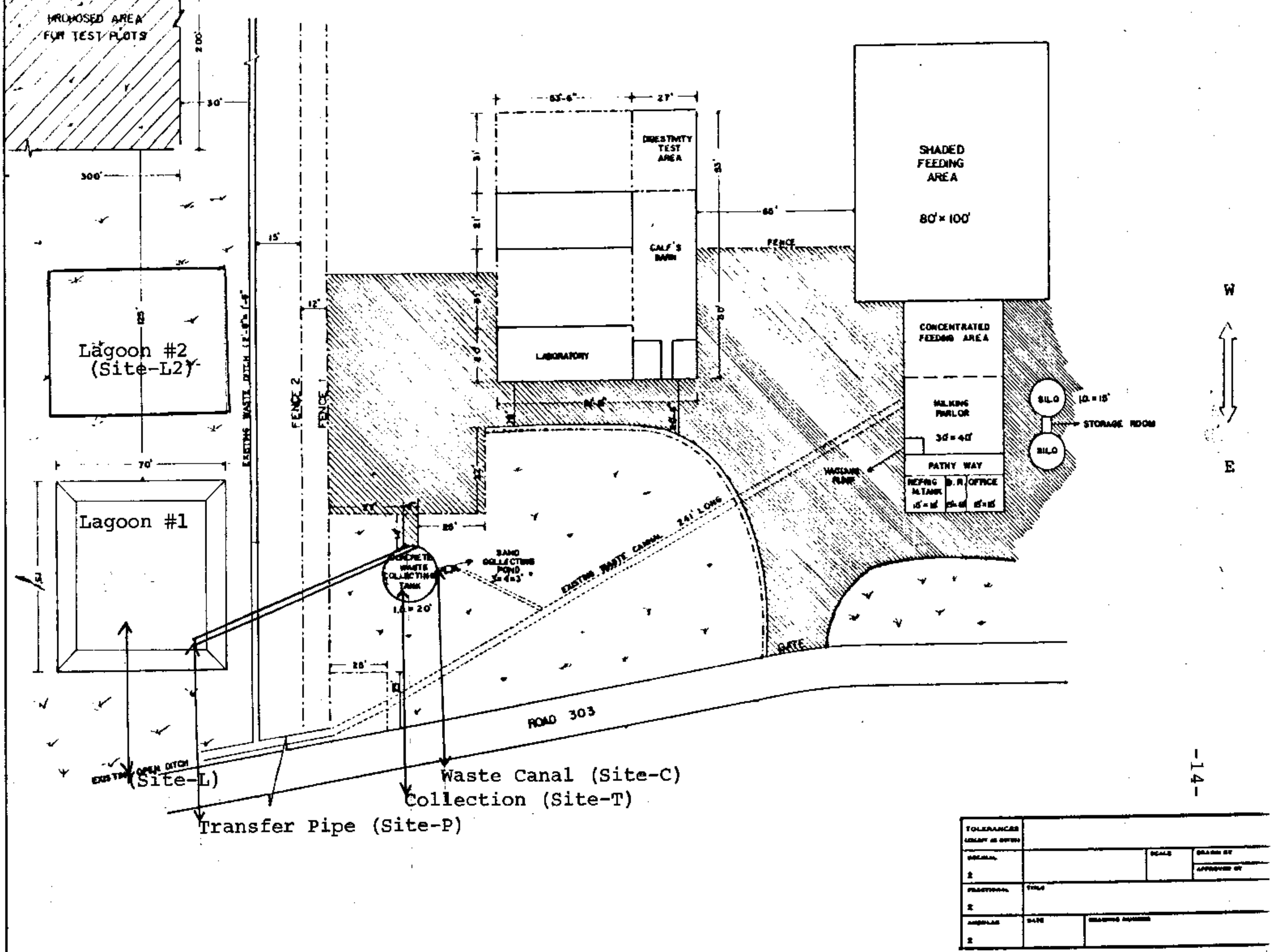
The station's dairy operation includes open pasture, shaded and concentrated feeding areas. The principal manure source is an 80 x 100 ft shaded feeding area and concentrated feeding area, as well as the milking parlor.

Manure from the shaded feeding area is scrubbed by a front end loader from paved,shaded feed lot into the gutters leading to the gutters of the concentrated feeding area. Manure from the concentrated feeding area is flushed daily to the proper gutters so that all the manure from the shaded feeding area and concentrated feeding area flows to the main waste canal. The manure from the milking parlor is also flushed, ending up in the main waste canal. This canal is approximately 22 x 22 inches and 241 ft long and directs the total liquid manure to a 3 x 4 x 3 ft sand collecting pond. The sand collector is basically a sand trap, where the heavy particles of the manure will settle to the bottom of the pond and periodically will be collected and disposed of. In this way sand and other heavy material will be eliminated before reaching the concrete waste collecting tank where a homogenizing pump is located. The size of the concrete waste collecting tank is determined by the total quantity of manure produced at the areas, evaporation, location and required depth, gravity, slope of the area, and economic considerations. Based on the above criteria, the capacity of the concrete collecting and homogenizing tank was calculated. The tank measures 20 ft I.D. and has an effective height of 9 ft, resulting in a effective holding capacity of 2827.43 ft^2 (21,150 gallons) equivalent to about (78,000) liters. The concrete tank is equipped with a homogenizing pump having a discharge capacity of 1000 GPM in pumping and 1,500 GPM in agitation. The homogenizing pump is driven by a 230/460 volts and 25 hp electric motor.

The material that comes in the animal excretions is a source of nutrients that coud be used as plant food, however, the chemical content of manure may have adverse effects on the soil and plant system. To apply the excrement to the soil, the concrete collecting tank could work as a reservoir. Since the capacity of this tank is limited, two lagoons in series with an approximate total holding capacity of 250,000 gallons are used. The primary use of these lagoons is to store the liquid manure for proper land application as needed, meanwhile pan evaporation and solid separation will also take place in the lagoons.

Figure 1 shows that portion of the farm containing the waste management system. The sites where samples were taken are indicated in the following manner.

Figure 1: SCHEMATIC REPRESENTATION OF DAIRY WASTE HANDLING SYSTEM IN LAJAS (UPR-AES)



Site C is the end of the waste canal past the sand collecting pond where the animal waste/flushing water enters the collecting tank. Samples were taken by lowering a plastic bucket over the fence surrounding the tank to a point just below the end of the waste canal where waste/water was falling into the tank.

Site T refers to samples collected from the concrete collecting tank.

Site P is the lagoon end of the pipe (PVC) through which homogenized waste slurry is pumped into the lagoon. This site was sampled while transfer of slurry from the collecting tank to the lagoon was taking place.

Site L refers to samples taken from the surface of the operating lagoon (#1).

Site L2 refers to samples of ground/rain water taken from the second lagoon (#2) which was only dug just before the end of this project and had not yet had waste water introduced into it.

