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Quantification of Performances of the Bioreactor of La Vergne

Master's Thesis in the International Master's Programme Applied Environmental Measurement Techniques

JEAN-CHRISTOPHE AUGEY

Department of Civil and Environmental Engineering
Water Environment Technology
CHALMERS UNIVERSITY OF TECHNOLOGY

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Jean-Christophe Augey

QUANTIFICATION OF PERFORMANCES OF THE BIOREACTOR OF LA VERGNE

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Diffusion :

Britt-Marie WILEN Chalmers University of Technology	
Delphine LE BOURHIS	GRANDJOUAN ONYX
Gaëlle LELAY	SENETD
Michel GUERBOIS	GEOLIA
Nathalie SKHIRI	CREED

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Validé par : *Nathalie SKHIRI*

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ABSTRACT

Quantification of performance for the bioreactor landfill of La Vergne

More and more strict environmental legislation obliges Municipal Solid Waste Landfill (MSWL) operators to think about new storage forms. They have developed bioreactor landfills for this purpose. A few bioreactor landfills are operated, especially in the United-States, but the amount of scientific data about their optimizations and operation is still low.

Therefore the research program concerning the MSWL of La Vergne, where there is an anaerobic bioreactor cell, aims at understanding phenomena occurring inside the bioreactor and assessing their performances. In order to achieve these goals, liquids and gas are analyzed and quantified through periodical samplings, measurements and a continuous monitoring of the quantities going in and out for leachate, and only out for the biogas.

It has been possible to show the relvance of a weekly uptake during the relaxation week and to make a monitoring protocol for the leachate going out of the bioreactor. Lagoon leachate, which has been regularly monitored, has given results on the influence of meteorological conditions. It has been shown that this influence can be neglected, except for exceptional cases, but it's possible to follow the evolution of leachate quality thanks to calculations. Quantitative impact of recirculation has only been studied on a one-week and a half injection. These leachate quality analysis, combined with some biogas data, have also given signs, showing that waste inside the bioreactor landfill is globally at the methanogenesis stage, and also that some localized parts are aerobic.

This report focuses on methods and material, which have been used to monitor the bioreactor, and on its current performances.

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LIST OF ABBREVIATION

BOD : Biological Oxygen Demand

COD : Chemical Oxygen Demand

CREED : Centre de Recherche pour l'Energie, l'Environnement et les Déchets (Research Center for Energy, Environment and Waste)

MSW landfill : Municipal Solid Waste landfill

Ntotal : total Nitrogen

PET: Potential Evapotranspiration

Redox Potential: oxydo-reduction potential

TOC: Total Organic Carbon

TVA: Total Volatile Acid

I INTRODUCTION

Among the 24 million tones of municipal wastes, which have been produced in France in 2002, around 55 % have been treated by incineration, sorting valorization and biological treatment. The other 45 % have been buried in MSWL [ITOM, 2002], which shows how important the storage sector is in France. That's why it is necessary to develop better performing MSW landfills, particularly in the environmental impact domain, where European and French regulations are more and more strict.

The bioreactor landfill program is currently under development in France, USA, Australia, and in other developed countries in order to meet these new environmental objectives.

My master thesis focused on the study of an experimental bioreactor landfill, where research is carried out at industrial scale. That bioreactor landfill is located on the MSW landfill of La Vergne (Vendée, France) and is operated by the CREED (Centre de Recherche sur l'Environnement, l'Energie et les Déchets) and the local owners for three years already. Before being transformed into a bioreactor, the landfill has received household waste from municipalities, which has not been sorted for the most part of the time of operation. This project mainly aims at comparing environmental impacts of a bioreactor landfill to a conventional MSWL and at learning how to design and monitor the performance of a bioreactor. The study focused on the measurement and monitoring of key parameters to assess the performance of the bioreactor, and to understand more about the processes occurring in it.

The storage issue in France is studied in the first part of this report. The second part is focused on methodology and materials, which has been used to monitor the bioreactor landfill. Finally the current performances of the bioreactor is assessed.

II THE STORAGE ISSUE IN FRANCE

II - 1 Conventional MSW landfills

II.1.a) Working basis

Because of a recent law (arrêté du 9 septembre 1997), MSWL owners must adopt a new design in terms of confinement, isolation, collection and treatment of effluents, surveillance and preventing risks [ITOM, 2002]. The main characteristics of a MSWL are described in Figure 1. Wastes are put in cells; sub-divided into smaller cells to limit their exposition time with the atmosphere and to facilitate burying operations.

The aim of limiting environmental impacts is achieved through two types of barriers. The passive security barrier is made of a clay layer, which is between the geomembrane and the soil. That clay layer is made of a layer, which is 5 meters thick and has a permeability, k, of 10^{-6} m/s and another one, 1 meter thick, with $k = 10^{-9}$ m/s.

The active barrier is made of the geomembrane and draining network. The geomembrane is laid on the bottom of the landfill and on its sides, which prevent any leakage to the soil. Leachate is collected through a draining network and sent to a storage lagoon, where it has to be treated before being released into the environment.

A tight cover and a collecting biogas network on the surface have to avoid any direct biogas emission. As this gas is mainly composed of toxic and greenhouse components, it is burnt at a flare in the majority of the MSW landfills [ITOM, 2002].

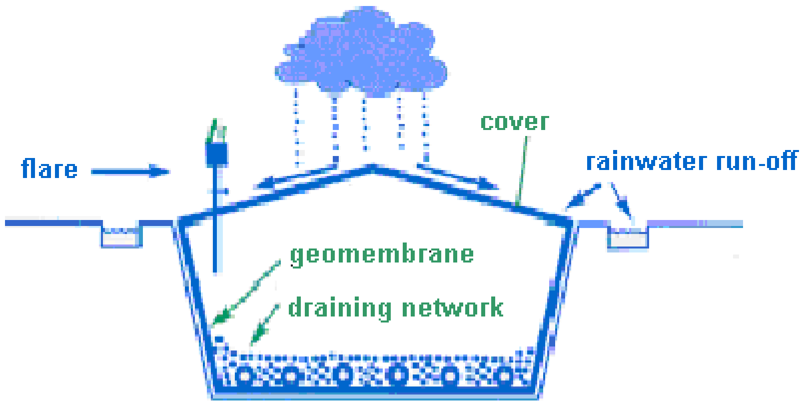


Figure 1: Simplified view of a landfill cell from a class 2 MSW landfill [ADEME]

II.1.b) Waste stabilization

After an exploitation period, when wastes are buried, the post-closure care begins. During this post-closure period, environmental regulations oblige owners to maintain the site in a good state for 30 years and to treat leachate and biogas. Then waste is supposed to be stabilized at the end of this period and should not harm the environment anymore. The land can finally be used for another purpose, such as parking lots or sport fields.

However a problem has appeared with tight covers. Indeed very little water seeps into theses covers and wastes remain dry, which slows degradation speed because humidity is a limiting factor for degradation. That phenomenon, also called « dry tomb », increases waste stabilization time and is a matter of concern for landfill owners.

II - 2 The bioreactor landfill, a new waste storage form

II.2.a) The bioreactor landfill concept

Waste storage industries are currently developing bioreactor landfills from already existing MSW or new MSW landfill in the course of filling to find an answer to the « dry tomb » problem and to have a shorter stabilization time.
The basic concept of bioreactor landfills is to raise the humidity rate of wastes through liquid injection. The aim is to create a homogeneous and optimal humidity content in the waste mass. Many bioreactor landfills have a tight cover, to prevent rejection of biogas, and air seeps inside the wastes and to get a good biogas quality. Different types of bioreactor landfills exist:

- ***Aerobic bioreactors***

In this kind of bioreactor, aerobic bacteria contribute to waste degradation. Air and water injection is favorable to their development (cf. Figure 2). The energy efficiency of aerobic respiration is higher than the anaerobic one, which accelerates waste degradation and the development of aerobic bacteria. However this important energy generation raises temperature in the waste mass and increase the risk of landfill fires. The required volume of added liquid is also higher because of the high temperature. Then post-closure costs could be higher [SWANA, 2000].

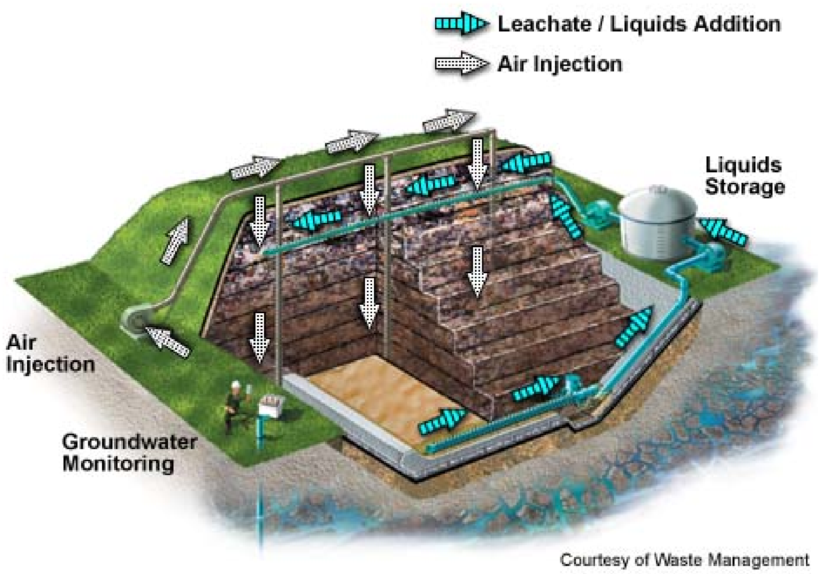


Figure 2 : View of an aerobic bioreactor [US EPA]

- ***Anaerobic bioreactor***

Anaerobic degradation is the basis of this type of MSW landfill. This degradation is slower than the aerobic one, but it presents fewer risks, particularly in the domain of landfill fires. Good development conditions for anaerobic bacteria are a humid environment and the absence of oxygen. The achievement of these conditions is done by a geomembrane, which covers the entire waste mass and by liquid injection, such as sludge water or leachate. Figures 3 and 6 show two types of liquid injection, the horizontal one (Figure 3), and the vertical one (Figure 6). The paragraph II.2.c) gives details about advantages linked to leachate recirculation in anaerobic conditions.

- ***Hybrid bioreactor***

This bioreactor combines both biodegradation types. Every layer of wastes is treated with the aerobic degradation, before being buried by another one. Then anaerobic degradation, which is enhanced by liquid injection, can begin in layers, where there is no air (Figure 3). The advantage of aerobic degradation is the fast reduction of carbon chains, which favors an early start of methanogenesis [SWANA, 2000]. The correlation between the size of carbon chains and the different anaerobic degradation stages is explained in paragraph II.2.c).

Figure 3 : View of a hybrid bioreactor

II.2.b) Description of the bioreactor landfill from La Vergne

This anaerobic bioreactor has a leachate recirculation system made of vertical injection wells, a geomembrane, which wraps up all the waste mass, and a biogas collection network (Figure 6). The site presents some particularities due to the framework of the R&D program, which has been launched by the CREED three years ago:

- A dense vertical well network.
- A draining trench.
- A lagoon dedicated to the bioreactor (injected leachate comes only from the bioreactor) in order to assess the effect of recirculation on leachate quality
- A test cell, which has the same kind of waste and is managed in a conventional way, to compare both types of waste management.

Figure 4 : Photo of the bioreactor cell before its filling

Figure 5 : Photo of the bioreactor cell after its filling (part recovered by earth) and of the test cell in the course of filling

Injection and biogas collection wells (Figure 6) have been added after the installation of the tight cover.

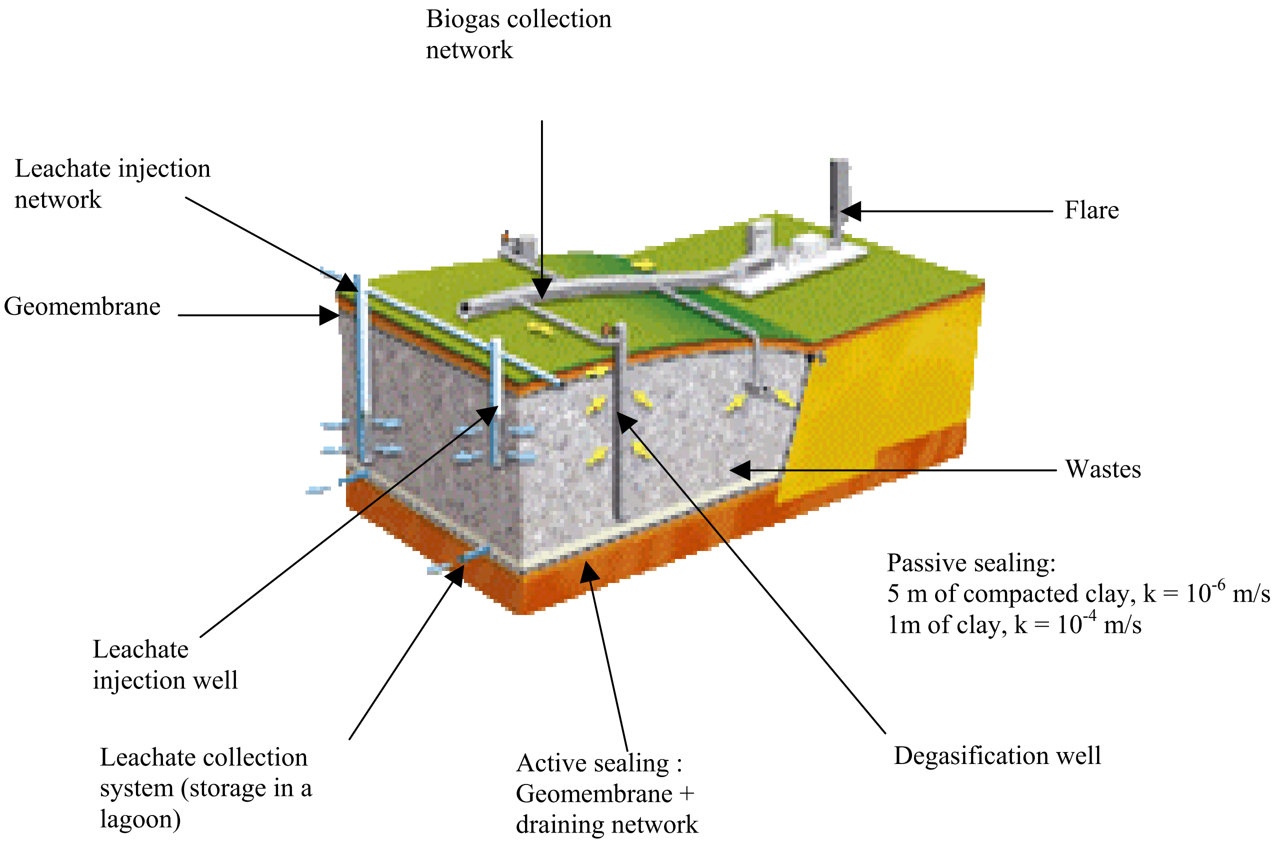


Figure 6: Simplified view of the bioreactor of La Vergne

The location of injection and biogas collections wells in the bioreactor is given in appendix IV.

II.2.c) Mechanisms of waste biodegradation:

♦ <u>Biodegradation phases</u>

The mechanisms, which are described is this paragraph, are only valid for the fermentable part of wastes. In the case of the bioreactor of La Vergne, that fraction represents on average 60 % of the waste mass [Skhiri, 2004]. Two main phases occur, with different stages for the anaerobic one:

- ***Aerobic phase***

Aerobic degradation occurs during the filling of the cell, when waste is still in contact with the air, until complete consumption of the oxygen. The activity of aerobic bacteria has two effects, which will favor the anaerobic phase:

- An increase in waste temperature: exothermal reactions of aerobic respiration produce heat and temperature can easily reach 50 to 70°C in the waste mass.
- A fast degradation of organic matter, which are easily hydrolysable [Delineau, Budka, 2000].

