



GREEK BIOGAS PRODUCTION FROM PIG MANURE AND CO-DIGESTIONS.

EVALUATION OF ANAEROBIC DIGESTION PROJECTS IN LIVESTOCK
UNITS.

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FINAL REPORT

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GREEK BIOGAS PRODUCTION FROM PIG MANURE AND CO-DIGESTIONS

FINAL CONSOLIDATED PROGRESS REPORT

for the period from **01-07-1999** to **31-01-2001**

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Final consolidated progress report

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Partners' Final Progress Reports

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2. SUC
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4. AUT
5. ZITA

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X. Karamanlis, A. Kamarianos and S. Kyriakis

Phase I. Survey of the environment and activities in the surrounding area of the two Greek pig farms (Crete and Sparta) and the wastewater disposal methods applied.

Introduction

The development of advanced zootechnical methods targeting the improvement of animal production led to gradual "industrialization" of the farms. The concentration of intensively breeding animals in big numbers into the farms caused the problem of the management of the large amounts of their wastes and wastewaters. The problem is increased in areas where the traditional use of animal wastes as fertilizers or soil improvers substituted by the use of chemical fertilizers or there is lack of cultivated land.

The use of technology improved the methods of animal waste treatment focusing the interest on the following main scopes:

- Recovery of nutrients (mainly N, P, K) by the means of using the treated wastes as fertilizers.
- Recovery of nutrients by the means of producing animal supplementary feeds
- Energy production by using them or their treatment byproducts (e.g. CH₄) as fuels.
- The protection of environment
- The protection of human and animal health.

The choice and the application of the management method depend on three main factors: The kind and the availability of the final receiver of the treated wastes or wastewaters, the cost of the installation and operation of the treatment method and finally on the standing legislation. Also the management, treatment and disposal of the treated wastes depend worldwide on some other factors as the size and the zootechnical method of the farm, the size and the other activities of the adjacent land, the existent pollution of the environment and finally on the religious and cultural individualities of each country. Although, "lagoons" is the most common management and treatment method for wastewaters from piggeries, last decade, a lot of researchers are developing treatment systems called more "natural friendly" or aiming on the reuse of treated wastewaters, such as the constructed wetlands (Polprasert, 1994, Cronk, 1996, Sievers 1997a and 1997b, Yang 1997).

In E.C. countries with intensive animal production, as Netherlands, Belgium, Germany, France, the limitations on the treatment and mainly on the disposal of

wastes and wastewaters are due to the lack of available land and the pollution of the environment (urban, agricultural, industrial origination).

In Greece, because of low animal and industrial production (in comparison to other E.C. countries), and the sparsely of the land, there is less skepticism about the pollution caused by animal wastes. Greek Legislation enacted the rules of animal farm establishment for the protection of the Public Health, the environmental health, as well the rules of handling, storing, treatment and disposal of animal wastes, (Ministerial Decision A1β/8181/5-2-87 and E1b/221/22-1-65). The standards for the wastewater disposal in natural receivers are specified by the decisions of the local Prefectures.

The amount and the composition of the pig farm wastes.

The amount and the composition of the wastes from piggeries depend on a lot of factors such as: animal species, gender, age, health status, nutrition, stabling system etc., (Karamanlis, 1989). Aarnink et al., (1992) created the mathematical model MESPRO which gives a good approximation (Hoeksma and Aarnink, 1996), of the amount and the composition of the slurries from fattening pig farms, based on pig weight (L.W.), water consumption by the animal or used for cleaning purposes, feed quality and consumption, environmental and slurry temperature and the duration of wastes storage. Data on wastes amount production and their concentration in dry matter (D.M.%) related to pig age, body weight and nutrition are given in table 1, (Grundey, 1980). From that data it could be concluded that the quantity and the quality of the wastes in relation to their contamination in dry matter can be controlled through the water supply method or its incorporation into the feed. It must be mentioned that water consumption in piggeries in Greece is higher than in North Europe due to climatologic conditions.