Site B refers to a stream of fresh well water which ran (except during extremely dry times) along the western side of the mapped area. This site was used as a background source of local ground water supposedly unaffected by the waste system.

During the period of this study the proposed system for irrigating test plots with the lagoon water was not yet put into operation and it was therefore impossible to collect samples from this part of the system.

PROCEDURES

SAMPLING

Samples were collected in clean, washed, rinsed, polyethylene bottles. The most common size sample taken was 500 ml, although samples of 100, 250 and 1000 ml were taken on occasion (using the same type of bottle). The bulk sample was taken using a plastic bucket to which was attached a rope, allowing samples to be lifted from distances greater than arm's length. The bucket was filled with sample and the sample discarded, 2 or 3 times in order to rinse the bucket. Care was taken that the rinse water was disposed of at a distance precluding its reintroduction into the sampling area. From the final sample taken, care was taken to avoid agitation of the sample in order to avoid mixing with atmospheric air.

The sample bottle was then lowered into the sample filled bucket (taking care to avoid hand contact with the sample) and the bottle was allowed to fill slowly with sample, again avoiding agitation of the sample. The sample collected was discarded again for rinsing purposes 3 times. On the final fill the bottle was completely filled and capped so as to preclude any air space within the sample collected. The samples were then transported back to Mayaguez (approximately 45 minutes) at ambient temperature. Analyses for pH, potassium (by electrode) and nitrate were usually carried out within the next few hours. Analyses for salinity, sodium, calcium, magnesium, zinc, lead, cadmium, and iron were carried out within a few hours to one week.

PH MEASUREMENTS

pH measurements were made immediately upon returning to the laboratory. These were made using a glass/Ag/AgCl combination electrode, calibrated with NBS buffers (pH 7 and 4) and a Pope model 1502 pH/Ion meter.

NITRATE MEASUREMENTS

Nitrate measurements were made using a Corning 476134 Nitrate Electrode. This electrode demonstrated a linear slope of 50 mV/-dec. over a range of 0.14 mgN/l to 140 mgN/l. Although response was not linear below 0.14 mgN/l the electrode did show response down to at least 0.014 mgN/l. In order to overcome any matrix effects due to the complex nature of the sample the electrode was used (after evaluation with a normal calibration procedure) in the standard addition mode. Three or four additions of a standard $NaNO_3$ solution (usually 1400 mgN/l) were made to the sample. The changes in solution potential after the first addition were used to calculate the electrode slope. This slope was then used with the original sample potential and the change in potential on addition of the first standard "spike" to calculate the original sample concentration of nitrate nitrogen. Although colorimetric methods for this analysis, which are more sensitive to lower nitrate concentrations, are available, the samples from the first two sample-sites were strongly colored. This precludes use of a spectrophotometric method unless the sample is first treated to remove this background. It was decided that the time necessary to determine a method for color removal which would not interface with the analyses being carried out was not available within the time limits of this phase of the project, and therefore all nitrate measurements were made by electrode. Dilution and rinse water used in all of these analyses (outside of the actual sample water) was Type I water (R>10 Mohms) prepared with a Gelman Water I system. All standard nitrate solutions were prepared with pure water and a standard nitrate (0.1000 M) obtained from Orion (920-706).

POTASSIUM MEASUREMENTS

Ionized potassium was also determined using a Corning potassium electrode (476132). Potassium was also determined by atomic flame emission. This method is described under the later section on flame emission measurements. The potassium electrode showed a linear response to potassium ion from 10 to 1000 mgK/l with a slope of 50 to 55 mv/dec. A lesser response was obtained for concentrations of 0.1 to 1 ppm. Again the method of standard additions was used to obtain the electrode slope and original potassium concentration in each sample. In this case the levels measured were all within the acceptable measurement range of the technique.

SALINITY MEASUREMENT

Salinity was measured directly on a few occassions using the conductivity method. Salinity can be related to conductivity in general by the relationship 640 mg/l salinity = 1 mS/cm. Conductivity measurements were made at ambient temperature with electronic temperature correction using a Yellow Springs Instruments model 33 Salinity, Conductivity, Temperature meter. The probe was washed 3 times with sample and measurements made on a fourth aliquot of approximately 100 ml.

SODIUM AND POTASSIUM MEASUREMENTS USING FLAME EMISSION SPECTROSCOPY

Since the values for sodium and potassium were expected to be relatively high (analytically speaking) and lamps were not available for atomic absorption measurements, atomic flame emission spectroscopy was used to determine these elements. In addition it was thought that the use of an alternative method for potassium determination could verify those results. Wavelengths used were 766.5 nm for potassium and 405.9 nm for sodium. Other conditions were set according to Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corp.. Lanthanum was added to all solutions to suppress ionization and samples were diluted with pure water to the extent necessary to bring the absorbance values within the linear range of the method. Standard solutions were prepared according to Analytical Methods using KCl and NaCl, reagent grade. The detection limit for this method is approximately 0.1 mg/l for both elements, well below the expected and encountered values.

CALCIUM, MAGNESIUM, IRON, ZINC, CADMIUM, LEAD AND COPPER DETERMINATIONS

The first two of these elements (Ca, Mg) were determined and the last four were screened for using atomic absorption spectroscopy. As in the flame emission measurements, both a Perkin-Elmer model 603 and a Perkin-Elmer 1420 Atomic Absorption Spectrophotometer were used. A pre-mix burner with flow spoiler and an a 10 cm single slot burner head was used with an air/acetylene flame in all cases. Standard conditions as listed in Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer, Corp. (Jan. 1982) were used in all cases. Samples were run directly with no treatment except for dilution and addition of lanthanum to the calcium and magnesium samples. Detection limits for zinc, cadmium, lead and copper were 0.005, 0.002, 0.05, and 0.01 mg/l. These four elements could not be detected under the conditions used. Trace amounts of iron (up to 0.1 to 1 ppm) were detected in some samples, but in general no iron was detected in the majority of samples at a detection limit of approximately 0.1 ppm.

RESULTS

As can be seen in Table 1, the pH values of the operational waste system including flushing canal, collecting tank, and lagoon (#1) are within the range of 6.5 to 7.1 (i.e. neutral). This means that the interpretation of nitrogen chemistry and microbial activity can be made in terms of neutral conditions and that neither acidic nor basic conditions prevail. The fresh water brook on the edge of the waste system area has a very low ionic strength (see salinity values in Table 2) and therefore can be expected to have a very low buffer capacity. This makes measurement of the pH of this sample difficult. However, the value of 7.4 was easily obtained on three successive days indicating a fairly reliable neutral value. The high (8.3 to 8.6) value of the ground water collected in the second, non-operational lagoon indicates the presence of alkaline salts in the soil of this area. The presence of large quantities of leachable salts is also indicated by the value of 1.85 mS (approximately 1.1 g/l salinity) for the conductivity of this water. Considering the apparently high salt content of the soil in this area it is very doubtful that the 0.7 mS conductivity of salinity contributed from the waste lagoon (#1) will have any effect on the surrounding land area.