- ***Anaerobic phase***

As soon as wastes are covered, oxygen is consumed and the anaerobic phase begins. Organic matter is decomposed in shorter and shorter organic chains at the different stages [Delineau, Budka, 2000]:

- Hydrolysis: lipids are transformed into fatty acids and glycerol, and protein in amino acids and peptides. This stage covers parts I and the first half of part II on Figure 7
- Acidogenesis: hydrolysis products are consumed and transformed in more simple organic alcohols and acids, such as volatile acids for example. There is an increase in the amount of volatile acids during this period (evolution of TVA on Figure 7). A decrease of the pH and a raise of total organic carbon (TOC, directly linked to COD) in leachate, as well as a CO_2, H_2 and NH_3 emission are also observed. That stage goes from the second half of part II until the first half of part III on Figure 7.
- Acetogenesis: products coming from acidogenesis are then decomposed in acetates, hydrogen and carbon dioxide, which produces an increase in pH and a decrease in total volatile acid. This stage begins from the second half of part III, and ends in part IV.
- Methanogenesis: that's the longest period and the most important one in the anaerobic degradation process. It allows the elimination of organic matter in waste by converting organic molecules from the acetogenesis to methane, carbon dioxid and water.
- Maturation: The least biodegradable part of organic matter is progressively decomposed in humic and fulvic acid, which are very stable but the other part of organic matter is stabilized. This is part V.

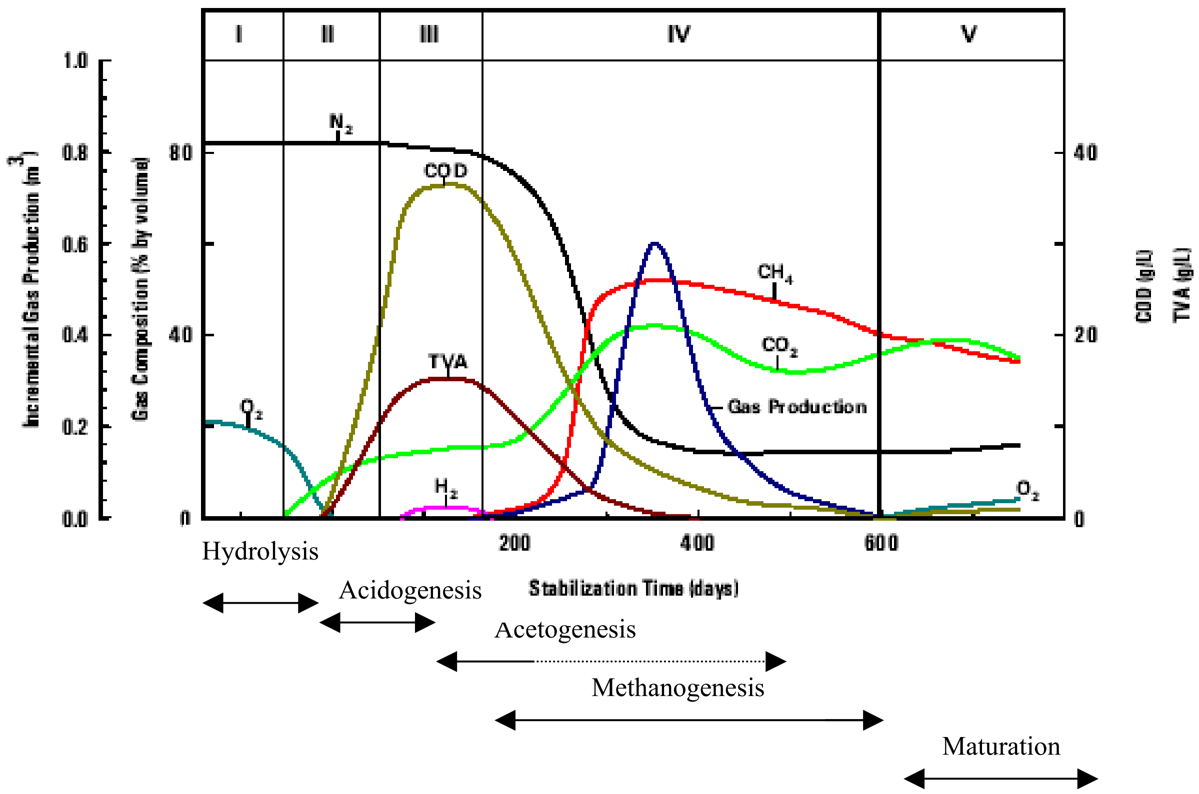


Figure 7 : Biogas composition according to the waste degradation phases [Pohland, 1986]

♦ <u>The methanogenesis</u>

Methanogenic bacteria, which live together with acetogenic bacteria, use hydrogen and acetate produced by them and release methane and carbon dioxide. There are three groups of methanogenic bacteria, the hydrogenophile, the acetoclaste and the methanogen methylotroph ones, and they occur in the following chemical reactions [J.Poulleau, 2002]:

- For hydrogenophile bacteria :
  - $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$
  - $HCOOH + 3\ H_2 \rightarrow CH_4 + 2\ H_2O$
- For acetoclaste bacteria :
  - $CH_3COOH \rightarrow CH_4 + CO_2$
  - $CH_3OH + H_2 \rightarrow CH_4 + H_2O$
  - $CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$
- For methylotroph bacteria:
  - $4\ CH_3OH \rightarrow 3\ CH_4 + H_2O$

The optimal development conditions for these bacteria are:

- A strict anaerobic environment with a redox potential value between -200 and –300 mV [D.B.Vance, 2002].
- A waste humidity rate between 45 and 65 % [SWANA, 2000]. The main goal of leachate injection into the waste is to reach that rate.
- A temperature between 34 and 41°C. The initial increase in temperature due to the aerobic phase is important because anaerobic reactions are less exothermal and produces less energy [J.Poulleau, 2002].
- A pH between 6 and 8.
- A stabilized sulfate concentration because the activity of sulfate-reducing bacteria can produce carboxylic acid, which lowers the pH and inhibits methanogenesis.
- Cation concentrations smaller than the ones given in Table 1.

Table 1: Elements likely to inhibit methanogenesis [T.Delineau, A.Budka, 2000]

Cations	Concentration levels involving a moderate inhibition of methanogenic bacteria (mg/l)
Sodium	3500 - 5500
Potassium	2500 - 4500
Calcium	2500 - 4500
Magnesium	1000 - 1500
Total Ammonia	1500 - 3000

The temperature increase and the fast degradation of the easily hydrolysable organic matter during the aerobic phase have beneficial effects on methanogenesis. As the thermal inertia of waste is high, temperature within the waste mass decreases very slowly. Then methanogenic bacteria find there a thermophilic (40-55°C) or mesophilic (30-40°C) environment, which favors their development. The rapid degradation of organic matters during hydrolysis phase also lowers the production of fatty acids, which are inhibitor factors for methane production [T.Delineau, A.Budka, 2000].

♦ Environmental impacts of methanogenesis

The products of waste degradation, which have been seen in the last paragraph, create two types of effluents. Rejections occurring during the methanogenesis phase are the following ones:

- ***Liquid rejections***

Leachate

According to the last paragraph, organic matter is consumed and leaves the bioreactor in the form of methane and carbon dioxide. A decrease in the TOC concentration (Total Organic Carbon) and in the biodegradable part can be seen during this phase [J.G. Pacey, 1999]. As organic compounds represent the most important part of the Chemical Oxygen Demand (COD), the leachate COD will decrease, as well as the index of waste biodegrability (BOD_5/COD). In the case of stabilized waste, the value of this ratio in below 0,1 [T.Delineau, A.Budka, 2000].

However the production of ammonia during methanogenesis reactions is going to create an accumulation of ammonia in the waste because of the pH, which is below 9,2 (pKa of NH_4^+/NH_3). An increase in ammonia concentration in the leachate could be an indicator of this phenomenon.

Mechanisms of complexation, precipitation and adsorption between metallic ions and organic matter and sulfur are important in the anaerobic phase. These mechanisms have the advantage to make metals insoluble and to immobilize them [C. Couturier, L. Galtier, 1998]. A research program, which had occurred in the 80's and 90's at the Sandtown bioreactor (Delaware, United States), has shown the increase in ammonia concentration and decrease in metallic ions ones in recirculated leachate [J.Morris, 2002].

Condensate

Biogas contains water vapor, which condenses in the biogas collection network. Very few studies have been done on that subject, but a study about search for microbial communities in condensate has shown that it was possible to find some methanogenic bacteria in condensate coming from waste, which are at the methanogenesis stage [M.Kim, 2004].

- ***Gaseous rejections***

Methane production reaches its maximal plateau during the methanogenesis, as well as the carbon dioxide one (Figure 7). Then the volume percentage of CH_4 is contained between 40 and 70 % and between 30 and 60 % for CO_2. The volume ratio CH_4 / CO_2 is contained between 1,2 and 1,5 [T.Delineau, A.Budka, 2000].

On the contrary, hydrogen consumption by methanogenic bacteria explains its decrease in the biogas composition. It's possible to find hydrogen sulfur and sulfurous hydrogen in biogas because of the combined action of sulfate-reducing bacteria and reducing conditions in the waste mass [T.Delineau, A.Budka, 2000].

The theoretical sealing of a bioreactor is achieved thanks to a geomembrane that wraps all the waste mass, and prevents any air infiltration in the waste. The creation of air pockets during the operational phase of the landfill is also avoided by waste compaction. As oxygen is supposed to have been completely consumed during the aerobic phase, and as there's no other source in the waste, the oxygen and nitrogen rates in biogas should be extremely low in waste at the methanogenesis stage.

♦ Environmental impacts of leachate recirculation

After having seen the impacts of methanogenesis, the effects of the other characteristic of the anaerobic bioreactor of La Vergne, the leachate recirculation, is going to be studied in this part.

- ***Positive effects***

Acceleration of waste degradation

Controlled leachate injection aims at reaching an optimal humidity rate in all the waste mass and creating favorable conditions for waste degradation because methanogenic bacteria need a humidity rate from 45 to 65 % [SWANA, 2000]. On the contrary, waste remains dry because of the waterproof cover and bacterial activity is reduced in a conventional MSW landfill.

Then the degradation of organic matter, which is a component of waste, should be faster in a bioreactor than in a conventional MSW landfill. The consequence is a reduction of the waste stabilization time.

Decrease in the post-closure time

The acceleration of waste degradation in a bioreactor causes an increase in the biogas production. That biogas production has been simulated with an EMCON/SWANA (AIRSPACE PLUS) model for two types of MSW landfill, a bioreactor (30 years, 6 millions tones in place at the closure), and a conventional MSW landfill (26 years, 5.2 millions tones in place at the closure) are presented in Figure 8 [Pacey, 1999].

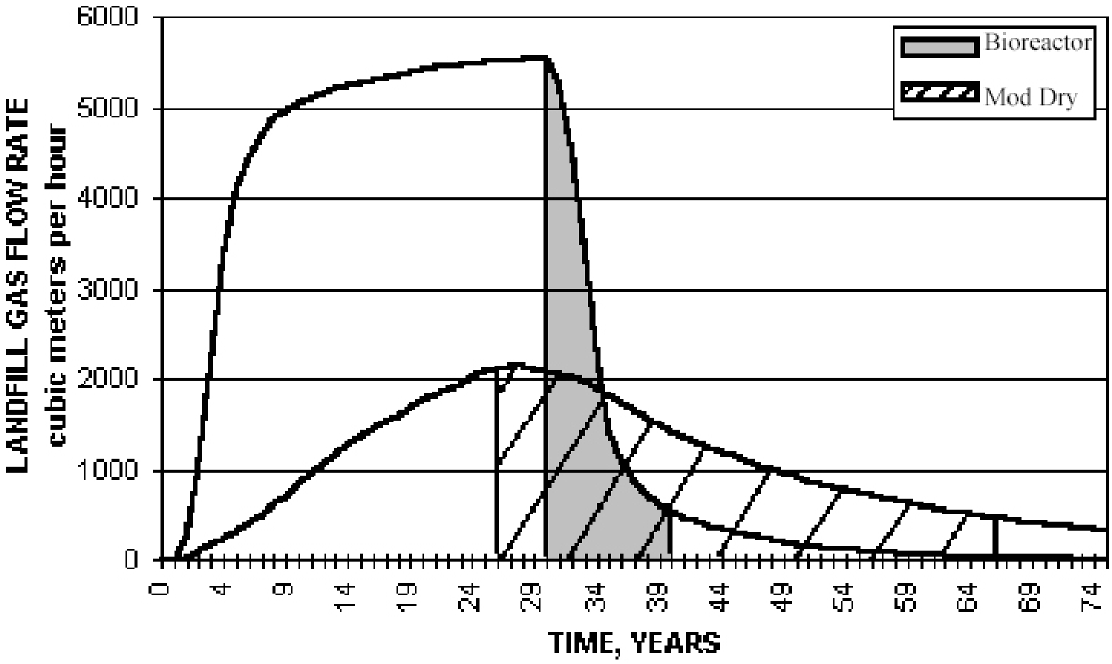


Figure 8: Simulation of biogas production for a bioreactor and a conventional MSW landfill [Pacey, 1999]

One of the conditions fixed by the law to stop the post-closure period is that biogas production has to reach a level, which is low enough not to have any significant impacts on the environment. The necessary duration to reach that level is shorter for the bioreactor (greyish part on Figure 8) than for a conventional MSW landfill (part with hatchings).

Increasing settlements

Waste degradation in a MSW landfill causes settlements, which can be seen at the surface. The acceleration of waste degradation in a bioreactor is going to lead to an acceleration of settlements. The injection of liquids in the bioreactor is also going to be in favor to waste compression and to the dissolution of solid soluble components. Then settlements will occur sooner and in a bigger extent in a bioreactor than in a MSW landfill. [J.G. Pacey, 1999]. The rapid availability of more airspace could be an argument for waste storage at bigger height.

A waste settlement simulation (EMCON/SWANA model, AIRSPACE PLUS) is presented in Figure 9 for diverse humidity rates, from the smaller one (Dry), to the most important one (Bioreactor), with the same parameters as the ones from the previous paragraph (30 year for the bioreactor and 26 years for the conventional MSW landfill). Two settlement curves have been drawn in Figure 9 in order to take into account the great variety of MSW landfills and the heterogeneity of waste biodegradation inside a landfill, a possible one (blue curve) and a probable one (back dotted line).

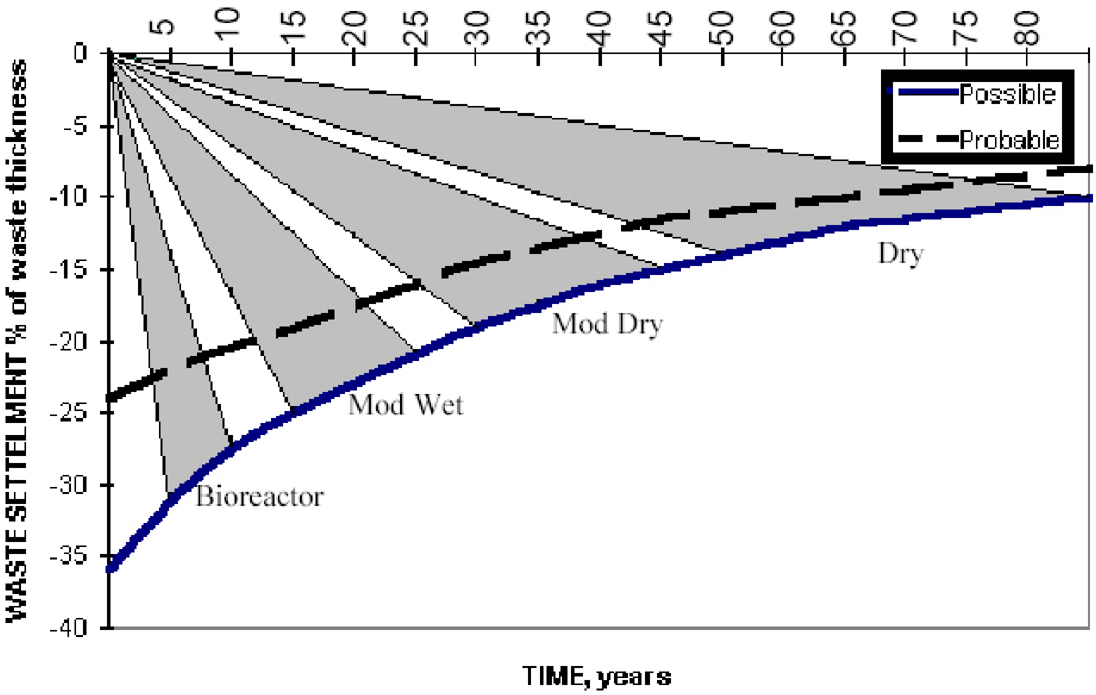


Figure 9: Settlement evolution according to the type of MSW landfill [J.G. Pacey, 1999]

Improved leachate treatment

The leachate from a conventional MSW landfill has to be stored in lagoons and have to be treated before being discharged into nature. Thanks to leachate recirculation and injection into the waste, bioreactors solve partly that problem [SWANA, 2000].