The composition of the wastes from pig farms, related to possible environmental impacts due to their disposal or a possible utilisation are given in table 2, (Furrer, 1974). B.O.D.₅ represents the high organic matter contamination of the wastes which in the case of pig wastes is translated to a population equivalent of 3 to 4 man per pig, although the biodegradation rate of pig wastes doesn't permit an accurate equivalence, (Markantonatos, 1986). The contamination of the wastes in volatile solids indicates the ability of biogas production under anaerobic treatment conditions. Finally, the fact of the significant difference in the concentrations of

nutrients (N, P, K) in faeces and urine indicates that the separation of the above portions acts on the quality of the wastes as well on the selection of their treatment and management method.

The impact of the pig farm wastes on the environment.

I. The impact on the atmosphere

Odours: The odours are bad smelling compounds (NH_3 , H_2S , volatile organic acids, mercaptanes, alcohols, aldehydes, cetones) produced during the anaerobic decomposition of the wastes. Although odours are not classified as typical «pollutants», they are very annoying and cause mainly a social problem. The storage of wastes in covered tanks, placed in appropriate position related to local wind directions as well their incorporation into the soil instead of spreading during fertilisation of the land could reduce the smell problem.

Production of toxic gases: Ammonia emissions from pig stalls, waste storage systems, field application of liquid manure can cause serious air pollution problems to the microenvironment of the farm as well to the total environment. Ammonia emissions contribute to the development of acid rain (Abbozzo et al., 1996). In Netherlands according to Groenenstein (1994), about 40-50% of the above fact is due to ammonia emissions. Continuous breathing of ammonia, even in low concentrations, increases the susceptibility of pigs and pig farm employers to respiratory diseases. Ventilation systems, manure and urine collection, management methods and diet manipulation, contribute to the reduction of ammonia as well as of other toxic gases (H_2S , CO_2) emissions. The eligible levels of the main toxic gases produced from pig wastes are given in table 5.

Table 5. Eligible levels of the main gases produced from pig wastes.

Gas	Smell	Eligible levels (ppm)
NH_3	acute	<10
H_2S	heavy	<10
CO_2	no	<300
CO	no	<7
CH_4	no	-

Balkamos et al., 1999

II. The impact on aquatic ecosystems.

The development of anoxic environment in aquatic ecosystems. The anoxic environment in aquatic ecosystems is due to the initially aerobic decomposition of the organic matter of the wastes. Later, after the total depletion of the dissolved oxygen, the anaerobic decomposition is developing and that cause the production of bad smelling as well as toxic gases (CH_4 , H_2S , CO_2 , CH_4).

Eutrophication of surface aquatic ecosystems. The development of eutrophication of the surface aquatic ecosystems due to the inputs of animal wastes refers to their high contamination in nutrients (N, P, K). As a result of eutrophication is the inordinate growth of aquatic plants (specially phytoplanktonic) which in many cases is desirable because it provides food to fish populations. In the case of hyper-eutrophication, the sun light penetration into the deep layer of the aquatic ecosystems is not permitted due to the thickness of phytoplanktonic population and the development of anaerobic activities take place. The decomposition of dead planktonic organisms on the sediment contributes to the development of the anaerobic environment.

The pollution of groundwater. The pollution of groundwater by the contaminants of the wastes from pig farms is mainly due to the soluble nitrate salts movement into aquifers. Nitrates are responsible for the appearance of the fatal infant disease called methemoglobinemia.

III. The impact on terrestrial ecosystems.

The impact of the unbounded waste application from piggeries on the land results on the change of its structure and its properties, decreases its draining ability and its penetration by air, reduces micro-organism activities because of the high concentration of heavy metals (Cornforth, 1973), develops unsuited pastures for grazing and contributes on the infection of diseases and the production of unpleasant odours.

Pig farming and waste management in Greece

Although, there is no tradition on pig production in Greece and the contribution of Greek pig production in E.C. is low (0,89%), «industrial type» farms are also established (Katsaounis and Spais, 1998). Characteristically, according to

E.C. data of 1996, the 81% of the pigs in Greece are produced in large farms (>100 sows) that represent only the 2% of the total pig farms of the country, (E.C., 1997).