In addition, using the equation for sodium absorption ratio (see theory), with concentrations in units of milliequivalents/ liter, the average SAR for the lagoon (#1) water is 2.9. This number is far below the value of 12, above which sodium absorp-

TABLE 1

(pH AS A FUNCTION OF SAMPLE SITE)

Sample	Site-C	Site-T	Site-P	Site-L	Site-L2	Site-B
9 (5/20)		6.58	6.60	6.83	8.61	7.48
10 (5/21)		6.57		6.80	8.32	7.33
11 (5/22)	7.02	6.60	6.48	6.71	8.31	7.46
Average:	7.0	6.6	6.5	6.8	8.4	7.4

TABLE 2

(SALINITY AS A FUNCTION OF SAMPLE SITE)
(mS)

Sample	Tap H 0	Site-T	Site-P	Site-L	Site-L2	Site-B
10 (5/21)	0.240	0.720		0.680	1.850	0.210

tion is considered to be a possible problem.

Table 3 shows the results for nitrate concentration (in mgN/l) obtained over the length of the project. As can be seen all of these results are close to or below the detection limit of 0.1 mgN/l. An attempt was made to measure ammonium and nitrate nitrogen toward the end of the project. The ammonium electrode proved to be too slow in response to allow useful method development and use for analysis within the present time scale. Some preliminary nitrite values were obtained. These, however, were not numerous enough to overcome doubts concerning their unreasonable values and scatter. Further work with these two species will be carried out in the future. As was explained in the theory the nitrate values should be most indicative of the functioning of the anaerobic lagoon.

The results for potassium concentrations are given in Tables 4 and 5 for the ion selective electrode and flame emission techniques, respectively. There is a most obvious difference in the results obtained by the two methods. The results for flame emission are always much higher than those measured by the electrode. Table 6 shows a comparison of the results obtained for this element using the two methods in the collection tank and the lagoon (#1). Although the ratio of the numbers obtained by the two methods is definitely not constant, an overall average ratio of 4.8 for the results by flame emission divided by those for ISE is obtained for both lagoon and collection tank samples. The most obvious difference in these two methods is that the electrode responds to the activity of ionized potassium and will therefore

TABLE 3

NITRATE CONCENTRATION (mgN/l)
(SPECIES' CONCENTRATIONS AS A FUNCTION OF SAMPLE SITE)

Sample (Date)	Site-C	Site-T	Site-P	Site-L	Site-L2	Site-B
1 (2/4/86)		0.2				0.2
2 (2/19)		0.1		0.1		<0.1
3 (3/3)		1.0	0.2	0.3		
4 (3/4)		0.5		0.4		
5 (3/10)				0.1		
6 (3/24)				<0.1		
7 (3/25)		0.3		0.2		0.3
8 (3/26)	0.3			0.1		0.1
9 (5/20)	(0.8)	0.4	<0.1	0.1	0.2	0.2
10 (5/21)		0.6		0.1	0.2	0.1
11 (5/22)		(5)*		(3.8)		0.1
12 (5/27)		(5)		(3.1)		0.2
Average:	0.3	0.4	0.2	0.2	0.2	0.2

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* Values in parenthesis are considered doubtful and not used to compute average values.

TABLE 4

POTASSIUM CONCENTRATION (mgK/l)
(DETERMINED BY ION SELECTIVE ELECTRODE)
(SPECIES' CONCENTRATIONS AS A FUNCTION OF SAMPLE SITE)

Sample (Date)	Site-C	Site-T	Site-P	Site-L	Site-L2	Site-B
1 (2/4/86)						4
2 (2/19)		15		18		0.4
3 (3/3)		30	18	27		
4 (3/4)		25		13		
5 (3/10)				32		
6 (3/24)				40		
7 (3/25)		28		60		0.9
8 (3/26)	21.5			60		1.5
9 (5/20)	19.2	24		20	3.9	
10 (5/21)		8		2	2.9	3.6
11 (5/22)	28.7	12		14	(22.5)*	0.6
12 (5/27)	(115)*	15		17	3.0	3.0
Average:	23	20	18	27	3.3	2.0

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* Values considered doubtful and not averaged in.

TABLE 5

POTASSIUM CONCENTRATION (mg/l)
(DETERMINED BY FLAME EMISSION SPECTROMETRY)
(SPECIFIES CONCENTRATIONS AS A FUNCTION OF SAMPLE SITE)

Sample (Date)	Site-C	Site-T	Site-P	Site-L	Site-L2	Site-B
1 (2/4/86)		75		88		
2 (2/19)		84		93		13
3 (3/3)		109	52	117		
4 (3/4)		015		130		
5 (3/10)				124		
6 (3/24)				149		
7 (3/25)		77		140		12
8 (3/26)	126			190		65
9 (5/20)						
10 (5/21)						
11 (5/22)						
12 (5/27)						
Average:	126	90	52	129	--	30

TABLE 6

POTASSIUM CONCENTRATION AS A FUNCTION OF ANALYTICAL METHOD

Sample	Collection Tank			Lagoon (#1)		
(Date)	ISE	FE	Ratio (FE/ISE)	ISE	FE	Ratio (FE/ISE)
1 (2/4/86)						
2 (2/19)	15	84	5.6	18	88	4.9
3 (3/3)	30	109	3.6	27	93	3.4
4 (3/4)	25	105	4.2	13	117	9.0
5 (3/10)				32	130	4.1
6 (3/24)				40	124	3.1
7 (3/25)	28	77	2.7	60	149	2.5
8 (3/26)				60	140	2.3
9 (5/20)				20	190	9.5
10 (5/21)						
11 (5/22)						
12 (5/27)						
Average:	20	90	4.5	27	129	4.8

FE = Flame Emission
ISE= Ion Selective Electroce

be effected by high ionic strength and will not detect unionized potassium (i.e. potassium attached to particles).

Tables 7, 8, and 9 show the data obtained for sodium, calcium and magnesium during the project. As is to be expected sodium is by far the most common of these, although as demonstrated above, not so much so as to cause difficulties with preferential absorption.

Only barely detectable amounts of iron were detected in a few samples and no lead, cadmium, copper, or zinc could be found within the detection limits of the methods employed.

Tables 10-15 show the same data of species concentrations as the previous tables, but these tables show each species' change with time at each specific sample site. This makes it easier to compare the changes of each species with the others, with the passage of time and to decide if perhaps there are any interactions or relationships evident from such a comparison.