Moreover the elimination of organic matter from the waste during the methanogenesis causes a decrease in the quantity of TOC (Total Organic Carbon), COD (Chemical Oxygen Demand) and BOD (Biological Oxygen Demand) in the leachate. They should be found in very low concentrations when recirculation ends because of the waste stabilization, which limits the final treatment cost of leachates.

Concerning metallic ions in recirculated leachate, they can complex, precipitate and be reduced thanks to reducing conditions in the waste. Then their concentration in recirculated leachates should decrease [J.G. Pacey, 1999].

Both phenomena, the decrease in organic matter and metal concentration in recirculated leachate have been seen on the bioreactor of Sandtown [J.Morris, 2002].

Finally the quantity of leachate and the number of pollutants to treat should decrease thanks to recirculation

Energy valorization of biogas

The strong and stable biogas production of a bioreactor, concentrated on a limited number of years, as well as its composition (mixture CH4 - CO2 with a small quantity of O2), make it possible to consider energy valorization projects of greater width and more profitable than for a conventional MSW landfill. The model of biogas production presented in the figure below uses the same parameters and model as in the paragraph bearing on the reduction in the post-closure duration
Figure 10 gives an outline of the potentialities of a bioreactor and a conventional MSW landfill as regards to energy production.

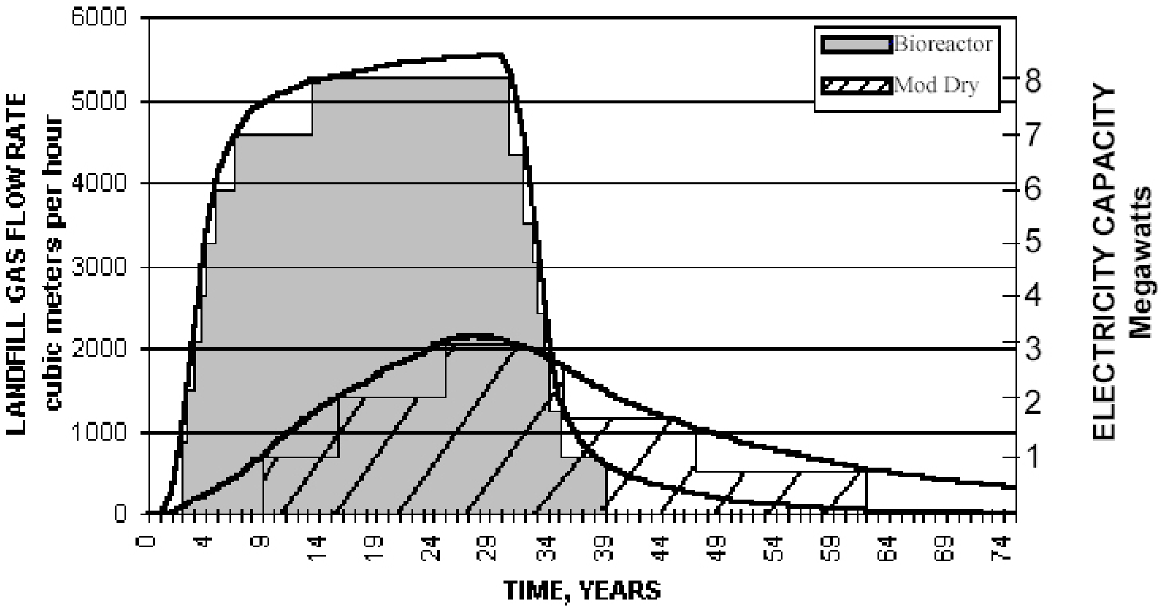


Figure 10: Energy potential of a bioreactor and of a MSW landill
[J.G. Pacey, 1999]

In addition to limit the treatment cost of leachate and to reduce the post-closure time, the bioreactor could thus be a source of income during the post-closure.

- ***Negative effects***

Increase in the salt concentration in recirculated leachates

Mineral salts, on which the reducing conditions and the methanogenesis do not have any effect, are easily soluble and should be carried along with the reinjected leachate. It is a scrubbing effect. In the case of bioreactors where recirculated leachate is not treated, an increase in the salt content should occur [T.Delineau, A.Budka, 2000] and it will then be necessary to take care not to reach the inhibiting thresholds for the methanogenesis (cf. Table 1).

Increase in ammonia concentration

It has been previously shown that the reactions of methanogenesis produce ammonia. This species is soluble in aqueous environment and will naturally pass into the leachate during its passage in waste. The ammonia concentration should increase continuously in the reinjected leachate. Moreover ammonia can inhibit methanogenesis, therefore its concentration should be regularly measured in order not exceed thresholds values (1500 - 3000 mg/l) [T.Delineau, A.Budka, 2000]. Some authors recommend to nitrify ammonia in the lagoon, then, anaerobic bacteria will operate a denitrification process and release nitrogen from the waste [SWANA, 2000].

Potential increase of odors [Foth& Van Dyke Associate, 2004]

In a bioreactor, the increased production of biogas can increase the risk of odors if the system of biogas pumping is not powerful enough. The odors can also come from the lagoon where the recirculated leachate is stored, without being treated by ventilation. However, this increased production of biogas is taken into account in the dimensioning of the degasification system (optimized). The tight cover has also an obvious effect on the biogas emissions.

III METHODS AND MATERIALS

III - 1 Sampling places

It is necessary to compare the quality of leachate before and after its passage through the bioreactor in order to know the impact of leachate recirculation and to understand the phenomena occurring in the waste mass in terms of stabilization (degradation). Then samples have been taken both at the collecting station (Figure 12), where the leachate leaving the bioreactor passes trough before being stored in a lagoon, and in the lagoon (Figure 11), where leachate is pumped in order to be injected into the waste.

Figure 11: Photo of the lagoon reserved for the bioreactor

Figure 12: Photo of the collecting station

III - 2 Monitoring parameters of the bioreactor

III.2.a) Leachate analysis

The following monitoring parameters are going to be studied: COD (Chemical Oxygen Demand), total nitrogen and ammonia concentration, conductivity and pH. The evolution of these parameters according to the number of injection cycles has to be linked to degradation phenomena, which take place within the waste mass (cf. paragraph II.2.c), as well as a scrubbing effect produced by the injection of leachate on soluble components or fine particles.

The pH is characteristic of the anaerobic phase of waste degradation. If the waste mass is in Acidogenesis, the pH will be lower than 6. If it increases, waste is in the acetogenesis phase, and if it lies between 6 and 8, then methanogenesis can take place.

The conductivity χ is connected to ion concentrations C_i present in the leachate, to equivalent conductivities λ_i and to electric load numbers z_i with the following formula:

$$\chi = \Sigma\, z_i \,.\, C_i \,.\, \lambda_i \text{ [Handbook of Chemistry and Physics] (Equation 1)}$$

The variation of conductivity is due to the three following phenomena:

- The scrubbing effect, whose consequence is the solubilization of salts in the reinjected leachate·
- The increase in the production of ammonia, which is the sign of a development of methanogenic bacteria.
- The reduction in the quantity of mobile metal species, related on reducing conditions and complexation, precipitation and adsorption, which take place within waste (cf. paragraph IV.1.b).

The first two phenomena produce an increase in conductivity, whereas the last one makes it decreasing. Moreover, the recirculation should accelerate each of the three phenomena; therefore an increase in conductivity should occur during the recirculation.

Organic compounds represent the greatest part of the Chemical Oxygen Demand (COD) and the regular monitoring of COD should thus make it possible to follow the waste degradation progress. The increase in COD between the entry and the exit of the bioreactor results from a scrubbing effect. Organic particles are indeed solubilized when injected leachate crosses waste layer. On the contrary, stabilization and reduction of the COD of the leachate taken at the exit of the bioreactor is a sign of an intense activity of methanogenic bacteria which would then start to consume organic matter present in the injected leachate [Morris, 2003].

Ammonia has a concentration threshold beyond which it becomes toxic for methanogenic bacteria. It is therefore important to measure its concentration in the leachate coming from the lagoon, before its injection into the bioreactor. It is a methanogenesis product and variations of the ammonia concentration in the leachate going out of the bioreactor are likely to give information on the methanogenesis phase in the waste mass.

In the case of a bioreactor in the methanogenesis phase, with nonventilated leachate, total nitrogen is mainly made up of ammonia. Nitrates and nitrites are minority components and the total nitrogen and ammonia concentrations are thus much closed.

Standardized complete analyses are also carried out, with the measurement of metal ions, sulphur species, BOD_5 and salts. The relationship between these parameters with the recirculation and the methanogenesis is described in the paragraph II.2.c) and the study of their variations and levels could allow having information about waste degradation within the bioreactor and about the effect of recirculation, but they require a long term monitoring to be well-interpreted.

III.2.b) Biogas analysis

Methane, carbon dioxide and oxygen contents are regularly measured in each degasification well to follow the quality of biogas. These parameters are also continuously measured at the flare, before burning the biogas. These composition measurements allow:

- To verify at which degradation state the waste is (cf. Figure 7), locally for measurements in biogas wells and globally for the ones done at the flare.
- To detect potential air intake. In case oxygen is consumed, the following phenomenon is observed:

$\%CH_4 + \%CO_2 + \%\ O_2 + \%N_2 < 100$ because the percentage in nitrogen is not measured, but calculated from the measurement of the percentage of oxygen.

The continuous monitoring of the biogas flow is done at the flare, where all biogas pipes join; with a distinction between the bioreactor cell and the conventional cell. The aim of that measurement is at assessing the biogas production at the bioreactor of La Vergne. The comparison of this biogas production to the potential gas production of the waste mass should allow estimating the degradation state of the waste. Other measurements are also carried out (depression in the waste mass, humidity, temperature, flow well by well…), but they will not be studied in this project.

III.2.c) Material

A spectrometer Dr Lange Lasa 100 has been used with Dr Lange kits for fast liquid analysis. Conductivity has been measured with a WTW conductimeter, and continuously with a data logger Consort R315.

♦ <u>Measurements on leachate taken at the exit of the bioreactor :</u>
- COD :
  Dr Lange Kit LCK014, (1000–10000 mg/L), no dilution.
  Dr Lange Kit LCK114 (150–1000 mg/L), dilution at 1:10
- Total nitrogen : Dr Lange kit LCK338 (20–100 mg/L), dilution at 1:20
- Ammonia : Dr Lange kit LCK302 (47–130 mg/L), dilution at 1:20

♦ <u>Measurements on leachate taken from the lagoon :</u>
- COD :
  Kit Dr Lange LCK014 (1000–10000 mg/L), no dilution
  Kit Dr Lange LCK114 (150–1000 mg/L), dilution at 1:10
- Total nitrogen : kit Dr Lange LCK338 (20–100 mg/L), dilution at 1:10 and 1:20
- Ammonia : in October, the Nessler method has been used (dilution at 1/300), then from November to February, Dr Lange kits LCK303 (2–47 mg/L) with a dilution at 1:20 and 1:40

The measurement of ammonia concentration has necessitated a study on fast analysis kits to establish a protocol and to obtain valid results. A technical note, available in appendix I, has been written on that subject.

♦ <u>Biogas measurements:</u>

Measurements in biogas wells are done with a GA2000, a temperature probe and an anemometer, and the continuous monitoring, with a continuous monitoring system.

III - 3 Establishment of a monitoring protocol for the leachate coming from the bioreactor

The variability of leachate quality is monitored in order to study the representativity of a punctual sampling on one day, one week and one month. The validity of that representativity is necessary to establish a monitoring protocol of the leachate coming from the bioreactor.
A measurement campaign has taken place during the injection of leachate in September 2004, then in October and November 2004. The COD, total nitrogen and ammonia concentrations, conductivity and pH have been measured at the following intervals:
- Twice a day to study daily variability,
- During 10 days to study weekly variability,
- Between two months

pH remained at a fixed value for all the length of that measurement period and is not studied here for that reason.

III.3.a) Quality monitoring while injecting leachate

Conductivity is representative of the salt and ammonia concentration and is studied in this part in order to assess the scrubbing effect of injected leachate on the bioreactor. That's also the parameter, on which the highest number of measurements is available, thanks to a probe and a data logger, which allow to make hourly measurements. Figure 13 presents the evolution of the conductivity at the exit of the bioreactor for ten days. It shows that conductivity increases rapidly during the injection, then tends to stabilize and to reach a plateau. Part III.3.b) is going to confirm the existence of that plateau that appears after the injection of leachate.

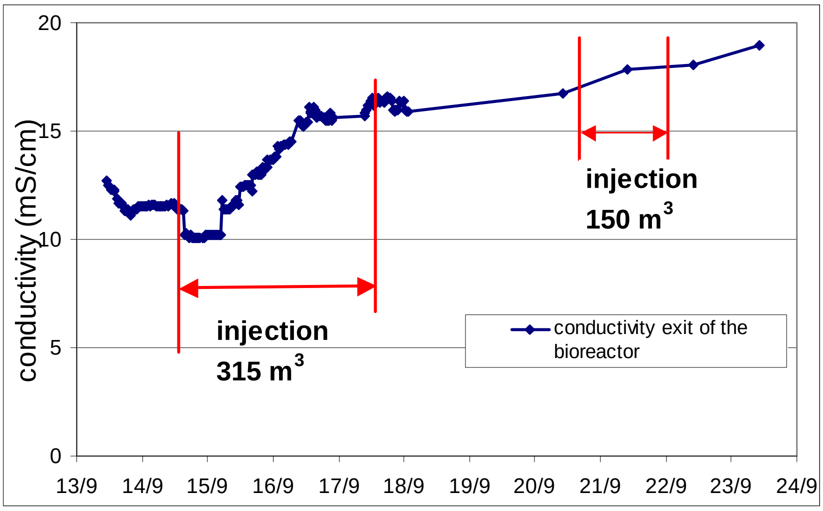


Figure 13 : Monitoring of the conductivity during and right after the injection of leachate

During the injection phase, COD seems to present the same evolution as the conductivity (increase, then plateau, cf. Figure 14), but not enough data are available to confirm this fact. Organic matter and salts coming from the waste could have been taken from the waste by the injected leachate during the injection week. No variation has been detected on the pH (value close to 8).

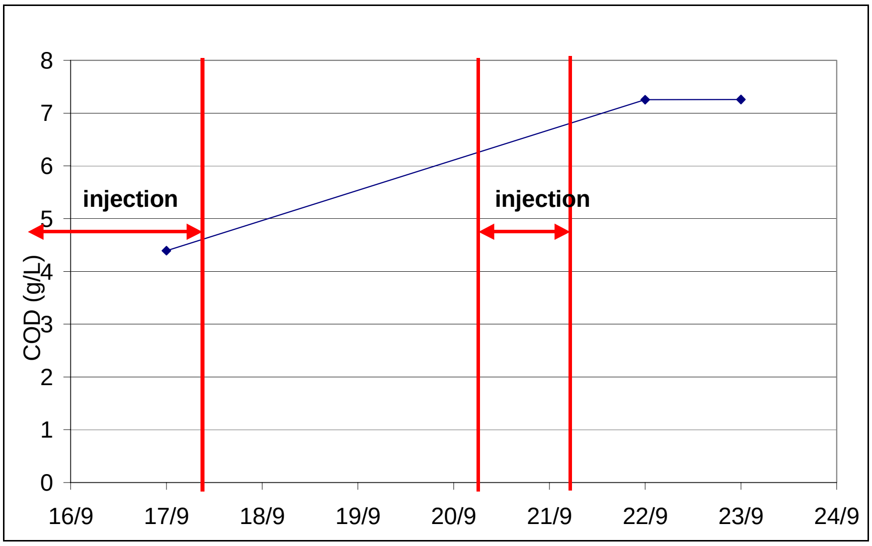


Figure 14: Monitoring of the COD at the exit of the bioreactor during the injection campaign

III.3.b) Evolution of leachate quality during the relaxation period

- Monitoring of daily variations

- ***COD***

Table 2 shows daily variations of COD between 9 am and 14:30 pm. Only one injection has been carried out, on the 20/10/04.