In piggeries the management, treatment and disposal of their wastes, varies depending on the size of the farm and the possible other productive activities of the enterprise, such as slaughter house, meat factory, that operate nearby.

According to the Greek Ministry of Agriculture (Katsaounis and Spais, 1998), the 17.5% of the pig farms of the country has installed a wastewater treatment system, but in many cases this is not in use because of the high operational cost. Also, in practice, in the case of well-designed and installed systems exist the problem of the sludge or the treated wastewater disposal, because of the lack of the appropriate final receiver. In many cases, the treatment efficiency of the installation is low because of the incorrect maintenance.

The most common management and wastewater treatment methods in pig farms in Greece are (Karamanlis et al., 1998):

- The use of stabilization tanks (lagoons) in farms over 500 sows.
- The use of the channels under the slatted floor or lagoons in farms sized $100 < \text{sows} < 500$.
- Land spreading in the case of farms < 100 sows.

In two cases in Greece (Korinthos area, Naxos island) the application of anaerobic treatment methods targeting biogas production from pig slurries was unsuccessful (C.R.E.S., 1997).

Also, the international experience on the production of biogas by the anaerobic digestion of exclusively pig slurries was rather disappointing. Contrary, Willers and Zeeman (1996), suggest that the co-digestion of pig slurries and other wastes, such as urban, dairies, agricultural is more efficient for biogas production.

Depending on the housing system and the waste management methods swine manure is handled either as solids or slurries and liquids. The wastes in the form of «slurries» (4-8% or up to 15% solids) can stored in under-floor storage pits or outdoors into above or belowground, tanks. As «liquids» (<4% solids) swine wastes are transferred, retain and treated in stabilisation ponds (lagoons). Lagoons can be either aerobic (up to 1.5 m depth) or anaerobic (up to 6 m depth). Anaerobic lagoons demand less land area for their establishment but they produce odours. Covering anaerobic lagoons by a floating cover helps to the collection of the produced biogas and reduces the odour emissions.

Using treated wastes from piggeries as land fertilisers is the most common practice in waste management. The Greek Ministry of Agriculture (1994) published the «Code of good agricultural practice» of the rational application on land of the wastewater from pig farms.

Possible sources and the quality of their effluents related to biogas production in Greece.

Targeting biogas production by co-digestion of piggery wastes and others of agricultural origination, CRES and partners focused on two areas in South Greece: Sparta (Peloponnese) and Rethymnon (Creta island). These areas are rather known for olive oil and fruits (orange) production activities as well for goat milk products. Additionally, Crete island as well Sparta are very attractive areas for tourism and that means a high sensitivity on environmental protection and a high care for the Public Health. Coincidentally, because of the very low cattle production, in these areas exist two of the biggest Greek pig breeding enterprises combining pig farms, slaughterhouses and meat factories. Also, in the nearby area exist a number of olive oil mills, orange processing factories and cheese-dairies. According to information collected, the problem of waste management in all of the above-mentioned enterprises is of a great importance.

Except of the two main pig farms, representative industries of olive oil mills, fruit treatment and dairies were selected for the specification of their waste and wastewater quality, as follows:

I. The area of Sparta.

a) The main source (pig farm, slaughterhouse, meat factory).

In a sort distance (10km) from the city of Sparta is situated the "Tsikakis - Yannopoulos" enterprise consisted of a 650 sows pig farm, a slaughterhouse and a pork meat factory.

The pig production of the farm is about 14,200 fattening pigs per year. According to the breeding system used the daily animal population of the farm consists of about 650 sows, 1,090 suckling piglets, 1,640 weaners, 1,910 growers and 1,910 fatteners. Animal wastes (slurries) are treated to a private aerobic treatment plant next to pig farm. It is well known that the final quantity and the quality of pig farm effluent is related to several parameters such as nutrition, water intake,

physiological stage of the sows, housing system, water used for cleaning and sanitation, etc. The wastewater from "Tsikakis - Yannopoulos" pig farm is collected in a tank following by mechanical screening for solids separation. The amount of wastewater produced (in average) is about 100m^3 per day according to estimations made two years ago for the designing of the aerobic treatment plant (Environmental Mechanics Ltd., personal communication).