Aside from the daily input of animal waste and flushing water into the system, the total system volume will also be effected by loss of water due to evaporation and gain of water due to rain (the only form of precipitation in this area). The area of the dairy farm is a dry one subject to long periods of no precipitation during which considerable evaporation can be expected due to very high amounts of direct sunlight and high average temperatures. The average daily temperature in the area for the first five months of the year was 75 degrees F with daily average highs of more than 85 degrees F. In addition in one four day period in May (5/11-5/14) 10 inches of rain fall on the area. As these

TABLE 7

SODIUM CONCENTRATION (mgNa/l)
(DETERMINED BY FLAME EMISSION SPECTROMETRY)
(SPECIES CONCENTRATIONS AS A FUNCTION OF SAMPLE SITE)

Sample (Date)	Site-C	Site-T	Site-P	Site-L	Site-L2	Site-B
1 (2/4/86)		180				20
2 (2/19)		105		101		16
3 (3/3)		27	45	49		
4 (3/4)		30		50		
5 (3/10)				51		
6 (3/24)				81		
7 (3/25)		23		70		10
8 (3/26)	51			90		40
9 (5/20)						
10 (5/21)						
11 (5/22)						
12 (5/27)						
Average:	51	73	45	70	--	21

TABLE 8

CALCIUM CONCENTRATION (mgCa/l)
(DETERMINED BY ATOMIC ABSORPTION SPECTROMETRY)
(SPECIES CONCENTRATIONS AS A FUNCTION OF SAMPLE SITE)

Sample (Date)	Site-C	Site-T	Site-P	Site-L	Site-L2	Site-B
1 (2/4/86)		8.5				4.0
2 (2/19)		1.1		1.5		4.0
3 (3/3)		6.5	5.0	3.5		
4 (3/4)		7.0		3.6		
5 (3/10)				3.6		
6 (3/24)				4.4		
7 (3/25)		5.3		6.4		1.6
8 (3/26)	6.8			5.8		4.2
9 (5.20)						
10 (5/21)						
11 (5/22)						
12 (5/27)						
Average:	6.8	5.7	5.0	4.1	--	3.4

TABLE 9

MAGNESIUM CONCENTRATION (mgMg/l)
(DETERMINED BY ATOMIC ABSORPTION SPECTROMETRY)
(SPECIES CONCENTRATIONS AS A FUNCTION OF SAMPLE SITE)

Sample (Date)	Site-C	Site-T	Site-P	Site-L	Site-L2	Site-B
1 (2/4/86)						
2 (2/19)		49		20		26
3 (3/3)		20	10.5	11.5		13
4 (3/4)		12		11.2		
5 (3/10)		13		11.5		
6 (3/24)				7.5		
7 (3/25)		7.0		7.5		4.3
8 (3/26)	6.8			7.0		4.3
9 (5/20)						
10 (5/21)						
11 (5/22)						
12 (5/27)						
Average:	6.8	20	10	11	--	12

TABLE 10

CANAL FROM BARN TO CONCRETE COLLECTION TANK
(SPECIES CONCENTRATIONS AS A FUNCTION OF TIME)

Sample (Date)	Nitrate (ppm)	K (elec.t) (ppm)	K (AA) (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)
1 (2/4/86)						
2 (2/19)						
3 (3/3)						
4 (3/4)						
5 (3/10)						
6 (3/24)						
7 (3/25)						
8 (3/26)	0.3	21.5	126	51	6.8	6.8
9 (5/20)	0.8	19.2				
10 (5/21)						
11 (5/22)	??	28.7				
12 (5/27)	??	(115)				

TABLE 11

CONCRETE COLLECTION TANK
(SPECIES CONCENTRATIONS AS A FUNCTION OF TIME)

Sample (Date)	Nitrate (ppm)	K (elec.t) (ppm)	K (AA) (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)
1 (2/4/86)	0.2		75	180	8.5	49
2 (2/19)	0.1	15	84	105	1.1	20
3 (3/3)	1.0	30	109	27	6.5	12
4 (3/4)	0.5	25	105	30	7.0	13
5 (3/10)						
6 (3/24)						
7 (3/25)	0.3	28	77	23	5.3	7.0
8 (3/26)						
9 (5/20)	0.4	24				
10 (5/21)	0.6	8				
11 (5/22)	(5)	12				
12 (5/27)	(5)	15				

TABLE 12

PIPE FROM CONCRETE COLLECTION TANK TO LAGOON (1)
(SPECIES CONCENTRATIONS AS A FUNCTION OF TIME)

Sample (Date)	Nitrate (ppm)	K (elec.t) (ppm)	K (AA) (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)
1 (2/4/86)						
2 (2/19)						
3 (3/3)	0.2	18	52	44	5.0	11
4 (3/4)						
5 (3/10)						
6 (3/24)						
7 (3/25)						
8 (3/26)						
9 (5/20)	<0.1	24.2				
10 (5/21)						
11 (5/22)						
12 (5/27)						

TABLE 13

LAGOON #1

(SPECIES CONCENTRATIONS AS A FUNCTION OF TIME)

Sample (Date)	Nitrate (ppm)	K (elec.t) (ppm)	K (AA) (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)
1 (2/4/86)			88			
2 (2/19)	0.1	18	93	101	1.5	20
3 (3/3)	0.3	27	117	49	3.5	11.5
4 (3/4)	0.4	13	130	50	3.6	11.2
5 (3/10)	0.1	32	124	51	3.6	11.5
6 (3/24)	<0.1	40	149	81	4.4	7.5
7 (3/25)	0.2	60	140	70	6.4	7.5
8 (3/26)	0.1	60	190	90	5.8	7.0
9 (5/20)	0.1	20				
10 (5/21)	0.1	2				
11 (5/22)	(3.8)	14				
12 (5/27)	(3.1)	17				

TABLE 14

LAGOON #2

(SPECIES CONCENTRATIONS AS A FUNCTION OF TIME)

Sample (Date)	Nitrate (ppm)	K (elect.) (ppm)	K (AA) (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)
1 (2/4/86)						
2 (2/19)						
3 (3/3)						
4 (3/4)						
5 (3/10)						
6 (3/24)						
7 (3/25)						
8 (3/26)						
9 (5/20)	0.2	3.9				
10 (5/21)	0.2	2.9				
11 (5/22)	??	(22.5)				
12 (5/27)	0.2	3				