Table 2 : Daily COD variations

date	COD exit of the bioreactor (g/L)	daily variation (%)
18/10/04 9:00	5,49	8,2
18/10/04 14:30	5,94	
19/10/04 9:00	6,04	0,0
19/10/04 14:30	6,04	
20/10/04 9:00	5,74	-3,1
20/10/04 14:30	5,56	
21/10/04 9:00	4,44	6,8
21/10/04 14:30	4,74	
10/11/04 9:00	4,98	1,2
10/11/04 14:00	5,04	

A previous study on Dr Lange kits [Redon, 2003] has shown that the average deviation between two measurements with the Dr Lange kits is equal to 4 % for the COD. Then COD variations are not significant on the 19/10/04, 20/10/04 and 10/11/04.
In such conditions (relaxation time after an injection campaign), daily variability is not significant.

- ***Total nitrogen and ammonia***

According to tables 3 and 4, daily variations for total nitrogen and ammonia concentrations are below 10 %, except on the 12/10/04, where it is equal to 44 % for total nitrogen.

Table 3 : Daily variation for total nitrogen concentration

date	Ntotal exit of the bioreactor (mg/L)	daily variation (%)
12/10/04 9:00	960	43,8
12/10/04 14:30	1380	
18/10/04 9:00	1697	-3,7
18/10/04 14:30	1634	
19/10/04 9:00	1748	-7,8
19/10/04 14:30	1612	
20/10/04 9:00	1376	-3,9
20/10/04 14:30	1322	
21/10/04 9:00	1428	1,0
21/10/04 14:30	1442	
10/11/04 9:00	1376	-1,8
10/11/04 14:00	1351	

Table 4 : Daily variation for ammonia contcentration

date	NH_4 exit of the bioreactor (mg/L)	daily variation (%)
19/10/04 9:00	1646	-8,1
19/10/04 14:30	1512	
20/10/04 9:00	1240	-0,7
20/10/04 14:30	1231	
21/10/04 9:00	1186	4,4
21/10/04 14:30	1238	
10/11/04 9:00	1212	-1,3
10/11/04 14:00	1196	

The measurement incertitude on Dr Lange kits is around 10 % [Redon, 2003]. That's why all those variations are not significant, except for the one on the 12/10/04. The important variation measured on the 12/10/04 is certainly due to the entry of rainwater in the collecting station by the condensate pipe, which is connected to it. Indeed, that pipe is not completely waterproof and water coming form heavy rains could leak in it. Regardless some special cases, daily variation of ammonia and total nitrogen concentrations are negligible.

- ***Conductivity***

Table 5 indicates that daily variations on the conductivity of the leachate going out of the bioreactor vary between 0,3 and 3 %, except on the 12/10/04, where it is equal to 25 % (cf. daily variations of total nitrogen).

Table 5 : Daily variations of conductivity

date	conductivity exit of the bioreactor (mS/cm)	daily variation (%)
12/10/04 9:00	12,23	25,2
12/10/04 14:30	15,31	
18/10/04 9:00	17,55	1,4
18/10/04 14:30	17,8	
19/10/04 9:00	18,4	-0,3
19/10/04 14:30	18,35	
20/10/04 9:00	16,28	-3,1
20/10/04 14:30	15,78	
21/10/04 9:00	15,8	2,3
21/10/04 14:30	16,16	
10/11/04 9:00	16,68	-1,1
10/11/04 14:00	16,5	

As the precision on conductivity measurements is approximately 2%, daily variations of conductivity are negligible, excluding the case of the 12/10/04.

That paragraph has just shown that parameter variations within one day during the relaxation period are not significant. Finally one punctual sampling a day is representative of leachate quality during this day.

♦ Monitoring of the variation between two days

- ***COD***

Table 6 presents COD variations between two days. The average value has been taken every day, when two measurements were available. It also should be noticed that there is a two-week difference between the 22/10/04 and the 09/11/04.

Table 6 : COD variations between two days in October and November 2004

	date	COD exit of the bioreactor (g/L)	variation Between 2 days (%)	
	12/10/04	4,34		
2 days	14/10/04	5,73	32	
4 days	18/10/04	5,72	0	
	19/10/04	6,04	5	
	20/10/04	5,65	-7	
	21/10/04	4,59	-23	
	22/10/04	5,19	13	-8 *
2 weeks	9/11/04	5,28	2	
	10/11/04	5,01	-5	

* between the 20/10 and 22/10 (cf. explanation in the text about the 21/10)

Apart from two high variations, the first one on the 12/10/04 (cf. paragraph bearing on daily variations of total nitrogen), and the second one on the 21/10/04, COD variations are between +5 % and –8 %. At the exclusion of these two particular points, the average COD value is equal to 5,5 g/L, the inferior limit to 5,0 g/L and the superior one to 6,0 g/L. Moreover COD variations can be considered as being small, taken into account the measurement incertitude of 4 % [Redon, 2003].
The important decrease on the 21/10/04 is surely due to the arrival of an important volume of leachate from the bioreactor (25 m^3 between the 20 and the 21/10 instead of 5 m^3 on average). The injection from the previous day may have caused it and, because of that fast passage inside the bioreactor, leachate has certainly not taken the same amount of organic matter as it could have if it had stayed several days in the waste mass. However, in the case of an hydraulic short-circuit, this decrease should have been far more important, taken into account the COD level of the injected leachate (2,61 g/L). A part of the leachate injected in the well PLS24 and a leachate pocket, with a higher COD could have gone out at the same time.

- ***Total nitrogen and ammonia***

Table 7 shows a strong variation (78%) of the total nitrogen concentration between the 12th and October 14, like the COD. The particularly weak total nitrogen concentration on the 12/10/04 (1170 mg/L) and the relatively high one on the 14/10/04 are responsible for such a variation. The variations of the other days lie between -20 and +10 %. These variations are rather weak taking into account the uncertainty of 10 % to the measurements and, over these four weeks, the average total nitrogen concentration is equal to 1578 mg/L, the upper limit to 2080 mg/L, and the lower limit, to 1364 mg/L.

Ammonia (Table 8) varies in almost the same proportions, between -22 and 13 %, presents an average concentration of 1387 mg/L and varies between 1820 mg/L and 1046 mg/L over the four weeks of study.

Table 7 : Variation of total nitrogen concentration during 9 days

date	Ntotal exit of The bioreactor (mg/L)	variation between 2 days (%)
12/10/04	1170	
14/10/04	2080	78
18/10/04	1666	-20
19/10/04	1680	1
20/10/04	1349	-20
21/10/04	1435	6
22/10/04	1576	10
9/11/04	1471	-7
10/11/04	1364	-7

Table 8 : Variation of ammonia concentration during 7 days

date	NH_4^+ exit of The bioreactor (g/L)	variation Between 2 days (%)
14/10/04	1820	
19/10/04	1579	-13
20/10/04	1236	-22
21/10/04	1212	-2
22/10/04	1046	-14
9/11/04	1182	13
10/11/04	1204	2

The case of the 21/10/04 is particularly interesting. Indeed, instead of having a fall of the total nitrogen and ammonia concentration because of the fast crossing of the waste mass by the injected leachate the previous day, their variations are not significant (+6 % for total nitrogen and -2 % for ammonia). The same explanation as for the COD, a mixture between a pocket of leachate with a higher total nitrogen and ammonium concentration and the leachate coming from the injection by the well PLS24, could be the cause.

- ***Conductivity***

Measurements available for October, September and November have been gathered on the same graph (Figure 15) to have an outline of the variations over these three months.

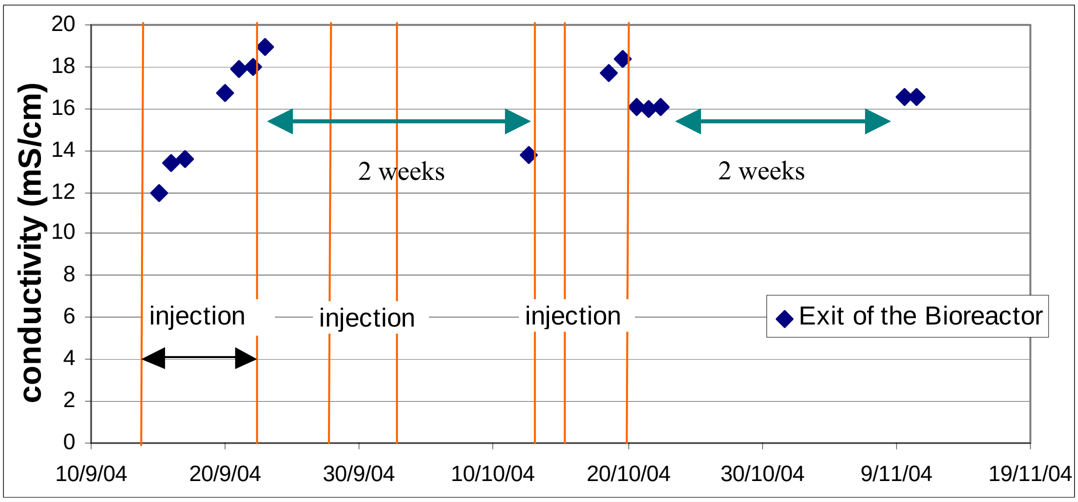


Figure 15 : Monitoring of conductivity from September to November 2004

According to Figure 15, the conductivity of leachate, which leaves the bioreactor, increases during the injection, then is stabilized at a stage, between 16 and 19 mS/cm for all the relaxation period, until December. The particularly low value of October 12 is due to the rainwater arrival in the collecting station and to the effect of dilution which it caused. During these three months, the average conductivity of leachate, which leaves the bioreactor after injection, is equal to 17 mS/cm. Moreover, the three weeks which separate the measurements taken in September from the ones in October, and

the two weeks between the ones of October and November, do not seem to have an impact on conductivity. In the same way, the important exit of leachate of October 21, consecutive with the injection on the 20th, does not seem to have an effect on the conductivity, which remains constant.
The weekly variability of conductivity during the relaxation week (no injection) is thus not significant and a measurement per week should be sufficient.

Even if the variations of the various parameters between two days are more important than the daily ones, they remain weak and only one measurement per week seems to be representative.

III.3.c) Proposal for a monitoring protocol for the leachate coming from the bioreactor

Finally, it can be considered that the different parameters representative of the leachate quality vary between two limits around an average value (Table 9), at the exclusion to some special points (one out of 18 for the COD and one out of 15 for total nitrogen and ammonia).

Table 9 : Variation intervals of the studied parameters between October and November 2004

	average	inferior limit	variation average/inferior limit (%)	superior limit	variation average/superior limit (%)
COD (g/L)	5,5	5,0	9,1	6,0	9,1
total nitrogen (mg/L)	1578	1364	13,6	2080	31,8
ammonia (mg/L)	1387	1046	24,6	1820	31,2
conductivity (mS/cm)	17	16	5,9	19	11,8

After an injection week, it seems that the quality of leachate evolves from a plateau to another one. However, only one complete injection week has been studied in the present case and the quality of leachate should be monitored on several injection weeks for two or three months to validate that result. If the injection protocol remains the same as the initial one, that is to say, one injection week followed by a relaxation week, samples should be taken at the following times (cf. Figure 16):

- 1 sample for the laboratory analysis per month
- 1 (or more) samples for analysis with Dr Lange kits per month

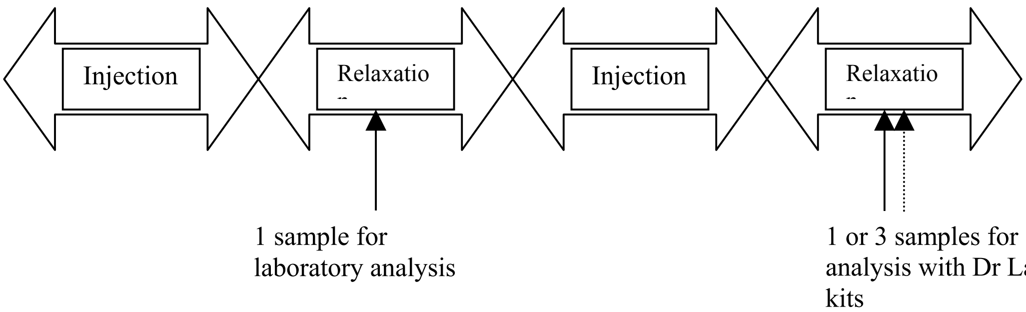
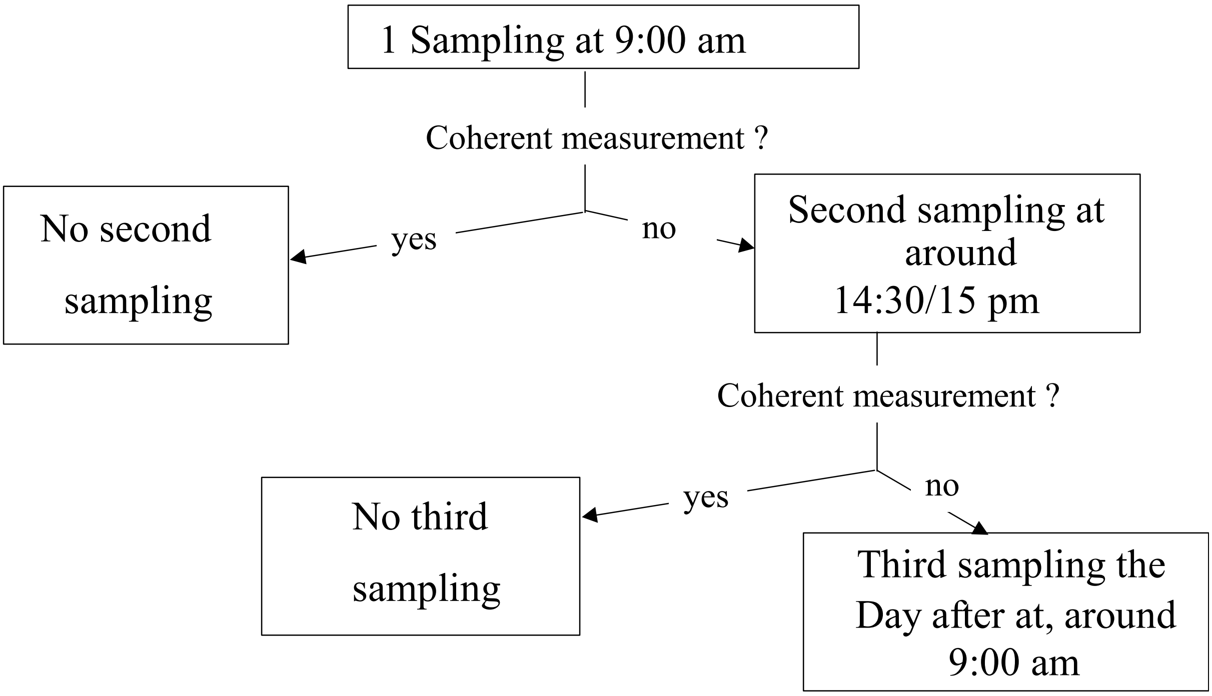


Figure 16 : Monitoring protocol for the leachate leaving the bioreactor for one month

The sampling should be done, while there is no injection in order to avoid short-circuit effects and to have a stabilized measure. The possibility to make easily several measurements with Dr Lange kits should eliminate special points. The following protocol for measurements with Dr Lange kits will be used, taken into account the easy use of these kits:



To check, whether the measurement is coherent or not, it is necessary to compare the measured value with the previous ones and to check if, the previous day, there no were disturbing elements such as an intense rain, a very important arrival of leachate in the lagoon, or a hydraulic short-circuit. The limited volume of the collecting station makes it possible to have a fast renewal of the leachate, and thus to be freed from these constraints.

III - 4 Study of the correlations between COD, total nitrogen, ammonia and conductivity

The objective of this paragraph is to find correlations between the key parameters. If good correlations appear between certain parameters, it will be possible to reduce the number of measured parameters or to reduce their measurement frequency. It is particularly interesting to study conductivity since it is measured uninterrupted in the leachate, which leaves the bioreactor, and in the lagoon. Then the study of correlations between COD, the concentrations in total nitrogen, ammonia, and conductivity will be carried out.