The wastewater from the slaughterhouse and the meat factory are also treated to the same plant after their passage from a Dissolved Air Flootation system (DAF). The sludge collected by DAF system is about 1.5 m^3 per day.

Because of the lack of any other slaughterhouse in the greater area of Sparta, the "Tsikakis - Yannopoulos" slaughterhouse is also used for the slaughtering of cows, sheep, pigs from other farms, etc. That makes difficult the estimation of the quantities as well the quality of the effluent and the comparison with other bibliographic references. The quantification of the slaughterhouse effluent is based on the amounts counted two years ago for the planning demands of the aerobic treatment plant and the quality is based on analyses that AUTH made for the current case. The average of wastewater produced by slaughterhouse and meat factory activities is about 100m^3 per day.

Bones, fat, other byproducts or no consumable parts of the fatlings are chopped, heated by steam and finally are centrifuged for oil and grease extraction. The management of the residue (given in the past as feed) is now a serious problem. It is estimated that 400 Kg of oil and grease and 400 Kg of "bone-meat" residues are produced daily. The produced oil and grease, is used -after melting- in a spray form to increase the energy value of dried olive husk which is the main combustible source to produce steam for several uses in the slaughterhouse, the meat factory and the treatment-sanitation of their solid wastes.

The flow chart of the wastewater treatment system in "Tsikakis-Yannopoulos" pig farm is given in Figure I.

The results of the analyses of the quality parameters of the above wastes and wastewater related to biogas production are given on Table I.

b) Other sources for co-digestion in anaerobic treatment plant.

In a 25Km rad distance from "Tsikakis - Yannopoulos" enterprise also exist a number of olive oil mills, orange processing factories, cheese-dairies and another (of

the same ownership) pig farm. The animal population of that farm consists of 250 sows and 5400 fattening pigs/year. According to the breeding system used the daily animal population of the farm consists of about 250 sows, 420 suckling piglets, 630 weaners, 735 growers and 735 fatteners.

The oil mill waste production consists of the olive processing wastewater (commonly called *katsigaros*) and the solid wastes as "olive husks". The olive husks are treated in a nearby factory to produce the olive husk oil and the residues of the processing consist a dry olive husk wood. The later is used for combustion in several cases but there is no extended commercial interest. The use of "*katsigaros*" and olive husks as alternative sources of co-digestion materials is temporary limited because of the olive oil mills operate only a few months in a year (November - February). The amount of "*katsigaros*" produced is related to the type of olive oil mill. According to Michelakis and Koutsaftakis, (1989) the traditional type (pressure) of olive oil mills produces 0.65 lt./kg of treated olives and the centrifugal type produce 1.0 lt./kg of treated olives. The results of the quality characteristics for the above wastewater and wastes from olive oil mills are given in Table I.

Another possible source to feed the anaerobic digester is the orange processing factory named "Lakonia". The total amount of oranges treated for the production of orange juice is about 50,000 ton per year. The 30-40% of the above mentioned amount of oranges consists the orange juice and the residues are wastes. At the moment the factory uses a drying system to pelletize the orange residues to sell them as animal feed but there is decreased interest by the side of farmers. The operation of "Lakonia" is also related to the period of orange production and that is from November (about 2,000 ton), December - March (about 10,000 ton/month), to April - May (about 8,000 in total). The results of the quality characteristics of the wastes from orange processing factory are given in Table I.

Finally in the above-mentioned area exist a number of cheese-dairies that produce the Greek traditional Feta cheese. The wastewater from cheese-dairies consists mainly of whey (commonly used for the production of other types of cheeses e.g. "*mitzithra*"), water for the freezing of the milk and water for cleaning and sanitation purposes. The yield of milk treatment to produce cheese depends on the composition and the origination of the milk (goat, sheep, cow milk). For "feta" cheese production the yield is about 3.5 - 4 kg milk/1.0 kg "feta" (the rest is whey). According to information collected in situ, the yield of milk/"feta" is about 5/1. The

water used for freezing is about equal to the amounts of the treated milk and the water used for cleaning is about the 1/5 of the milk used. The use of wastewater from cheese dairies as organic source for anaerobic digestion is also temporary depended, because the above dairies operate from the end of October till the end of the June. The results of the quality characteristics of the wastewater from cheese-dairies are given in Table I.