TABLE 15

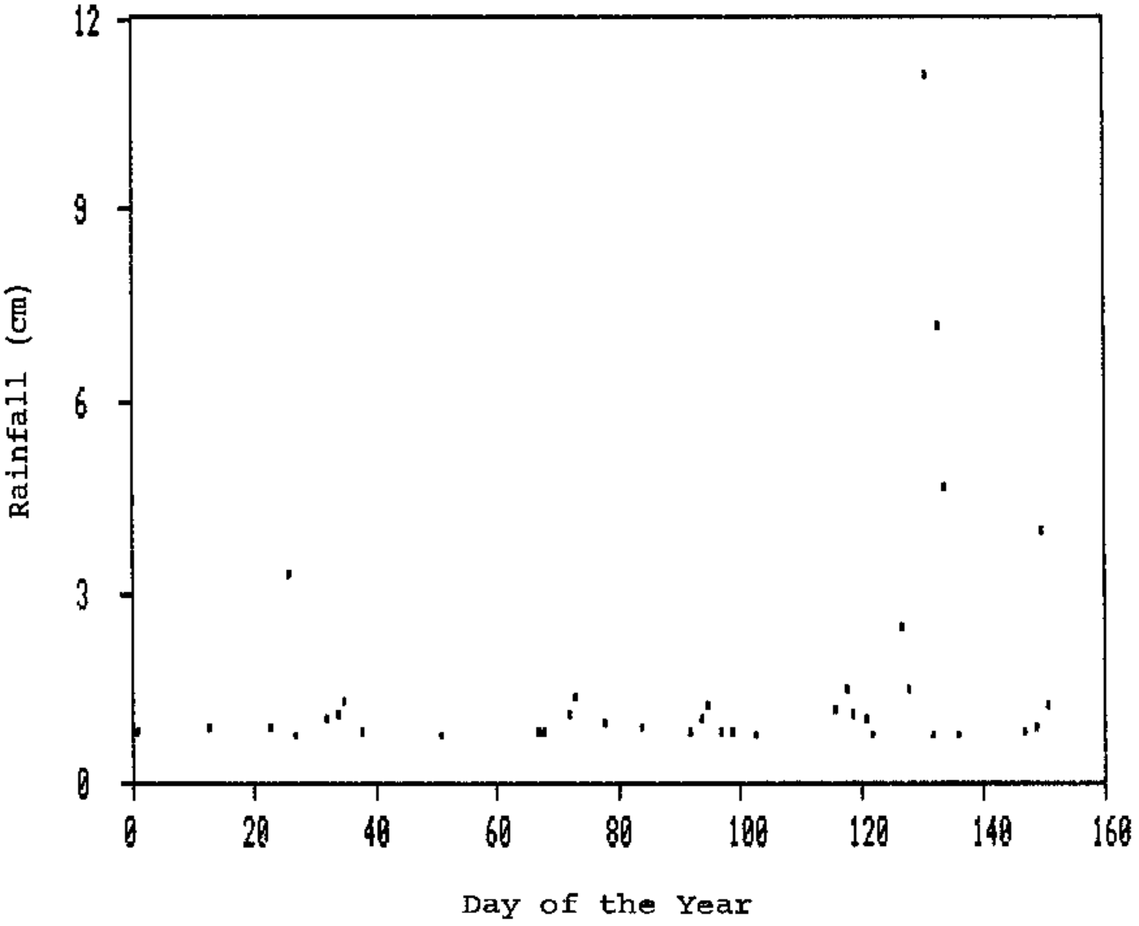
BROOK

(SPECIES CONCENTRATION AS A FUNCTION OF TIME)

Sample (Date)	Nitrate (ppm)	K (elec.t) (ppm)	K (AA) (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)
1 (2/4/86)	0.2	4		20	4	26
2 (2/19)	<0.1	0.4	13.2	16	4	13
3 (3/3)						
4 (3/4)						
5 (3/10)						
6 (3/24)						
7 (3/25)	0.3	0.9	12	10	1.6	4.3
8 (3/26)	0.1	1.5	65	40	4.2	4.3
9 (5/20)	0.2					
10 (5/21)	0.1	3.6				
11 (5/22)	<0.1	0.6				
12 (5/27)	0.2	3.0				

conditions could be expected to effect waste system concentrations a plot of daily rainfall recorded at the farm during the first 5 months of 1986 is shown in Figure 2.

Figure 2: Daily Rainfall at Lajas (1/1-5/31/86).

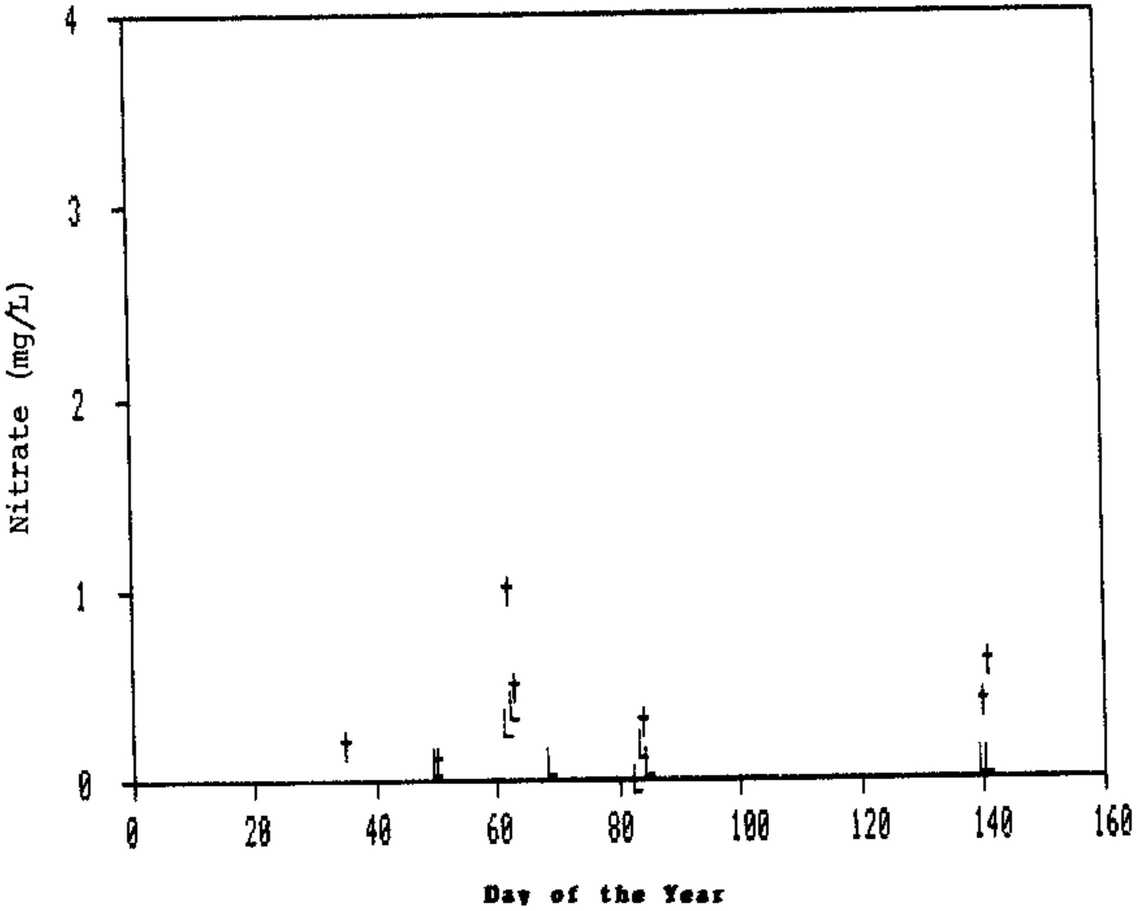


DISCUSSION

As mentioned in the results section, the neutral pH values found within the waste collection system will lead to normal chemical/biological processes such as described in the theory section. In addition there need be no worries about the effect of lagoon effluent on either soil, crops or an anaerobic methane digester from the pH stand point. The measured values of salinity and sodium absorption ratio indicate no difficulties in applying this effluent to agricultural land.