The correlations between the parameters of the leachate from the lagoon are not studied because this system suffers from too many variations of its characteristics (recharging of the lagoon, important variation of the volume of leachate when it is pumped and sent into the bioreactor).

A statistical tool, the principal components analysis (PCA), has been used to highlight possible correlations between COD, total nitrogen, ammonia and conductivity. The goal of the APC is to represent a great number of statistical data in a space of much lower dimensions (2 or 3). The processed data obtained on various dates (cf. appendix II) makes it possible to place the variables, here the measurement parameters (COD, NH_4^+, total nitrogen, conductivity), on the correlation circle. As three eigenvalues of the matrix of the correlations provide 99,4 % of information, the variables have been projected and graphically illustrated on the three principal axes (cf. Figure 17 and Figure 18). The detail of the calculations can be found in appendix II.

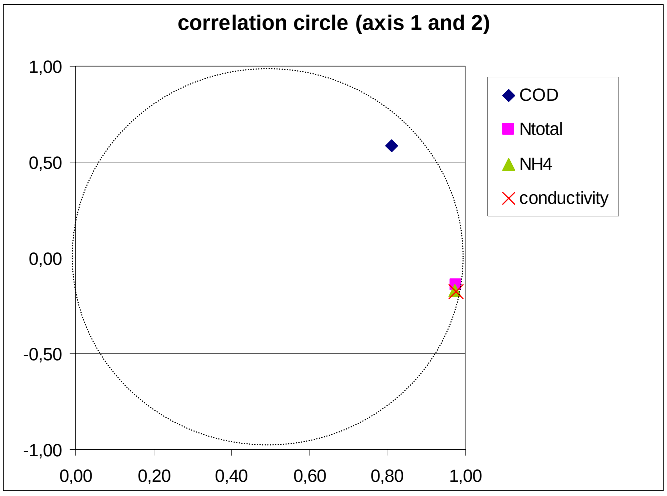


Figure 17 : Representation of the correlation circle on the principal axes 1 and 2 (*)

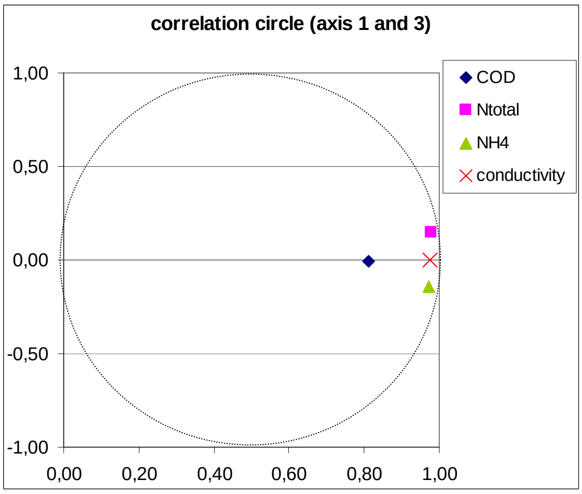


Figure 18 : Representation of the correlation circle on the principal axes 1 and 3 (*)

(*) explanation about axis available in appendix II

The proximity of the points representative of conductivity, total nitrogen and ammonia, shows that these variables are correlated. On the other hand, the distance between the COD and the other points shows the absence of correlation.

In Figure 19, the total nitrogen and ammonia concentrations according to conductivity are traced, and confirm this correlation: the correlation coefficient (R^2) of the average lines is close to 1. Moreover, the average deviation between the total nitrogen concentration and the ammonia one is low and seems to be practically constant. This characteristic comes from the fact that ammonia is a breakdown product of the methanogenesis and that the waste mass is an anaerobic environment (cf. paragraph II.2.c). The total nitrogen is thus mainly made up of ammonium in the leachate outgoing of the bioreactor.

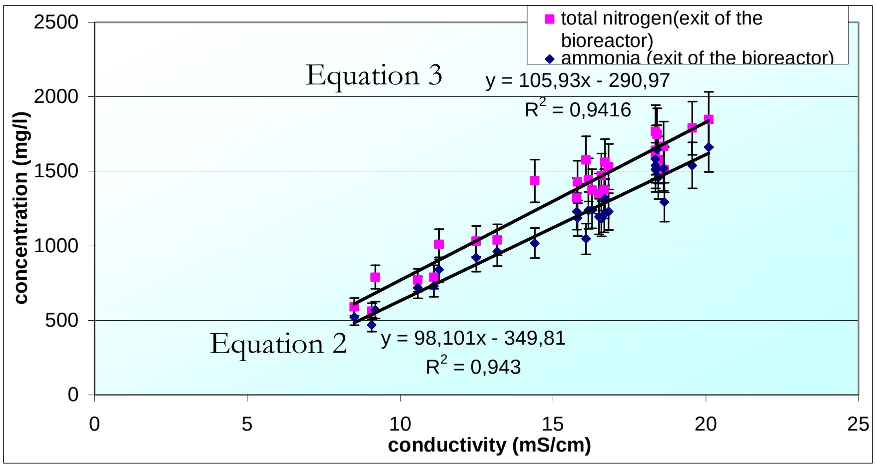


Figure 19 : Representation of total nitrogen and ammonia according to conductivity

Leachate of different qualities has been injected into the bioreactor, but these differences in qualities do not seem to influence the correlations, only on the values. Indeed, the points with conductivity lower than 14 mS/cm correspond to injection of leachate with a lower content in total nitrogen and ammonia than the others, which can explain these various levels of concentration.

Finally, a linear relation can be established between:

- total nitrogen concentration and conductivity : [Ntotal] = 105.93 χ – 290.97 (Equation 2)
- ammonia concentration and conductivity : $[NH_4^+]$ = 98,101 χ – 349,81 (Equation 3)

This result is valid when the waste mass of the bioreactor of La Vergne is in methanogenesis, independently to the quality of the injected leachate. As the methanogenesis should last several years, it would be interesting to continue to follow these correlations. Then it could be possible to obtain the total nitrogen and ammonia concentrations from conductivity.

IV STUDY OF THE PERFORMANCES OF THE BIOREACTOR OF "LA VERGNE"

Quantifying the performance of the bioreactor requires to make a rigorous monitoring of what enters (injected leachate), and what leaves (leachate and biogas) the system. A detailed study of the injected leachate will be presented, then the entering and outgoing quantities of the bioreactor will be compared, and finally, thanks to these data, the waste degradation state in the bioreactor will be assessed.

IV - 1 Monitoring of leachate injected into the bioreactor

IV.1.a) Influence of meteorological conditions on the lagoon

A possible influence of the exposure of leachate to the air (rain, evaporation and oxidation of the upper layers) on its quality could produce difficulties to interpret the results in the study of the recirculation effect on the leachate quality. If such an influence were detected, it would be necessary to cover the lagoon, where leachate is stored.

Figure 20 shows the system set up to study this influence. Two reservoirs, one open, the other close and the lagoon LB' (dedicated to the bioreactor) will be followed qualitatively and quantitatively. The contribution of rainwater and leachate by the connection to the bioreactor are the principal parameters, which intervene. Their effects will be studied through studies on the reservoirs and the lagoon.
Evaporation in the lagoon and the open reservoir was negligible during October 2004 and September, whereas in July it caused a 4 cm level reduction in the open tank. The PET, (2,6 to 6,5 mm in July against 0,3 to 2 mm in September [Meteo France data]), seems to be the cause.

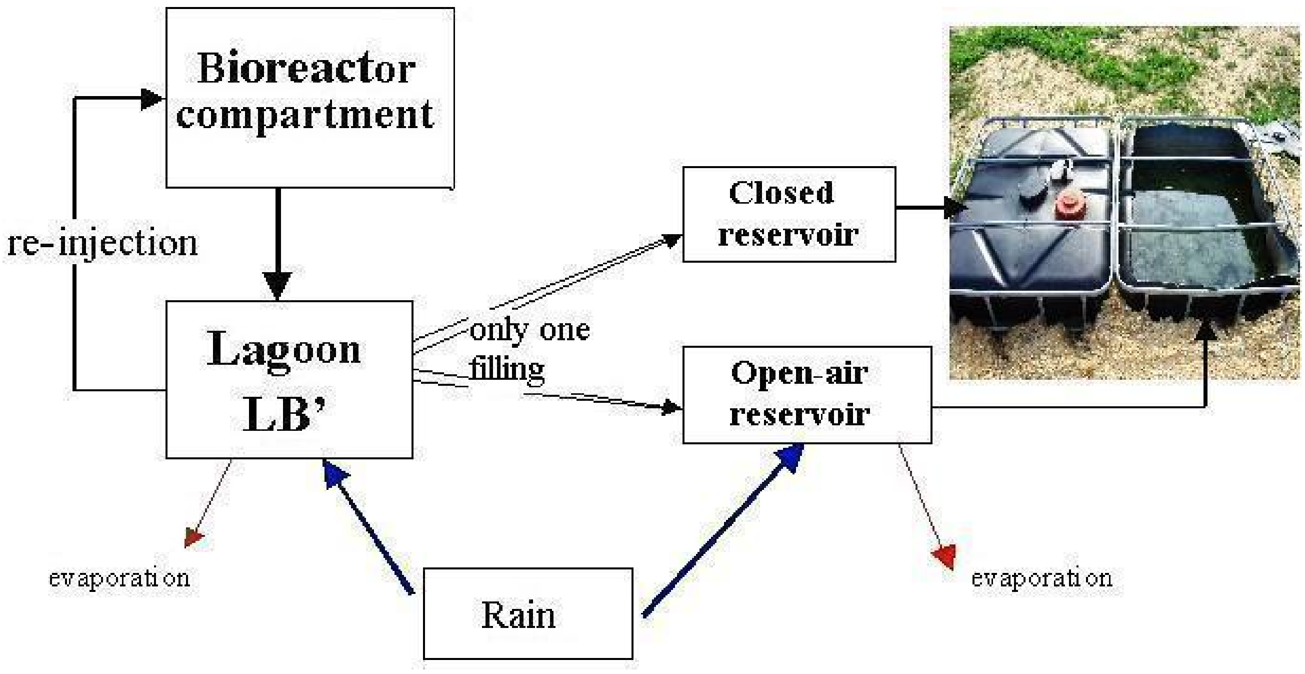


Figure 20: Studied system

♦ <u>Dilution effect</u>

- ***Monitoring of total nitrogen, NH_4^+, salts concentrations and COD***

From the 14th to 30th of September, it practically did not rain and no variation in quality and quantity was observed on the two reservoirs. Over all September, salt and total nitrogen concentrations, COD and the conductivity of the reservoir A (close) and B (open) is stable. The air and the PET during September did not thus have any effect on the leachate. The oxidizing effect of the air on the upper layers of the leachate contained in the lagoon and the reservoirs is not visible.

On the other hand, as soon as rain intervenes, all these parameters undergo a major reduction in the open reservoir. Figures 17, 18, 19, 20 show that this reduction is correlated with precipitation: it is about 8 to 9% for all the parameters between September 14 and October 11, then between the 11th and October 20, about 20% for the COD and even 45% for total nitrogen and ammonia.

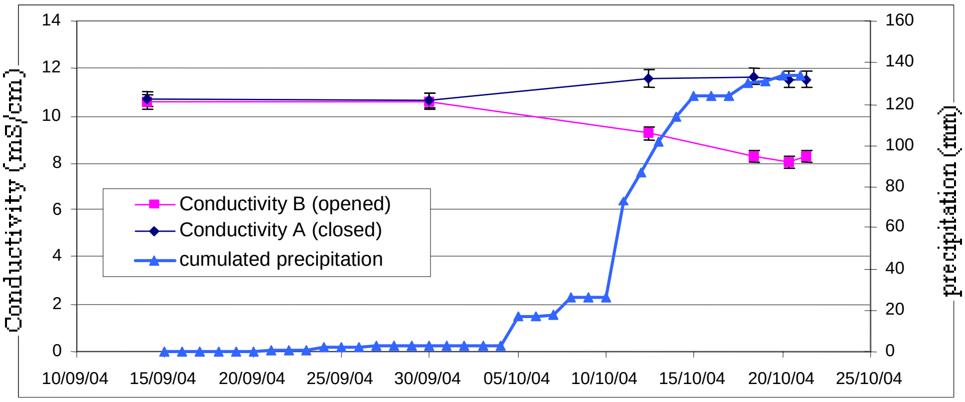


Figure 21 : Monitoring of the conductivity of the reservoirs A (close) and B (open) in September-October 2004

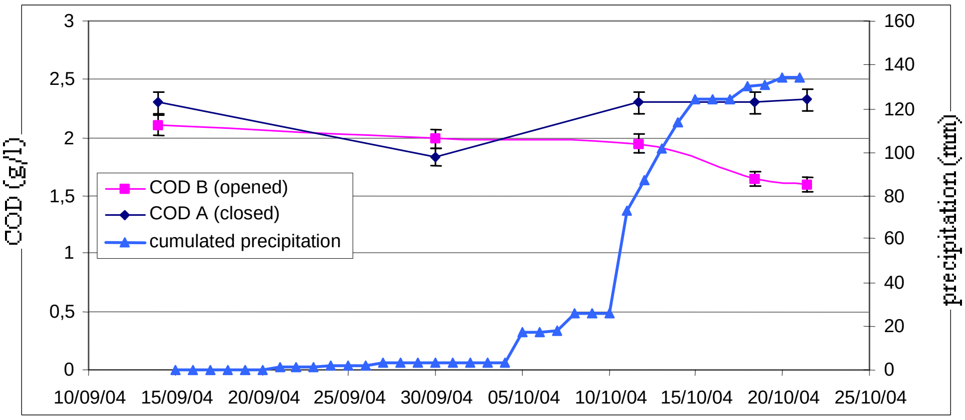
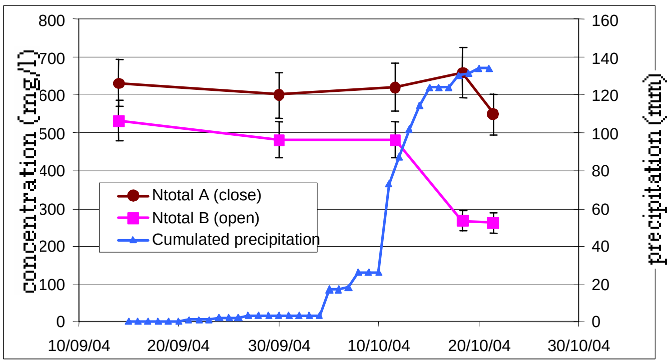


Figure 22 : Monitoring of the COD of the reservoirs A and B in September-October 2004



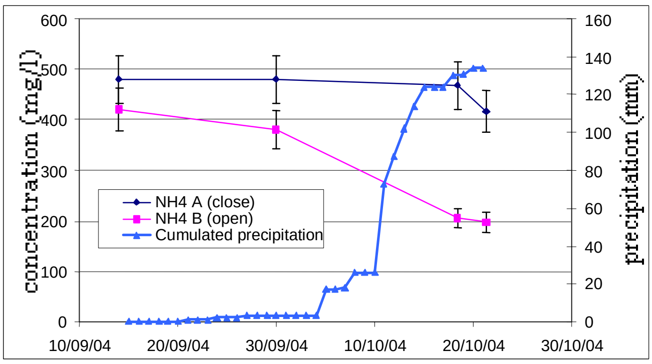


Figure 23 : Monitoring of the Ntotal concentration in the reservoirs A and B in September-October 2004

Figure 24 : Monitoring of the NH_4^+ concentration in the reservoirs A and B in Septembre-Octobre 2004

The following calculation highlights the effect of dilution in the open reservoir:

F represents the dilution factor.
$F = V_{initial}/(S_{reservoir} * Pluvio_{cumul} + V_{initial})$ Equation 4
With $V_{initial}$= 900 L (volume of the reservoir), $S_{reservoir}$= 1 m^2 (recovery surface of rainwater) and $Pluvio_{cumul}$= 134 mm (cumulated precipitation from the 14/09 to the 18/10/04)
F= 1,2
The following value is thus obtained: $DCO_{diluted} = DCO_{30/09} / F$ = 1,66 g/L ~ $DCO_{18/10}$ ($DCO_{18/10}$ = 1,65 g/l)

In fact, almost 100 mm of rain has fallen during the week from the 11th to the 18th of October, which is exceptional for the region. The study of the precipitation from the last two years did not make it possible to find such an important figure over one week. Normally, it can reach 50 to 65 mm to the maximum. It can thus be considered that this week constituted an extreme case in this study.