II. The area of Rethymnon (Crete Island).

a) The main source (pig farm, slaughterhouse, meat factory).

In a distance of about ten (10) kilometers from the city of Rethymon is situated the "Creta Farm" enterprise consisted of a 1,800 sows pig farm, a slaughterhouse and a pork meat factory. "Creta Farm" is one of the biggest pig farms in Greece.

The pig production of the farm is about 40,000 fattening pigs per year. According to the breeding system used the daily animal population of the farm consists of about 1800 sows, 2,500 suckling piglets, 3,340 weaners, 3375 growers and 6750 fatteners.

The slurries (animal excreta, water used for cleaning) produced from the pig farm are collected in a primary collection tank. About 250 m³ of slurry is daily produced. The wastewater is collected in a sedimentation tank after screening for solids separation. The settled solids are centrifuged and the de-watered solids are used as fertilizers. Wastewater from the sedimentation tank is farther treated in three (3) consecutive aerobic treatment tanks. The main volume of the treated wastewater is loaded in a final tank and then is used for irrigation and a small portion (mainly sludge) is used for refeeding the system.

The wastewater from the slaughterhouse and the pork meat factory (about 100 m³/day) is collected in a primary aeration tank. The pre-treated wastewater is farther treated to the main aerobic treatment system of the farm.

The flow chart of the wastewater treatment system in "Creta Farm" is given in Figure II. The results of the analyses of the quality parameters of the above wastes and wastewater related to biogas production are given on Table II.

b) Other sources for co-digestion in anaerobic treatment plant.

In the greater area of Rethymnon exist a number of olive oil mills and cheese-dairies. Also, in the city of Chania (about 70 Km away) exist an orange-grapefruit processing factory.

In relation to the area of Sparta, mentioned above, the olive processing in Rethymnon area is similar because of the use of the same centrifugal type oil mills. So, there are not expected differences between the quality characteristics of the wastewater produced during the oil mill processing in the above areas.

The oil mills as well the olive husk treatment plant (Association of Rethymnon Agricultural Units) operate from November to March. Suggestively, the dried olive husk production is about 4500 ton /period.

Opposite, the cheese-dairies in Crete island produce different types of cheese than in Sparta (feta cheese), follows a different treatment process. In a sort distance (15 km) from Rethymnon exist the "Plimakis" cheese dairy that produce traditional "hard cheese". The dairy operates from October to June treating about 1,000 ton of milk. The production of cheese is about 15 Kg of cheese/ 100 Kg milk. About 5% of the whey is reheated for "mitzithra cheese" production (12% yield). Although the cheese making process gives about 73% as wastewater the total amount of wastewater increases because of the water used for cleaning and freezing proposes. It is estimated that finally the wastewater produced is about 7 lit. of wastewater per litter of milk treated.

At the East side of Rethymnon also exist another cheese dairy of the Association of Rethymnon Agricultural Units ownership. The dairy also operates from October to June treating on average about 20 ton of milk monthly. The quality of its effluent is indicated as "cheese dairy II" in Table II.

The results of the analyses of the quality parameters of the above wastewater related to biogas production are given on Table II.

In a suburb of the city of Chania 70 Km from Rethymnon exists an orange-grapefruit-processing factory. The industry operates from December till September treating about 15,000 ton of oranges (mainly) and grapefruits for juice production. The 40% of the treated fruits are wastes as bark, the 1.5% as thick cut pulp and 1% as thin cut pulp. The barks are used as animal feed.

The results of the analyses of the quality parameters of the above wastewater related to biogas production are given on Table II.

Phase II. Determination of the opportunities for biogas applications in these potential customers.