The low values of nitrate nitrogen encountered in the lagoon also tend to indicate that, although more detailed information on nitrite and ammonium nitrogen concentrations within the system would be useful, in general it appears that the anaerobic lagoon system is reducing almost all of the nitrogen forms in the waste products to innocuous, volatile nitrogen gases. Although this leaves the lagoon effluent with little nitrogen fertilizer value, it makes it a negligible source of nitrogen pollution due to runoff once applied to the land. If one looks at a graph of the nitrate data as a function of time for the collection tank and lagoon samples (Figure 3) one sees that in general the nitrate values do not change much with time. The only apparent relationship in these values is that the nitrate values in the tank tend to be somewhat higher than those in the lagoon, verifying the nature of the function of the lagoon in reducing the available nitrogen under anaerobic conditions.

FIGURE 3: NITRATE ION AS A FUNCTION OF TIME IN THE COLLECTION TANK AND LAGOON (#1).

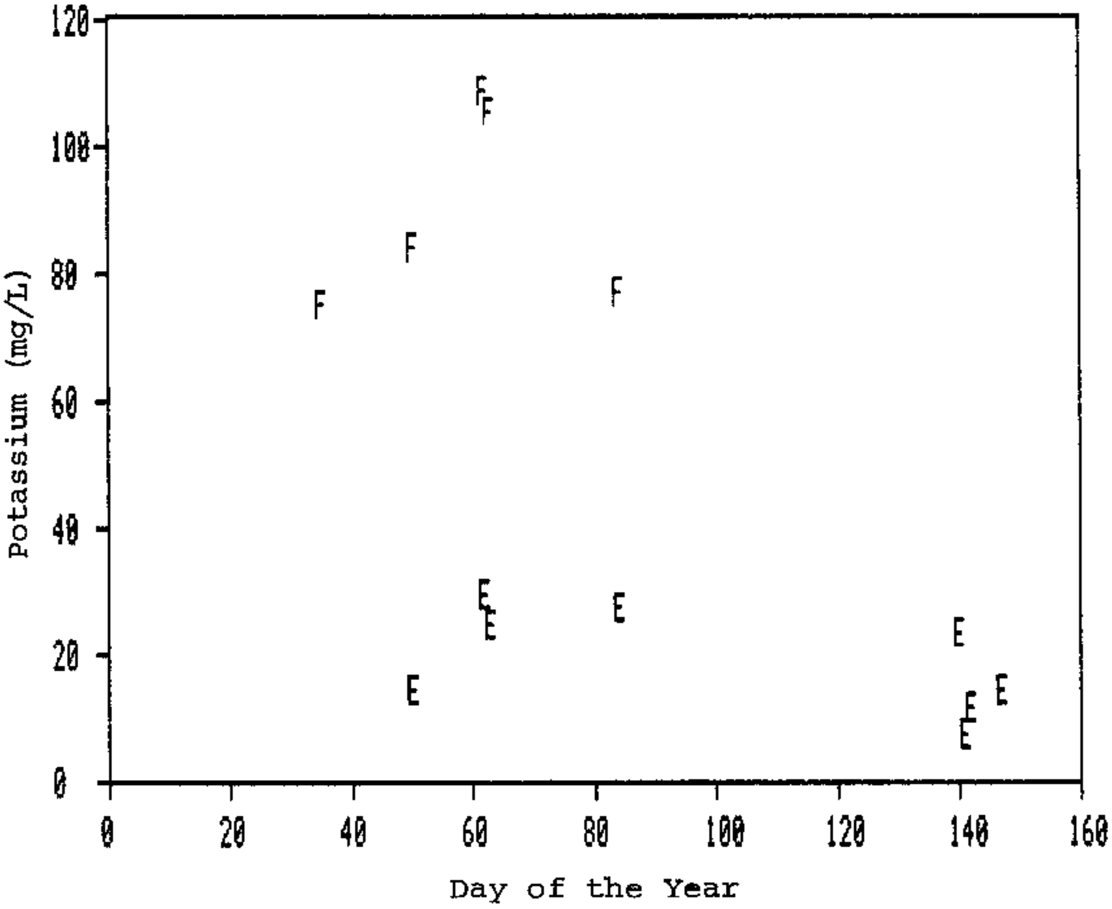


t = Collection Tank sample
L = Lagoon sample

The measured values of potassium (by whichever method) are also far lower than allowable limits in drinking water (1000 to 2000 mg/l) and therefore pose no pollution source. In addition, although not very high, this amount of potassium will have a fertilizer value when applied to any crops and as such could be used to replace a small amount of any necessary additional potassium. The difference in potassium measured by electrode or flame emission should be further investigated. The most probable next step would be to filter a sample of the lagoon water and measure the potassium by flame emission in the filtrate. If a great deal of the potassium is attached to colloidal particles, then the size of the filter used will effect the flame emission results of the filtrate. If this is not the case then the electrode method will have to be considered suspect. Samples number 8 collected on March 26, 1986 were analyzed by flame emission using the method of standard additions, which should have corrected for any matrix affects on the method. As seen in the results section these values are just as high in comparison to the electrode results as those flame emission results using a standard calibration curve.