The week from the 3rd to the 8th of October, with 23 mm of rain, is more representative of what usually occurs on the site during this season. Finally, by taking into account only results obtained until the 11th of October, it appears that rain caused a reduction from 8 to 12% of conductivity, COD, ammonia and total nitrogen concentrations. According to measurement uncertainties (10% for Ntotal and NH_4^+ and 4 to 10% for the COD), these variations are not significant.

This paragraph has just shown that the exposure to free air does not have an effect on the leachate quality and that the usual conditions of precipitation affect slightly the leachate from the lagoon. On the other hand, of the exceptional rain conditions over one week (100 mm) will have an important influence on the quality of the stored leachate. However it is possible to simulate the effect of the rain by calculation.
In the paragraph about the concentration/dilution effect in the lagoon, an additional parameter, the contribution of the leachate from the bioreactor, will be added to the system.

- ***pH monitoring***

Figure 25 shows that, contrary to other parameters, the pH of the open reservoir remains equal to the one of the closed reservoir, even with an important rainwater contribution. This is probably due to the high buffer effect of the leachate.

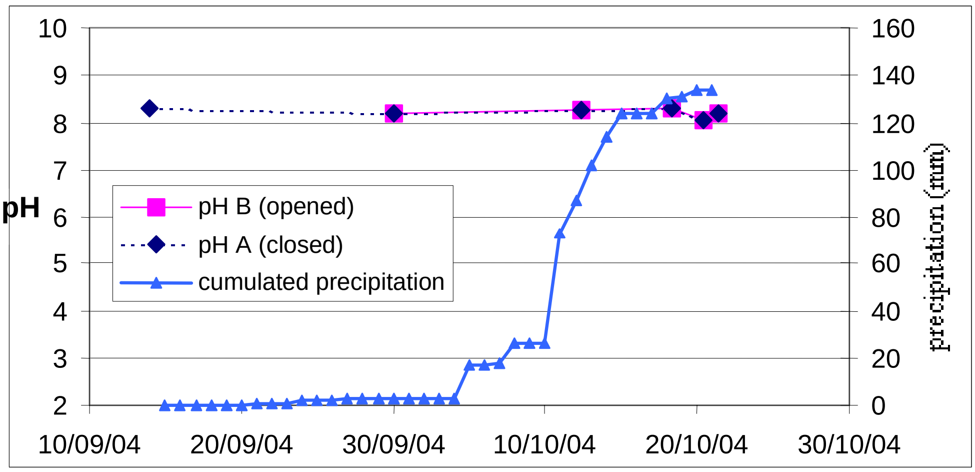


Figure 25 : Monitoring of the pH on the tanks A (close) and B (open) in September-October 2004

♦ <u>Concentration/dilution effect in the lagoon LB'</u>

- ***Monitoring of the concentrations in different species***

Between September 25 and October 12, the COD (Figure 27) and the conductivity (Figure 26) of the lagoon dropped, but this reduction is very weak for the open reservoir. Calculations and graphs presented in appendix III show that the decrease in COD and in the total nitrogen concentration in the lagoon is caused by volume effects. That volume effect is due to the arrival at the same time of liquid from the exit of the bioreactor and from the rain, as well as to the very low volume of the lagoon after the first injection week.

On the other hand, from the 12th to October 18, all the parameters measured in the lagoon remain constant, whereas precipitation was very important during this week. The leachate analyzed at the exit of the bioreactor the 14th and on October 18 was much loaded in pollutants than the one from the 12th and the outgoing flow of the bioreactor is also more important (7 m^3 instead of 5 m^3 per day). This arrival of more polluted leachate in the lagoon is likely to explain the stability of the parameters in the lagoon in period of strong rain (cf. figures 22, 23 and 24).

The following week, the one from the 18th to October 22, precipitation is very weak, even null, which is found in the composition of the open reservoir (no change) and in the one of lagoon LB' (increase in the various concentrations). Indeed, the fact of not having a contribution of water results in an increase in conductivity, COD, total nitrogen and ammonia in the lagoon due to the arrival of leachate coming from the bioreactor. The week from the 11th to October 18, this concentration phenomenon, related to the arrival of more polluted leachate from the bioreactor, had been counterbalanced by a very important precipitation (cf. Figure 28).

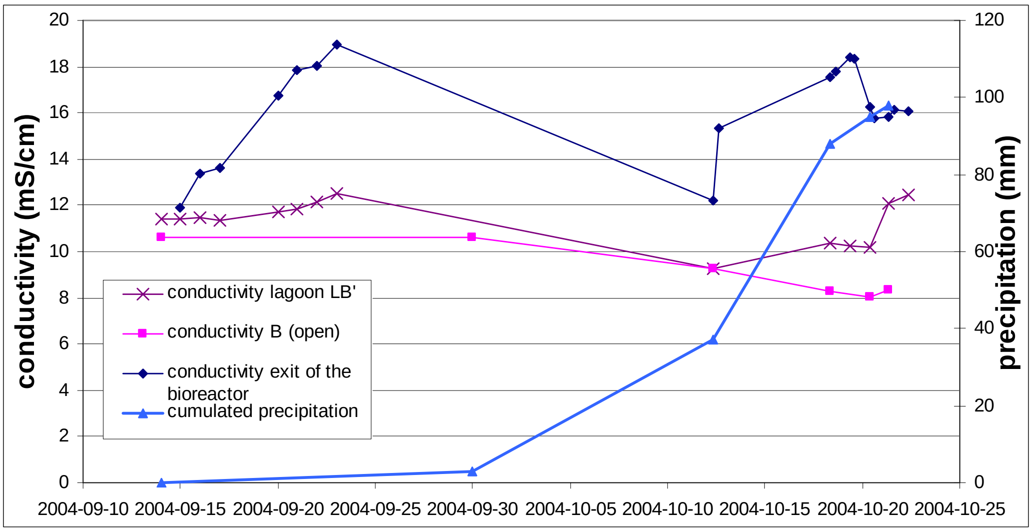


Figure 26 : Monitoring of the conductivity of the lagoon LB', the reservoir B and of the leachate going out of the bioreactor in September-October 2004

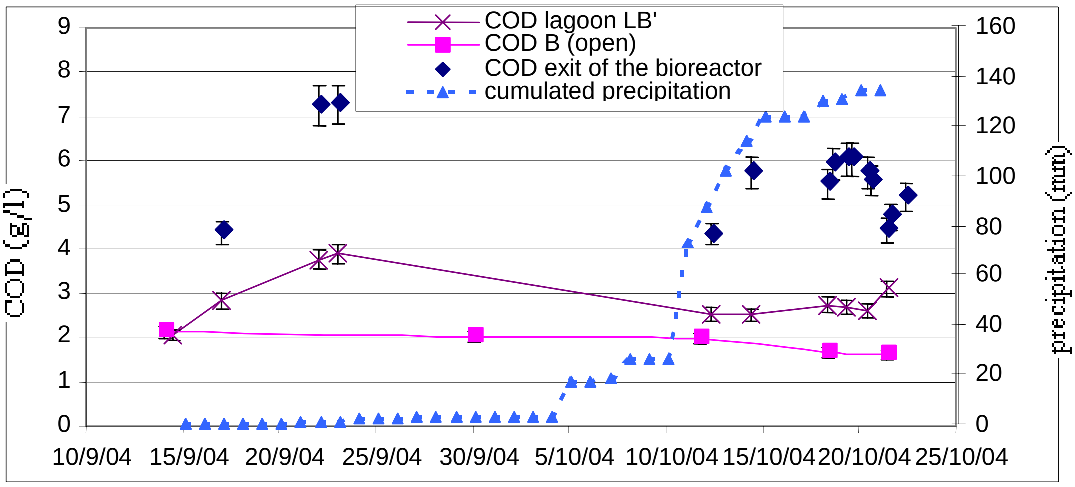


Figure 27 : Monitoring of the COD of the lagoon LB', of the reservoir B and of the leachate going out of the bioreactor in September-October 2004

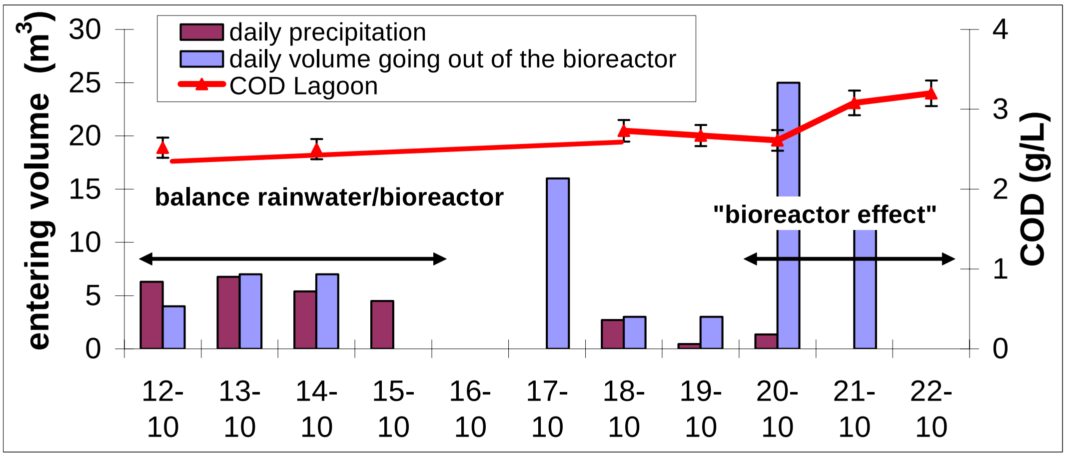


Figure 28 : Comparison of the effects of the different types of input on the COD of the lagoon

The paragraph concerning the dilution effect showed that it was possible to calculate the concentrations from the quantity of rainwater, which had entered into the open reservoir. To highlight the action of the rain on the lagoon, COD and the total nitrogen concentration were recomputed by removing the contribution of rainwater and only taking into account the outgoing leachate from the bioreactor. The PET, very low in October, has been neglected.

Example of calculation on the 12/10/04:

$$COD_{lagoon\ 12/10} = \frac{m_{COD\ exit\ bioreactor\ 12/10} + COD_{lagoon\ 11/10} * (V_{lagoon\ 12/10} - V_{rain} + V_{exit\ bioreactor})}{V_{lagoon\ 12/10} - V_{rain} + V_{exit\ bioreactor}} \quad \text{Equation 5}$$

with :

- Input of COD to the lagoon on the 12/10/04 : $m_{CODexit\ bioreactor12/10}$
- COD in the lagoon on the 11/10/04 : $COD_{lagoon\ 11/10}$ and on the 12/10/04 : COD $_{lagoon\ 12/10}$
- Volume of the lagoon on the 12/10/04 : $V_{lagoon\ 12/10}$
- Volume of rain entering in the lagoon on the 12/10/04 : V_{rain}
- Volume of leachate going out of the bioreactor le 12/10/04 : $V_{exit\ bioreactor}$

Table 10 : Effect of precipitation on the COD of the leachate from the lagoon

date	Real COD lagoon, with rain (g/L)	Calculated COD lagoon, without rain (g/L)	Decrease caused by the rain (%)
11/12/04	2,45	3,53	**-31**
12/10/04	2,52	4,35	**-42**
14/10/04	2,5	empty lagoon	
18/10/04	2,73	3,33	**-18**
19/10/04	2,67	3,70	**-28**
20/10/04	2,61	empty lagoon	

Tableau 11 : Effect of precipitation on the total nitrogen concentration of the leachate from the lagoon

date	Real Ntotal lagoon, with rain (mg/L)	Calculated Ntotal lagoon, without rain (mg/L)	Decrease Caused by the rain (%
11/10/04	750	1015	**-26**
12/10/04	790	1236	**-36**
14/10/04	750	empty lagoon	
18/10/04	727	971	**-25**
19/10/04	669	1073	**-38**
20/10/04	737	empty lagoon	

Tables 10 and 11 show that the calculated values of the $COD_{without\ rain}$ in October are very closed to those measured on the 21st and 22nd of September. This can be explained by similar conditions between these two dates and the first half of October, particularly with the low volume of lagoon caused by the injections. Calculation thus makes it possible to show that, by removing the contribution out of rainwater, COD and the total nitrogen concentration would have been higher than what has been measured. Instead of having a stable quality over several days, the COD, total nitrogen and other species from the leachate of the lagoon would have increased because of the leachate leaving the bioreactor. Besides, this phenomenon is visible September the 21, 22 and after October 20 on figures 23 and 24.

Another manner of highlighting the role of the rain consists in eliminating the contribution in leachate going out of the bioreactor. The formula is the following one:

$$COD_{lagoon\,12/10} = \frac{COD_{lagoon\,11/10} * V_{lagoon\,11/10}}{V_{lagoon\,11/10} + V_{rain\,12./10}} \quad \text{Equation 6}$$

with :

- COD of the leachate on the 11/10 : $COD_{lagoon\ 11/10}$
- COD of the leachate on the 12/10 : $COD_{lagoon\ 12/10}$
- Volume of the lagoon on the 11/10/04 : $V_{lagoon\ 12/10}$
- Volume of the rain, coming in the lagoon on the 12/10/04 : $V_{rain\ 12/10}$

The COD of the 11/10 constitutes the initial value, and CODs of the following days are deduced starting from this initial value. Table 12 gives the results of these calculations.

Table 12 : Calculation of the COD of the lagoon without input of leachate coming from the bioreactor

date	real COD lagoon LB' (g/l)	volume of rain arrived in the lagoon (m^3)	volume of leachate in the lagoon (m^3)	calculated COD without input from the bioreactor
11/10/04	2,45	21	102	2,45
12/10/04	2,52	6	108	2,31
14/10/04	2,5	12	120	2,07
18/10/04	2,73	7	127	1,96
19/10/04	2,67	0	128	1,95
20/10/04	2,61	1	129	1,93
21/10/04	3,08	0	129	1,93
22/10/04	3,2	0	129	1,93

The comparison of this simulation with the real data of the lagoon and those of the open reservoir is graphically presented on Figure 29.

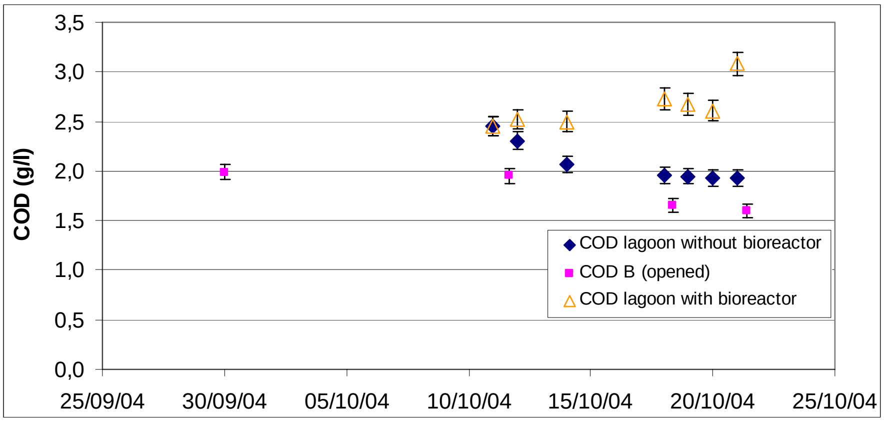


Figure 29 : Comparison between calculated COD (without bioreactor), real (with bioreactor) of the lagoon and COD of the open reservoir

Without contribution of the bioreactor, the leachate of the lagoon would thus undergo the same dilution as the open reservoir. Moreover, the COD of the open reservoir and the calculated COD evolve in parallel and their variation remains practically constant, equal to approximately 20 %.

With a full lagoon (450 to 600 m^3), the leachate coming from the bioreactor can be diluted between 50 and 100 times (outgoing volume ranging between 4 and 8 m^3 per day), which should limit its impact on the quality of the leachate of the lagoon.

Then two different dilution phenomena on the lagoon can be observed:

- Dilution of the leachate coming from the bioreactor, going into the lagoon because of the large volume of the lagoon (week of the 14th and on September 17).
- Dilution due to strong rains because of the low volume of the lagoon (week from the 11th to October 18).