The determination of the opportunities for biogas production by anaerobic co-digestion of the wastes and wastewaters of the previously mentioned sources is based on the estimation of the quality of the effluents as well the available quantities. The qualification of the waste and wastewaters produced was estimated as follows and the final results are represented in Tables I and II.

Materials and Methods

Double representative samples were collected from selected points of the above-mentioned enterprises. The selection of the sampling points was based on the effluent flow chart of each enterprise targeting the delineation of the wastewater quality.

The samples were collected in polypropylene sampling bottles (0.5 lit. cap.) and transferred in a portable refrigerator (4°C) at the Veterinary Faculty of the University of Thessaloniki.

Analyses of the samples took place at the Laboratory of Ecology & Protection of Environment of Veterinary Faculty AUTH, 24 hours after sampling, for a variety of parameters related to pollution potential of the wastewater or wastes, their nutritional value and to the aim of the program: the production of biogas from pig wastes and co-digestions. The samples were analyzed for the determination of Dry Matter content, Ash and Organic Matter, Organic Nitrogen (Kjeldahl), Total Phosphorus, Potassium, Oil and Grease, Biochemical Oxygen Demand (B.O.D.₅) and Chemical Oxygen Demand (C.O.D.).

All analyses were made according to Standard Methods (APHA, 1989) procedures as adapted by Karamanlis (1989) for animal waste analysis.

Dry Matter, Ash and Organic content.

Dry Matter (D.M.) content was estimated by drying the sample at 105°C till stable weight. Ash and Organic content was estimated by ignition of the pre-dried samples at 550°C in a muffle furnace.

Apparatus:

- Porcelain evaporating dishes, 90 mm diam.

- Melag drying oven for operation at 103°C – 105°C.
- Dessicator
- Heraeus muffle furnace for operation at 550±50°C.
- Sartorius analytical balance capable of weighing 0.0001 gr

Procedure:

A well-mixed solid sample volume ranged between 30 to 100 gr of w.w. sample or 160 ml of well-mixed liquid sample were transferred to preweighed and evaporated to dryness porcelain dish. The samples were dried overnight at 103-105°C, cooled in temperature room into the dessicator and weighed for D.M. estimation. The ash and organic content were estimated by the ignition of the dried samples first over a gas burner and then into a muffle furnace at 550±50°C.

Calculation:

$$\% \text{ D.M.} = (A-B) \times 100 / (C-B)$$

$$\% \text{ Ash} = (D-B) \times 100 / (A-B)$$

$$\% \text{ Organic} = ((A-D) \times 100 / (A-B))$$

A = weigh of dried residue + dish

B = weigh of dish

C = weigh of wet sample + dish

D = weigh of residue + dish after ignition

Organic Nitrogen.

Organic Nitrogen was determined by Kjeldahl method without ammonia removal followed by steam distillation and titration.

Apparatus:

Kjeldahl digestion flasks, 800 ml.

Heating device, 370°C.

Parnas-Wagner distillation apparatus.

Reagents:

Conc. Sulfuric acid

Sulfuric acid 0.02 N

Sodium Hydroxide 30%

Potassium Sulfate

Mercury oxide red

Boric acid 2%

Mixed indicator solution (200 mg methyl red indicator in 100 ml ethyl alcohol mixed with 50 mg methylene blue in 50 ml ethyl alcohol).

Procedure:

About 1 gr of solid sample or 10 ml of liquid sample were placed into a Kjeldahl flask follows by the addition of 20 ml conc. sulfuric acid 20 gr potassium sulfate and 0.4 gr mercury oxide red. The flask was heated on a heating device under a hood till the colored or turbid samples turned clear or straw-colored. After digestion the sample was diluted to 250 ml with distilled water. About 10 ml of the diluted sample was distilled in a steam distillation apparatus (Parnas-Wagner) by the addition of 10 ml of sodium hydroxide. Distillate was collected in an Erlenmeyer flask containing 50 ml boric acid plus few drops of mixed indicator solution. Finally the boric acid solution was titrated by the use of 0.02 N, sulfuric acid.