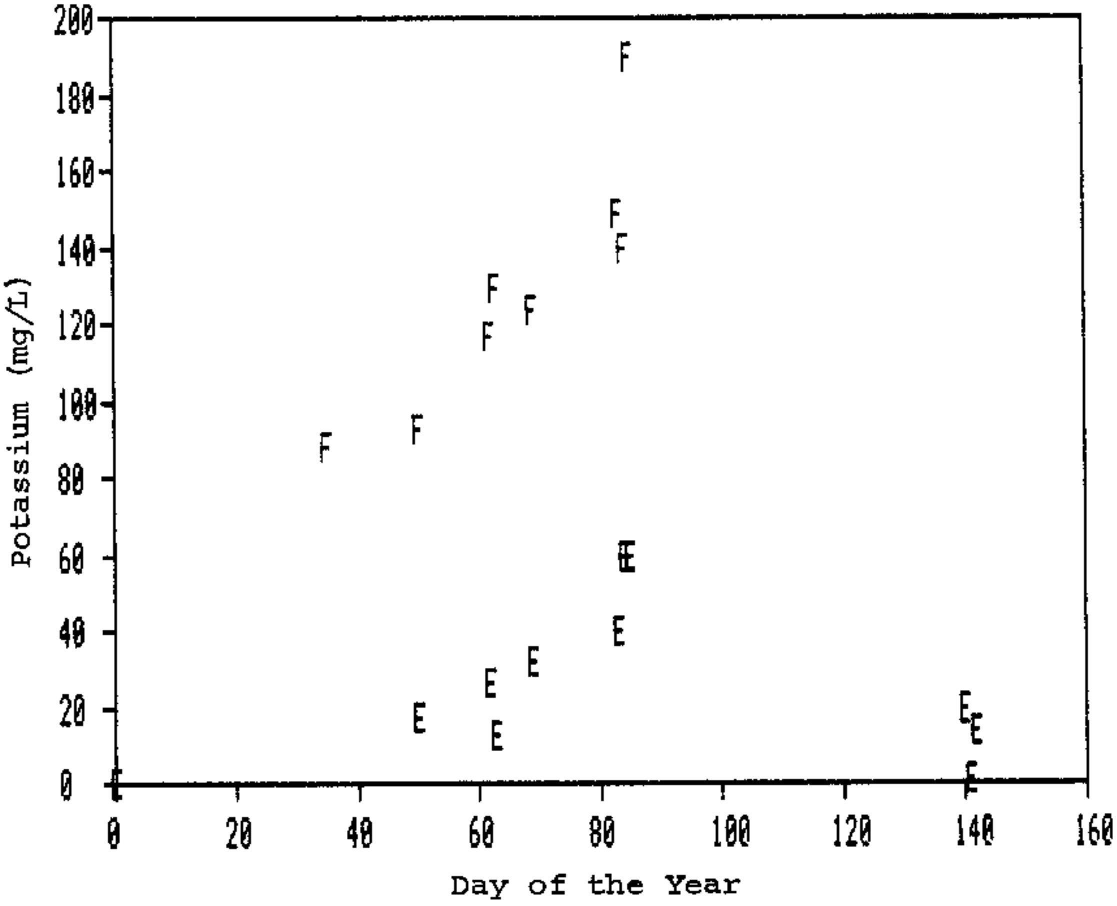
Plots of potassium concentrations as a function of time (both electrode and flame emission results) at both the collection tank (Figure 4) and the lagoon (#1) (Figure 5), again demonstrate that the flame emission values are higher than those determined by electrode. Other than that, the apparent trend in the results appears to be consistant for both analytical methods. Wether these apparent trends are real, can only be determined by taking samples more frequently over a period of time.

Figure 4: Concentration of Potassium in the Collection
Tank as a Function of Time and Method.



E = Determination by Ion Selective Electrode.
F = Determination by Flame Emission.

Figure 5: Concentration of Potassium in the Lagoon (#1) as a Function of Time and Method.



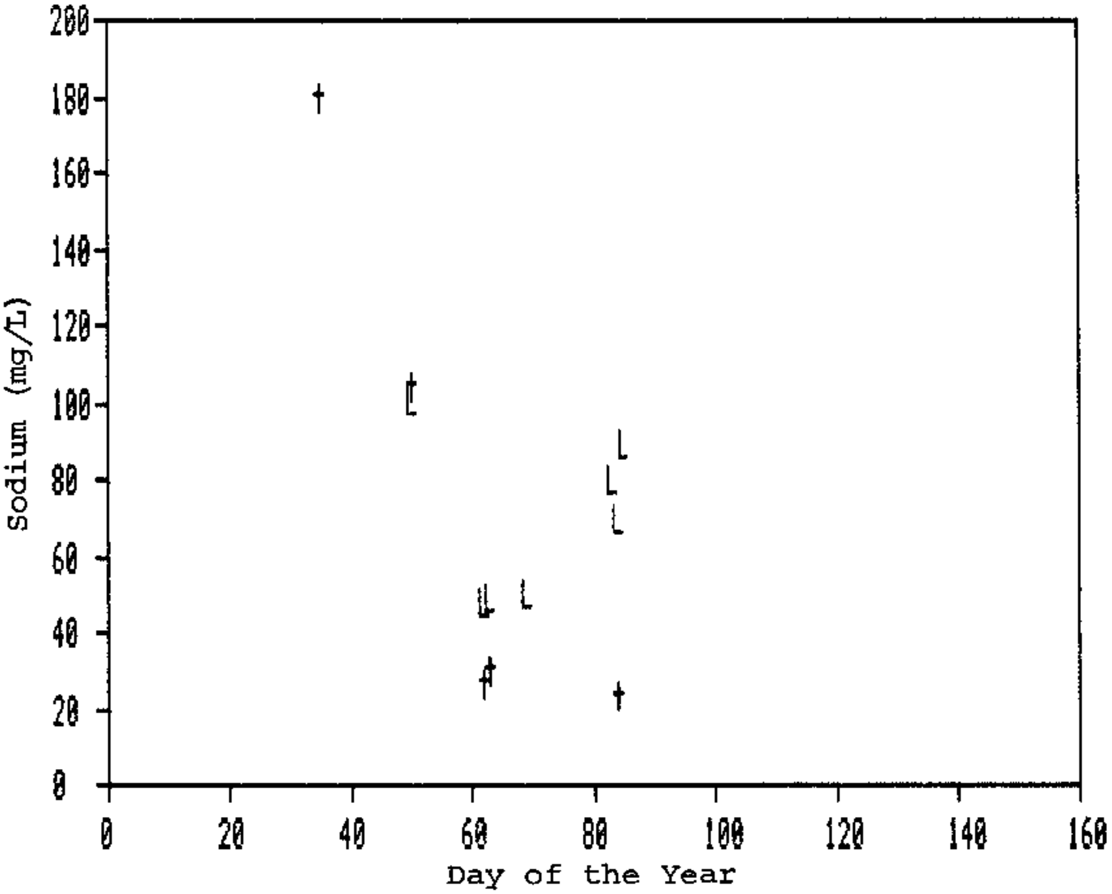
E = Determination by Ion Selective Electrode.
F = Determination by Flame Emission.

Plots of sodium, calcium and magnesium as a function of time for the collection tank and lagoon (#1) (Figure 6, 7, and 8) do not contain enough points to show any general relationships in terms of change with time or differences in concentration between the two sample sites. In general, these data indicate solely that the values are well within acceptable limits as far as use of the lagoon water is concerned.

The negative results obtained for iron, lead, cadmium, zinc, and copper indicate that toxicity or other possible problems due to these species should not occur from the application of waste from this system to the land.