- ***pH monitoring :***

No effect of precipitation on the pH of the lagoon or the open reservoir can be detected on Figure 30, which is representative of the buffer effect of the leachate.

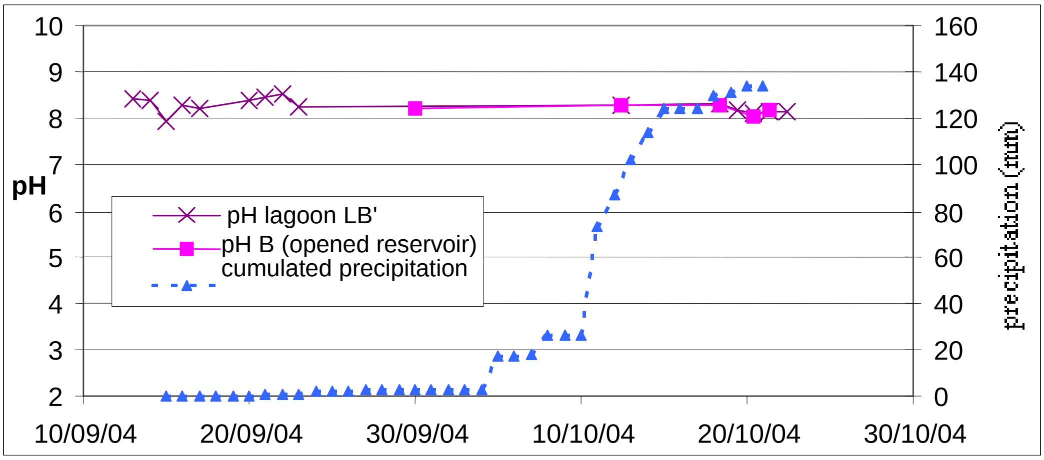


Figure 30 : Monitoring of the pH in the lagoon LB', the reservoir B and in the leachate coming from the bioreactor in Spetember-October 2004

♦ <u>Conclusion on the effect of meteorological conditions</u>

Apart one week of very intense rain (from the 11th to October 18), which modified the quality of the leachate of the lagoon and the open reservoir, there was no significant variation of this quality. Moreover, various weather conditions could be tested with the absence of rain in September, then moderate rains in the beginning of October and finally an extreme precipitation over one week.
As long as weather conditions are usual, almost no effect will be felt on the quality of the leachate of the lagoon. Moreover, it is possible to determine the effect of strong rains by making an assessment matter (calculation starting from the entering and outgoing quantities). The installation of a cover is thus not necessary.

IV.1.b) Impact of the injected leachate on methanogenic bacteria

The injected leachate contains compounds, which can have an effect on methanogenic bacteria and potentially affect the biological breakdown of waste. Two particularly toxic elements for anaerobic bacteria, chromium and oxygen, have been identified in the case of the bioreactor of La Vergne and their potential actions on these bacteria are studied in this part.

♦ <u>Influence of Chromium speciation on the methanogenesis</u>

Chromium has two main oxidation degrees: Cr(III) and Cr(VI). Cr^{3+} ions are almost insoluble for a neutral pH, whereas Cr^{6+} is soluble and can move very easily [T.L.Marsh, M.J.McInerney, 2001]. Some studies have shown that Cr(III) is less toxic than Cr(VI) [K.J. Bundy, F. Mowat, 1996]. Both species have an inhibitor action when their concentrations vary between 100 to 200 mg/l and become toxic when they reach 260 – 420 mg/l [C. Couturier, L. Galtier, 1998].

The total chromium concentration measured on the 9/11/04 is equal to 0,88 mg/l for the leachate leaving the bioreactor and to 0,79 mg/l for the lagoon, which is inferior to inhibition and toxicity thresholds. Then the soluble chromium concentration inside the bioreactor is low enough, not to have any inhibitor effect on methanogenic bacteria.

Moreover, part II.2.c) has shown that precipitation, adsorption and complexation mechanisms between metallic ions and organic compounds are very important and contribute to immobilize these ions, which become insoluble. As metals are dangerous when they are free [Couturier, 2002], the toxicity of chromium and other metals inside the bioreactor should be reduced thanks to these reactions.

♦ Impact of dissolved oxygen from injected leachate on the methanogenesis

Strict anaerobic methanogenic bacteria have different sensibilities to oxygen. Different mechanisms (creation of bacteria aggregates, adjustment of the redox potential, secretion of an enzyme) allow them to resist to the intrusion of oxygen in their environment, or to an increase in redox potential [Kato, Field, Lettinga,1997].

Bacteria, which are highly sensitive to oxygen, stop methanogenesis reactions and their development at a dissolved oxygen concentration starting from 0,01 ppm, or after an exposure to 0,1 % of gaseous oxygen, whereas others can survive to an exposure of four days to 7 ppm of dissolved oxygen. In the case of methanogenic bacteria from sludge granulate, the concentration of dissolved oxygen allowing an inhibition of 50 % of the methanogenesis varies between 0,05 and 6 mg/l. The presence of facultative bacteria, which consume oxygen around anaerobic bacteria, is the main mechanism of tolerance to the oxygen toxicity [Kato M.T., 1994]. According to different articles, the toxicity threshold of dissolved oxygen in anaerobic bioreactors should never be reached if the oxygen entering into the system is only under the dissolved form [Kato, Field, Lettinga, 1997].

- ***Consequences on methanogenic bacteria of the bioreactor of La Vergne***

In the case of the bioreactor of La Vergne, with the exception of leakages involving the air intake on the surface, the only source of oxygen, which could tackle methanogenic bacteria inside waste, comes from the leachate periodically injected.

On site redox potential measurements have been taken in the lagoon, at 10 cm under the surface and gave a redox potential equal to - 44 mV. The negative redox potential of the leachate of the lagoon is the sign of reducing conditions and a very low dissolved oxygen concentration. The leachate of the lagoon, which is injected into the bioreactor, should thus not have any effect on the reducing conditions existing within the waste mass, and dissolved oxygen, present in very small quantities in the injected leachate, should not impact on anaerobic bacteria.

IV - 2 Qualitative and quantitative impact of the recirculation on leachate

One week and half of injection had taken place in mid-September, followed by one waiting period from October to the beginning of December, so that all the injected leachate goes out. However, of the 750 m^3 of injected leachate, only 406 to 316 m^3 (cf. explanations on the hypothesis in Table 13) went out, therefore a little more than half of the leachate remained in the waste mass. Normally the waste mass should have retained a greater part since, theoretically, it is necessary to inject 44 000 m^3 of leachate to reach the field capacity, i.e. a water content of 45 % in mass [Skhiri, 2004]. An explanation to this phenomenon lies in the existence of preferential ways used by the injected leachate, which is rather frequent with the vertical injection systems [SWANA, 2000].

On the other hand, the concentrations measured at the exit of the bioreactor are the double of those measured in the injected leachate (cf. appendix IV). Table 13 compares the injected and outgoing quantities of the bioreactor of COD, total nitrogen, ammonia and highlights a quasi-equality between the injected and outgoing quantities. This quasi-equality comes from the fact that half of the volume of the injected leachate went out and that the concentrations and COD doubled between the entry and the exit of the bioreactor.

Table 13 : Assessment matter on the entering and outgoing quantities of the bioreactor after the injection campaign of September and October 2004

	injected quantities in the bioreactor	Outgoing quantities of the bioreactor	
		High hypothesis *	Low hypothesis**
COD (kg)	2081	2260	1764
Ntotal (kg)	582	627	488
NH_4^+ (kg)	509	549	427

* high hypothesis: all of the outgoing volume is counted
** low hypothesis: 1 m^3 (the background noise) is withdrawn each day from the total volume

IV - 3 State of the waste degradation in the bioreactor

IV.3.a) Indications given by biogas and leachate analyses

Seven characteristics of biogas and leachate indicate that waste is at the methanogenesis stage.

First of all, the fact that the bioreactor produces biogas, primarily made up of methane and carbon dioxide, shows that methanogenic bacteria are active and that the waste mass is in methanogenesis. Moreover, according to the data of the 18/02/05, the ratio of the volume percentages % CH_4 / %CO_2 is between 1,2 and 1,5 for seven biogas wells, which is an essential characteristic of waste at the methanogenesis stage.

The second indication comes from the pH of leachate leaving the bioreactor (cf. Figure 31), which is stable from September 2004 to February 2005, and which varies between 7,4 et 8,1. That stability and pH closed to 8 characterize the methanogenesis stage (cf. paragraph II.2.c).

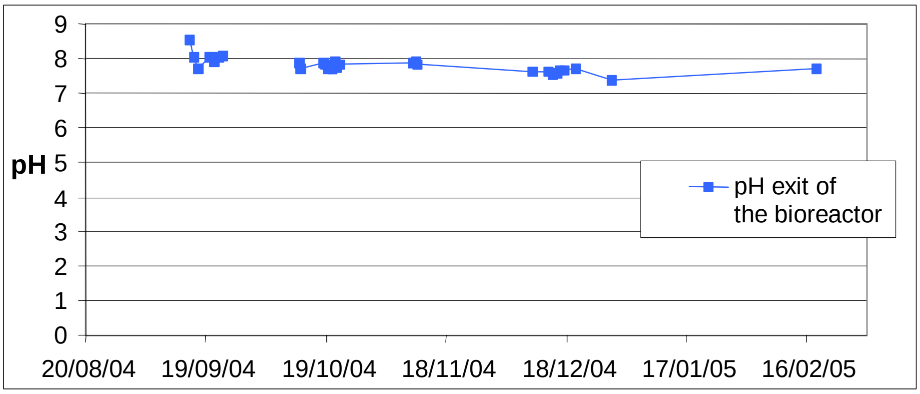


Figure 31 : Monitoring of the pH of the leachate leaving the bioreactor

The third point concerns the COD, which varies between 3010 mg/l and 7260 mg/l (cf. Figure 32), with a great number of measurements below 6000 mg/l. Moreover it has been established that COD could vary between 6000 and 60 000 mg/l during the Acidogenesis phase, and between 500 to

4500 mg/l during the methanogenesis [Ehring, 1983]. The variation domain of COD, in the case of the bioreactor of La Vergne, could be in the superior limit of the one valid for methanogenesis.

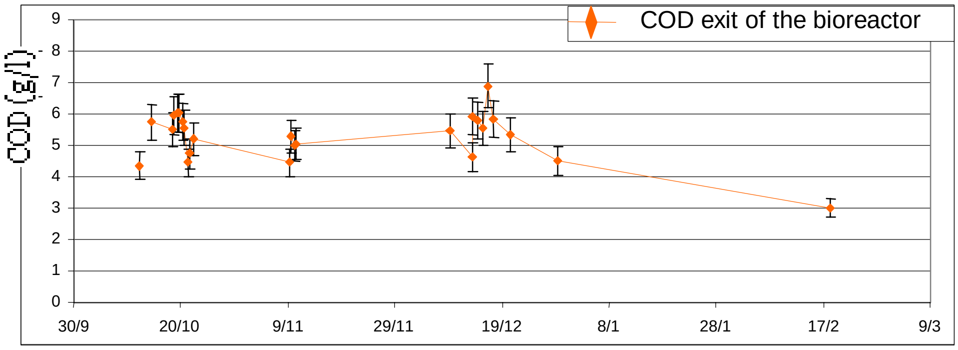


Figure 32 : Monitoring of the COD of the leachate at the exit of the bioreactor

The fourth point comes from the interpretation of ratio BOD_5/COD. Indeed, Table 14 shows that the ratio BOD_5/COD, characteristic of the progress of the biological breakdown, varies around 0,1; what could be a sign of the advanced waste degradation state. Such a value places the outgoing leachate of the bioreactor between the intermediate (age of waste ranging between 5 and 10 years) and stabilized (age of waste higher than 10 years) categories [Millot, 1986].

Table 14 : Calculation of the biodegrability index for the lixiviat going out of the bioreactor of La Vergne

	BOD_5 (mgO_2/l)	COD (mgO_2/l)	BOD_5/COD
14/10/04	540	5730	0,09
09/11/04	680	4450	0,15
13/12/04	440	4620	0,10

However, in the case of the MSW landfill of La Vergne, the oldest waste has at most 4 years (beginning of the exploitation in August 2001), therefore this low value of biodegrability index could come from the acceleration of the degradation of waste caused by the 6 months and half of recirculation of leachate.

The fifth point is provided by the ammonia concentration. Ammonia, which is a breakdown product of the methanogenesis, has a high concentration, higher than 1000 mg/l in the leachate which has crossed the waste mass (cf. Figure 33).

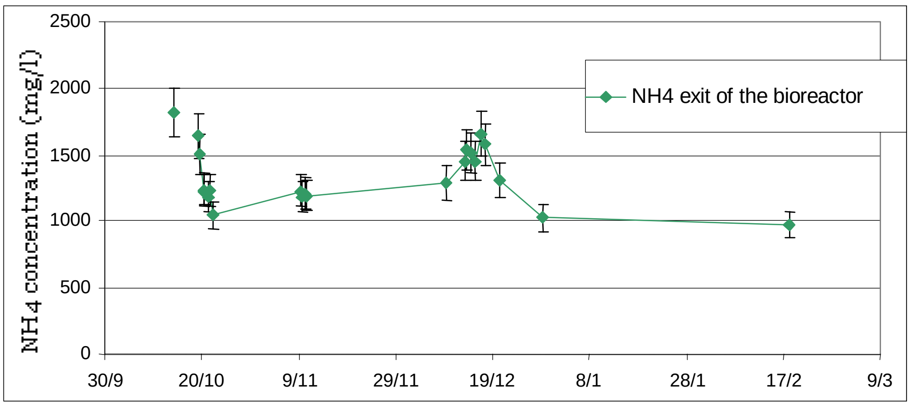


Figure 33 : Monitoring of ammonia concentration in the leachate leaving the bioreactor

The fact that ammonia is a methanogenesis product could explain such a level of concentration and the doubling of its concentration between the entry and the exit of the bioreactor. Moreover, ammonia is a soluble compound in an aqueous environment. Therefore it is easily pulled by the leachate, when this one crosses the waste mass.

The sixth point relates to the monitoring of the NH_4/Ntotal ratio. It can provide information on the anaerobic conditions which take place within the waste. Figure 34 shows that this ratio varies between 0,8 and 1, except for two particular points. The total nitrogen is thus primarily composed of ammonia. Nitrates and nitrites, which form the other part, are present in negligible quantities. There is no nitrification in the bioreactor, which is a consequence of the absence of oxygen in the waste and aerobic bacteria, where leachate passes.

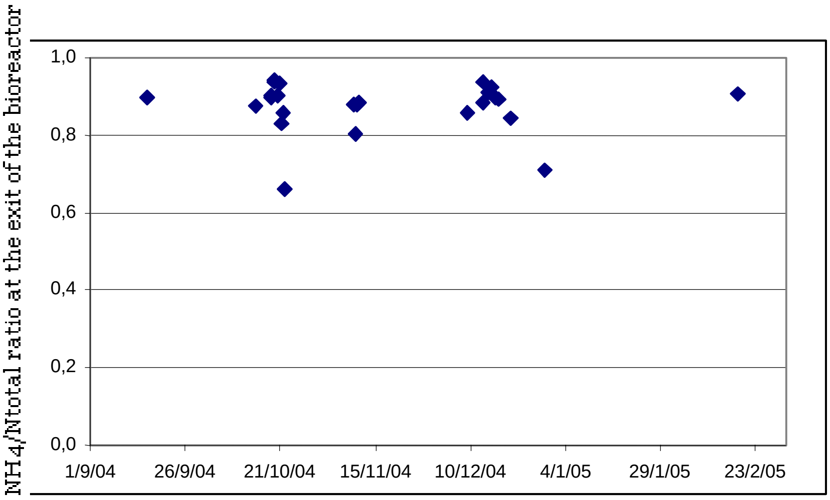


Figure 34: Evolution of the NH_4/Ntotal ratio

The last information is provided by the measurement of the redox potential in the leachate going out of the bioreactor. Indeed the redox potential is there equal to – 352 mV. Such a value of redox potential is a good indicator of reducing conditions, which exist within the waste mass and corresponds to a favourable environment with the development of methanogenic bacteria. Indeed, it has been noted, in the part II.2.c), that the redox potential favourable to the development of the methanogenic bacteria lies approximately between – 200 and – 300 mV.