Calculation:

$$\text{Organic N\%} = 0.0014 \times 100 \times N \times B / A \times C$$

N = ml of 0.02 N Sulfuric acid used in titration

A = gr or ml of the sample

B = the dilution of the sample after digestion

C = ml of the sample for distillation.

Total Phosphorus

Total Phosphorus was estimated spectrophotometrically by vanadomolybdophosphoric acid method.

Apparatus:

PH meter, WTW PH 90

Filtration apparatus and filter (Whatman no 42).

Spectrophotometer at 400 nm, (SHIMADZU UV-160A)

Reagents:

Conc. Hydrochloric acid

Activated carbon

Standard phosphate solution

Vanadate molybdate reagent (25 gr ammonium molybdate in 400 ml d.w. 1.25 gr ammonium vanadate in 300 ml d.w. and 300 ml conc. Hydrochloric acid. The solution was diluted up to 1 lit by d.w.)

Procedure:

The ash obtained from the ash content determination was diluted by the use of 1.5 ml hydrochloric acid and distilled water to a final volume of 100 ml. If the pH of the sample was less than 4, the sample was diluted 1:2 by distilled water. Any color was removed by filtration of the sample mixed with 200 mg activated carbon through a Watman no 42 filter. 35 ml of the sample and 10 ml of vanadate-molybdate reagent were placed in a volumetric flask and the final volume was 50 ml by the addition of distilled water.

A calibration curve was obtained by the use of 1, 5, 10, 15-ppm P-PO₄ solutions treated as the original sample. Total phosphorus content was estimated by the use of a SHIMADZU UV-160A, spectrophotometer at 400 nm.

Potassium

Potassium (K) was estimated by the use of flame photometer method.

Apparatus:

Porcelain cookers 4 cm (diam.)

Filtration apparatus and filter (Whatman no 42)

Heraeus muffle furnace for operation at 400-450°C.

Flame photometer (EEL Model 150).

Reagents:

Deionized – distilled water, (d.d.w.)

Potassium chloride solution, 200mEq K/lit

Conc. hydrochloric acid, HCl

Conc. ammonium hydroxide, NH₄OH.

Procedure:

A well-mixed solid sample volume ranged between 30 to 100 gr of w.w. sample or the residues of 160 ml of well-mixed liquid sample were transferred to

porcelain cookers. The ash obtained by the ignition of the dried samples first over a gas burner and then into a muffle furnace at 400-450°C was diluted with the help of 1 ml hydrochloric acid and d.d.w. up to the notch of a 100 ml volumetric flask. Neutralization of pH was taken place by adding ammonium hydroxide. A standard solution of 0.5 mEq K/lit was prepared for Flame photometer calibration. The results were expressed as mEq K/lit.

Oil and grease

Oil and grease was determined by Soxhlet extraction method for sludge samples (APHA, 1989).

Apparatus:

Extraction apparatus, Soxhlet

Sartorius analytical balance capable of weighing 0.0001 gr

Flask evaporator at 70°C

Extraction thimble, paper

Reagents:

Magnesium sulfate monohydrate dried at 150°C overnight

Trichlorotrifluoroethane

Procedure:

About 20±0.5 gr of the sample was mixed by stirring with 25 gr of magnesium sulfate into a porcelain mortar. Paper thimble was filled and extracted using Trichlorotrifluoroethane at a rate of 20 cycles per hour for about 4 hours. The solvent was distilled at 70°C in water bath. The weight of the residue represented the oil and grease content of the sample.

Biochemical Oxygen Demand (B.O.D.₅)

Biochemical Oxygen Demand was estimated by the use of an YSI model 51B oxygen meter.

Apparatus:

YSI model 51B, oxygen meter.

B.O.D.₅ bottles

Freezing incubator at 20°C

Procedure:

Sample was homogenized and multi-diluted with d.w. to a final dilution 1:2000 – 1:3000 depending on the sample origination. About 300 ml of the sample was seeded in B.O.D.₅ bottles at 20°C for 5 days. The difference in concentration of diluted oxygen as mg O₂/lit between the 1st and 5th day, multiplied by the dilution rate give the B.O.D.₅ value.