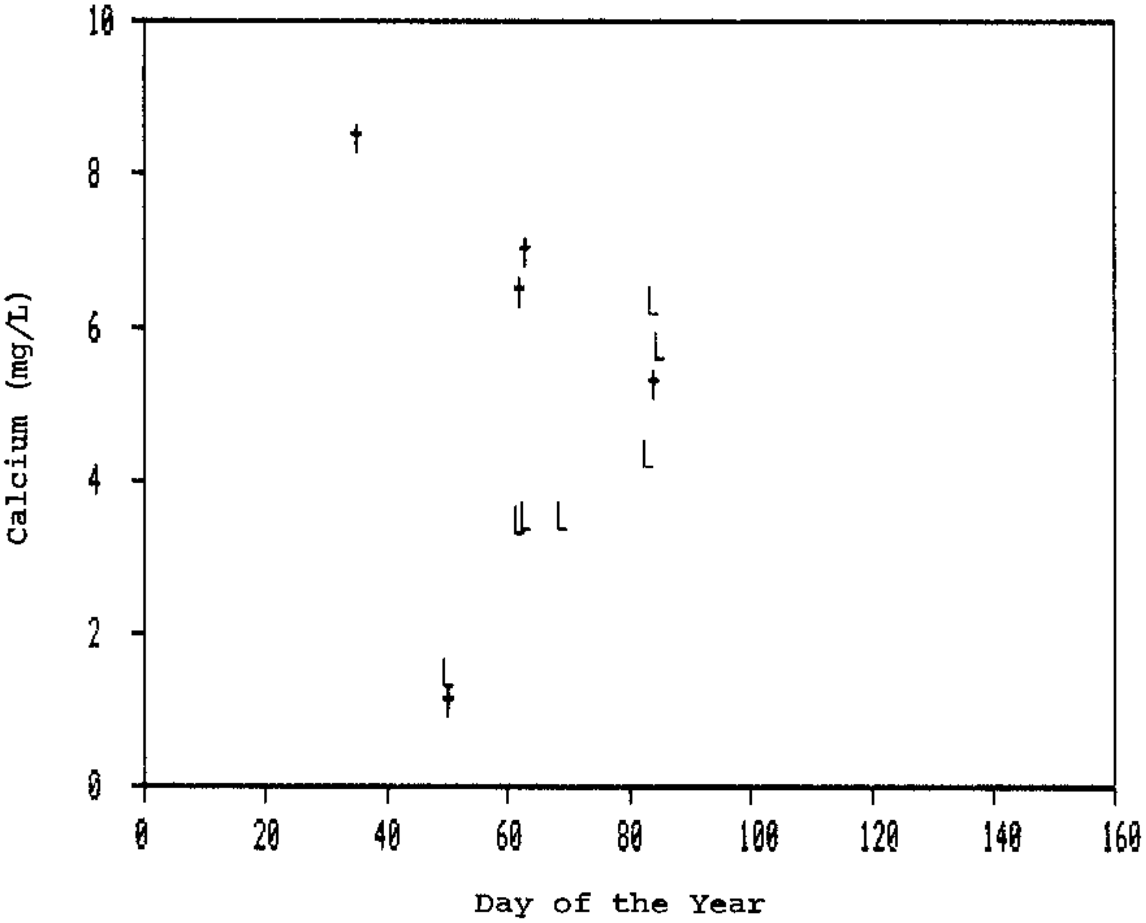
Overall, although 12 separate sets of samples including 70 separate samples were taken, on which more than 200 analyses (not counting cadmium, iron, lead or copper tests) were made, the overall model of this sytem is still very spotty and incomplete. The use of automated analysis procedures involving either electrodes or colorimetric methods in conjunction with automated atomic absorption/flame emission will definitely need to be used in order to complete a near comprehensive chemical model of this waste system. This will be particularlyy true when the irrigation system and test plots are added to the system. These particular results give us a general idea of the utility of the system and show specifically which types of analyses at what levels of detection should be automated for the continuation of this project.

Figure 6: Concentration of Sodium in the Collection Tank and Lagoon (#1) as a Function of Time.



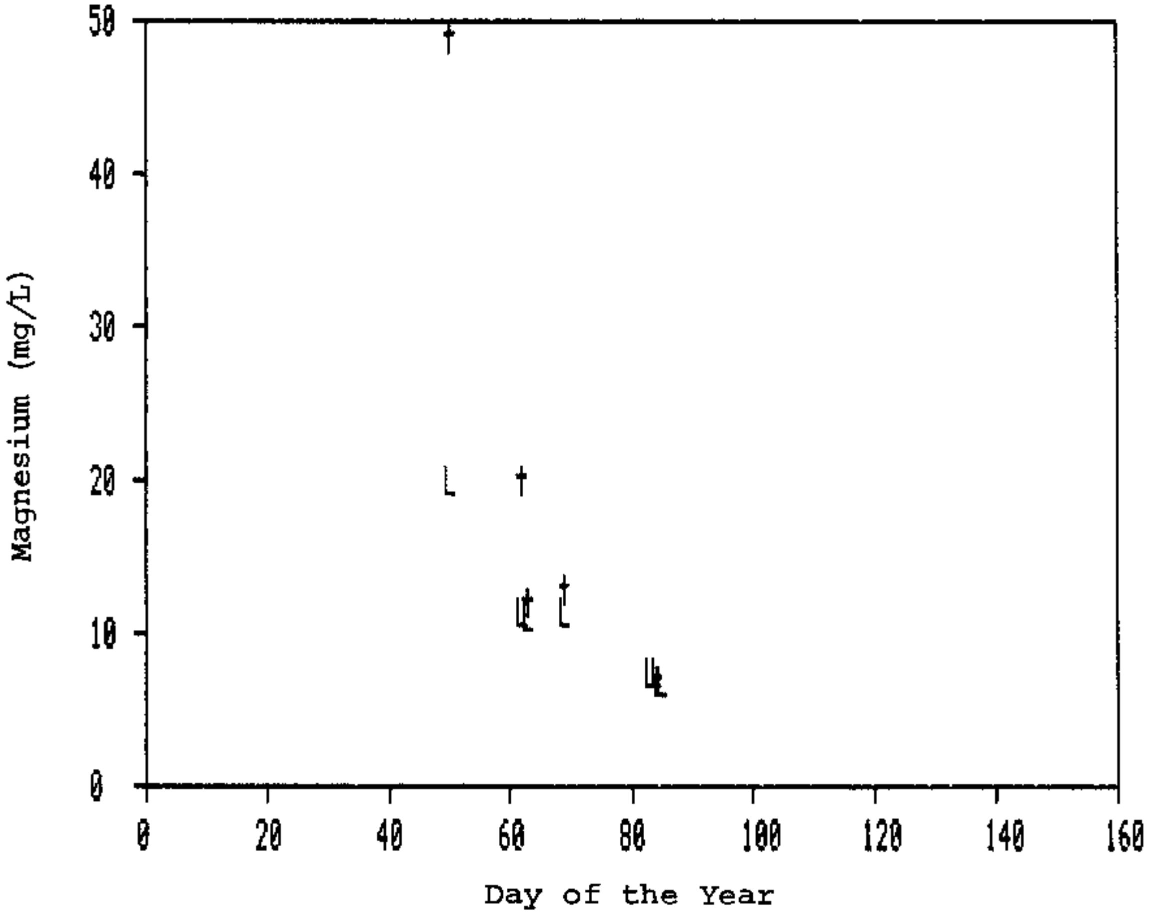
t = Collection Tank sample.
L = Lagoon (#1) sample.

Figure 7: Calcium Concentration in the Collection Tank and Lagoon (#1) as a Function of Time.



t = Collection Tank sample.
L = Lagoon (#1) sample.

Figure 8: Magnesium Concentration in the Collection Tank and Lagoon (#1) as a Function of Time.



t = Collection Tank sample.
L = Lagoon (#1) sample.

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