Chemical Oxygen Demand (C.O.D.)

C.O.D. were estimated by the use of a HACH, C.O.D. reactor. The analysis is based on the use of a strong oxidant as Potassium dichromate (K₂Cr₂O₇) for the oxidation of organic matter.

Apparatus:

HACH, C.O.D. reactor

Test tubes, 15 ml with Teflon cap.

Reagents:

Standard potassium dichromate solution 0.25 N

Sulfuric acid solution (22 gr AgSO₄ in 4 Kg H₂SO₄)

Standard ferrous ammonium sulfate titrant 0.1 N

Ferroun indicator solution

Mercuric sulfate

Procedure:

2 ml of the diluted (for B.O.D.₅ determination) sample was placed into a test tube containing 1ml of the sulfuric acid solution, 2 ml of potassium dichromate solution 0.25 N and 40 mg of mercuric sulfate. The tube was place into C.O.D. reactor at 140°C for about 2 hours. After cooling at room temperature, 2ml of d.w. and 2-3 drops of ferroun indicator solution was added and mixed. The final volume was titrated by standard ferrous ammonium sulfate titrant 0.1 N. The above procedure was applied for a "blank" sample consisted of 2 ml distilled water.

Calculation:

$$\text{C.O.D. (mgO}_2\text{/lit)} = (A-B) \times N \times 8000 / C$$

Where:

A = ml of ferrous ammonium sulfate titrant for blank titration

B = ml of ferrous ammonium sulfate titrant for sample titration
C = ml of the sample
N = Normality of ferrous ammonium sulfate titrant

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Table II. Production units and the quality of their effluents in the area of Rethymnon (Crete island).
The results are expressed as gr or mg per lt. or per Kg (W.W.) depending on the physical properties of the sample

Source	code	Sample units	D.M. gr/lt or Kg	Ash % D.M.	organics % D.M.	B.O.D ₅ mg/lt or Kg	C.O.D. mg/lt or Kg	Total - P mg/lt or Kg	Organic N N** g/lt or Kg	oil and grease mg/lt or kg	K mg/lt or kg
Pig farm collection tank	1	lit	18,1	31,3	68,7	10000	18150	544,7	3,25	175	1108,4
Sedimentation tank	2	lit	11,9	37,0	63,0	6400	13650	409,2	2,35	218	1289,6
Aeration tank	3	lit	2,5	38,0	62,0	5000	5800	60,8	0,34	19	75,5
Refeeding tank	4	lit	4,4	59,3	40,7	2200	4550	158,8	0,28	24	881,0
Solids after centrifugion	5	kg	629,4	39,7	60,3	3200	4550	29077,1	20,72	1350	2120,6
Treated effluent tank	6	lit	<0,1			2600	4350		0,11	15	140,4
Solids after screening	7	kg	260,1	21,9	78,1	1600	4350	8315,5	5,60	1526	2266,1
Slaughterhouse aeration tank	8	lit	0,6	54,3	45,7	2200	9100	5,9	0,11	22	2,8
Cheese dairy I (whey)*	9	lit	1,9	10,0	90,0	6200	40900	11,0	0,73	189	22,3
Cheese dairy I total effluent*	10	lit	4,4	15,6	84,4	8800	63600	21,4	1,34	70	70,5
Cheese dairy II	11	lit	2,5	5,7	94,3	4800	18150	12,3	0,67	416	19,9
Orange processing wastes	12	kg	110,8	5,3	94,7	4000	13650	188,2	7,28	2045	1577,9
Thick cut orange pulp	13	kg	136,1	3,7	96,3	3600	4550	228,9	4,48	1077	1695,6
Thin cut orange pulp	14	kg	107,6	4,1	95,9	6400	13650	327,7	3,36	2045	2220,7

Codes 1 - 8 are related to "Crete farm".

* "Plimakis" cheese dairy.

** Kjeldahl Nitrogen without ammonia removal.