IV.3.b) Highlight of heterogeneities in the bioreactor

Biogas coming from various degasification wells is regularly analyzed and its composition is given. Between the various parts of the bioreactor, differences in performance of the methanogenesis were highlighted thanks to this measurement of the biogas composition. Generally, biogas coming from wells located at the center of the waste mass has a better quality (gas composed of methane and carbon dioxide, no oxygen and very little nitrogen) than those located at the edge of the cell.

For example, measurements on a well located at the center, on the D3 cell (cf. appendix V) gave a composition of 57 % of methane, 42 % of carbon dioxide, 0,1 % of oxygen, whereas the measurements taken on another well, located close to the edges, on the I1 cell (cf. appendix V), gave 38 % of methane, 34 % of carbon dioxide, 1,7 % of oxygen, and 26,3 % of not identified gas, probably nitrogen. In the first case, the values are in conformity with those of waste in a methanogenesis phase, whereas in the second case, the infiltration of air into waste, detected by the oxygen contents and nitrogen, disturbs the methanogenesis. This explains the low methane and carbon dioxide contents. The high percentage of nitrogen and the small percentage of oxygen are also the sign that oxygen is consumed, whereas nitrogen, which is an inert gas, crosses waste and passes inside the biogas network.

However, external parameters, such as the depression applied at the flare or the sealing of the clay cover, which also depends on precipitation, have a strong influence on the air intake, and on the biogas composition. The interpretation of the collected data must thus hold into account of these other external factors.

IV.3.c) Conclusion on waste degradation in the bioreactor cell

The analysis of the measurements on the leachate coming from the bioreactor and biogas make it possible to affirm that the waste mass is overall in methanogenesis, with the ideal reducing conditions, but also that certain zones are locally under aerobic operation with a disturbed methanogenesis.

The low value of the biodegrability index, obtained for some 4-year-old waste, could be a sign of an acceleration of the waste degradation. However, the recirculation system has undergone many modifications, particularly with the change of the lagoon, and no downward trend of COD has still been observed, which is surely due to the low recirculation period, which has been, until today, of six months and half.

V CONCLUSION

This master thesis has partly filled one of the objectives of the Bioreactor program, which is to study the impact of the recirculation on the waste stabilization and on the leachate quality.
A monitoring protocol of the leachate leaving the bioreactor has been developed for that purpose. In addition, the validation of the use of the fast analysis kits Dr. Lange for the measurement of the ammonia concentration will make it possible to complete the standardized monthly analyses. It has finally been shown that conductivity, total nitrogen and ammonia in the leachate taken at the exit of the bioreactor are correlated. With the resumption of the recirculation, it would be interesting to continue to study these correlations, which should make it possible to have an uninterrupted monitoring of total nitrogen and ammonia concentrations thanks to conductivity measurements.

On the other hand, lessons brought by my master thesis for the part "optimization of the bioreactor" are weaker. As the bioreactor program is only at its beginnings and as the recirculation started only a few months ago (6 months out of the 5 to 10 years expected), the effect of the recirculation on the degradation of waste in methanogenesis could not be highlighted. But certain parameters, such as the biodegrability index, indicate a faster degradation than in a traditional MSW landfill. It has also been shown that weather conditions have a limited influence on the quality of the injected leachate and that this leachate does not have any negative impact on methanogenic bacteria. Lastly, analyses on biogas showed that the waste mass was overall in methanogenesis, but that some zones were also locally aerobic.

Finally, the monitoring and the optimization of a bioreactor are very complex to implement, mainly because of the constant evolution of this system and the problem of having an easy access to the heart of the waste. These two facts complicate the interpretation of the data collected at the exit of the bioreactor and consequently, the study of its performances. However, the experience gained thanks to this research program should make it possible to go further in this field of science, which is still largely unexplored.

VI PROSPECTS

A sampling system for condensate in the biogas wells is currently developed to obtain information about the local degradation state of the waste. Indeed, leachate taken at the exit of the bioreactor come from the three cells and does not allow knowing what occurs in a given zone of the bioreactor. When the sampling system is operational, samples will be taken on various wells and the measurements compared between them, like with the ones obtained on biogas. The correlations identified between these data, related to the mechanisms of waste degradation, should make it possible to interpret them. This track of research is very interesting, especially as practically no study is related to condensates of MSW landfill.

Moreover, the research programme on the bioreactor of La Vergne is only at its beginnings. A few years of recirculation and continuous monitoring of liquid and gas rejections should thus be necessary before being able to observe "the bioreactor effect" and to compare its performances with a conventional MSW landfill.

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US - EPA
http://www.epa.gov/epaoswer/non-hw/muncpl/landfill/bio-work/index.htm

http://www.epa.gov/epaoswer/non-hw/muncpl/landfill/bioreactors.htm

Waste Managment
http://www.wm.com/WM/environmental/Bioreactor/

APPENDIX I : TECHNICAL NOTE ON THE VALIDATION OF THE KITS DR. LANGE FOR THE MEASUREMENT OF THE AMMONIA CONCENTRATION

OBJECT: Evaluation of the fast analysis kits Dr. Lange for the measurement of the ammoniacal Nitrogen concentration within the framework of the Bioreactor program of La Vergne

Context:

The objective of this note is to validate the use of the fast analysis kits Dr. Lange for the measurement of ammonia and to provide recommendations to carry out a reliable measurement on the leachate of the bioreactor of La Vergne, like on those coming from other MSW landfill. It follows a first note from Estelle REDON (« Evaluation des kits d'analyse rapide DR LANGE suite aux analyses réalisées dans le cadre du programme PTB », 2003)
The values obtained with these kits are compared to standardized analyses of CAE laboratory, and measurements are carried out with various dilutions to estimate the reliability of the result.

Material and methods:

Effluent :
The analysed leachate comes from the following sampling places:

- recovery lagoon of the leachate coming from the bioreactor cell of La Vergne
- collecting station (transit place of the lixiviats leaving directly the bioreactor before their passage in the lagoon)

Standardised Analyses:
The measurement incertitude for ammonia is equal to 10% with the method NF EN 1899-1/ISO 5664(1984) (Laboratoire Central CAE)

Fast Analyses:
The assessment of ammonia concentration with the kits Dr. Lange is based on spectrometry. Colorimetric measurement is done with a spectrometer Lasa 100. The use of these kits requires to dilute the effluent to reduce the concentrations of substances interfering with the measurement of NH_4. The list of the principal disturbing ions, and their concentration levels from which they distort measurement (levels checked separately ones from the others), is provided with the kits and is given in table 1.

Table 1 : Principal interfering substances with the NH_4 measurement

Ions	Threshold concentrations
Cl^-, SO_4^{2-}	1000 mg/l
K^+, Na^+, Ca^{2+}	500 mg/l
CO_3^{2-}, NO_3^-, Fe^{3+}, Cr^{3+}, Cr^{6+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}	50 mg/l
Fe^{2+}	25 mg/l
Sn^{2+}	10 mg/l
Pb^{2+}	5 mg/l
Ag^+	2 mg/l

However these threshold concentrations could be lower since cumulative effects of these ions have not been studied by the manufacturer. As the studied leachate contains the majority of these compounds at more or less high concentrations, it is necessary to dilute sufficiently the sample to be sure, not to overpass thresholds and to avoid possible measurement disturbances.

In the case of the leachate coming from the bioreactor of La Vergne, the measured concentrations on the 9/11/04 are the following ones:

- chlorine :1670 mg/l at the exit of the bioreactor (EB) and 1300 mg/l for the lagoon LB'
- potassium :690 mg/l for EB and 550 mg/l for LB'
- sodium :1190 mg/l for EB et 950 mg/l for LB'

These concentrations are higher than the threshold concentrations and it is then necessary to dilute at least at 1:20 or 1:40 to mask their effects.

The other important parameters that should be taken into account are:

- the temperature, since the analysis tanks must be stored between +2 and +8°C, but the reaction has to be done at 20°C. The manufacturer states clearly that "different temperatures influence the exactitude of the results".
- the pH of the sample, which must lie between 4 and 9.

Finally, for the concentrations thresholds of the disturbing elements, it is necessary to dilute the sample at least at 1:20 and, by taking into account the preceding standardized analyses, levels of NH_4 concentrations have been assessed and the corresponding kits are given in table 2.

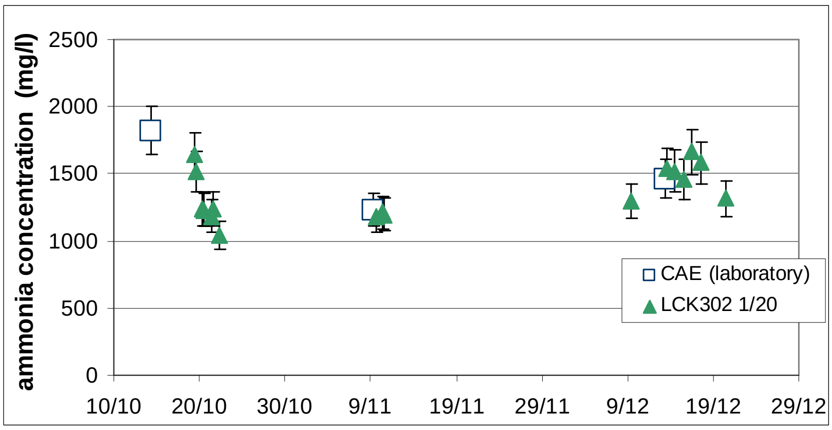
Tableau 2: Characteristics of the kits Dr Lange used for the measurement of NH_4

Sampling place	dilution	Measurement range	reference
Collecting station	1/20	47 – 130 mg N/l	LCK302
Lagoon LB'	1/20	2 – 47 mg N/l	LCK303
	1/40	1 – 12 mg N/l	LCK305

Results

Comparison between the kit LCK302 and the CAE measurements:

The results of the analyses carried out by the means of the two methods (Dr. Lange and laboratory CAE) were gathered on graph 1. A dilution at 1/20 was carried out for the Dr. Lange analyses.

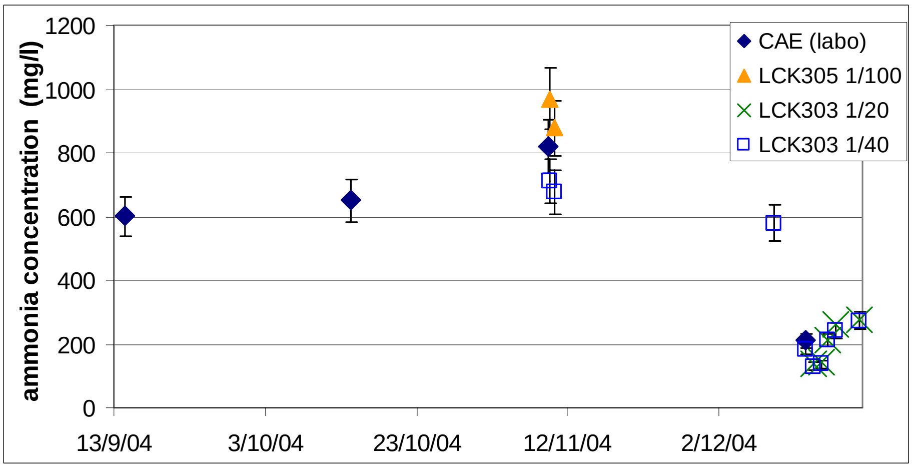


Graph 1: Comparison between Dr Lange and CAE measurements

A variation of 4 and 5% appears when the sampling for Dr Lange and CAE laboratory analyses are carried out on the same day and of 11% when there is a five days difference. However, measurement uncertainty is equal to 10%; therefore these variations are not significant. Moreover, the curve of ammonia concentration follows the one of total nitrogen accurately, which reinforces the coherence of the result since these two parameters are closely dependent ([NH_4] ≤ [Ntotal]). Finally, the comparison with the CAE analyses makes it possible to validate the use of the kit for this type of leachate.

<u>Comparison between the kits LCK303 et LCK305 and the CAE measurements :</u>

In the lagoon, the ammonia concentration is roughly lower by half than the one of the leachate coming from the bioreactor, and it was thus necessary to use kits LCK303 and LCK305, which present lower concentration ranges. Graph 2 presents the results obtained with these various analysis methods and the dilutions used for each of them.



Graph 2 : Comparaison des différentes méthodes d'analyse de l'ammonium

Graph 2 shows that the dilution test on the kit LCK303 gives good results (variation from 1 to 8 % between dilution at 1:20 and 1:40), and that the values obtained with this kit are very close to the CAE analyses (variations of 12 and 13 %). The kit LCK303 is thus well adapted to the measurement of the ammonia concentration in the leachate of the lagoon.

However, the analyses carried out with the kit LCK305 are incompatible with measurements of total nitrogen concentration. Indeed, they give: [NH4+] > [Ntotal] and this kit is not adapted to the measurement of ammonia concentration in the lagoon.

Conclusion

In the case of the bioreactor of La Vergne, it is possible, with a dilution at 1/20 for the kits LCK302 and LCK303, to be freed from the measurement disturbance caused by certain elements present in large quantities in the leachate. Finally, the kits Dr. Lange, whose range is adapted to the ammonia concentration, are the following ones:

- LCK302 for the leachate sampled at the exit of the bioreactor
- LCK303 for the leachate sampled in the lagoon

These kits, with a dilution at 1/20 of the sample, will be used for the next analyses. However, as the quality of the leachate is likely to change, it will be necessary to control regularly the concentrations of the elements responsible for the disturbances, as well as the evolution of the ammonia concentration and to change the range if it is necessary.

More generally, standardized analyses at the laboratory will bring confirmation that the sample is in the good range and that the potential disturbing elements do not exceed the limiting concentrations. Then the regular monitoring of the leachate, thanks to the fast analyses, will make it possible to adapt the dilution and the type of kit to the analyzed leachate. Two other important parameters, the pH and the temperature, have also to be checked during the test.

APPENDIX II: ANALYSIS IN PRINCIPAL COMPONENTS

Basis of the APC:

In the field of statistics, the lines of a table of data are called "individuals", and the columns, "variables". The goal of the analysis in principal components is to represent these statistical data in a space of two or three dimensions, with the minimum of information losses. This method makes it possible to study the relations between the variables, the individuals, or between variables and individuals. In this case, only the relations between variables (columns of table 1) will be studied.

Detailed calculation:

Three stages are necessary to be able to project the variables on the principal axes :

- First stage : calculation of the reduced centered data

As variables (COD, Ntotal, NH_4^+, and conductivity) have different unit scales, reduced centered data should be used.
x_i is the initial data. The reduced centered data x_i' is obtained by withdrawing x_i from the average variable X and by dividing the whole by the standard deviation of this variable.

Table1 : Initial data

Date	COD (g/l)	Ntotal (mg/l)	NH_4^+ (mg/l)	Conductivity (mS/cm)
03/04/03	2,37	770	720	10,57
12/05/03	6,55	790	570	9,18
26/06/03	2,61	560	470	9,06
24/07/03	1,68	1040	960	13,17
21/08/03	5,34	1030	920	12,49
18/09/03	2,42	790	730	11,1
16/10/03	4,71	1790	1540	19,56
13/11/03	3,71	1530	1230	16,82
11/12/03	2,37	1010	840	11,27
08/01/04	1,47	590	520	8,49
19/10/04 9:00	6,04	1748	1646	18,4
19/10/04 14:30	6,04	1612	1512	18,35
20/10/04 9:00	5,74	1376	1240	16,28
20/10/04 14:30	5,56	1322	1231	15,78
21/10/04 9:00	4,44	1428	1186	15,8
21/10/04 14:30	4,74	1442	1238	16,16
22/10/04 9:00	5,19	1576	1046	16,08
09/11/04 14:30	5,28	1471	1182	16,58
10/11/04 9:00	4,98	1376	1212	16,68
10/11/04 14:00	5,04	1351	1196	16,5
09/12/04 09:30	5,46	1511	1293	18,64
13/12/04 12:00	5,92	1642	1539	18,36
14/12/04 12:00	5,8	1668	1521	18,62
15/12/04 12:00	5,54	1576	1458	18,45
16/12/04 12:00	6,88	1848	1662	20,1
17/12/04 12:00	5,84	1768	1582	18,35
20/12/04 12:00	5,34	1559	1316	16,7
29/12/04 10:00	4,5	1436	1019	14,4

Table2 : Reduced centered data

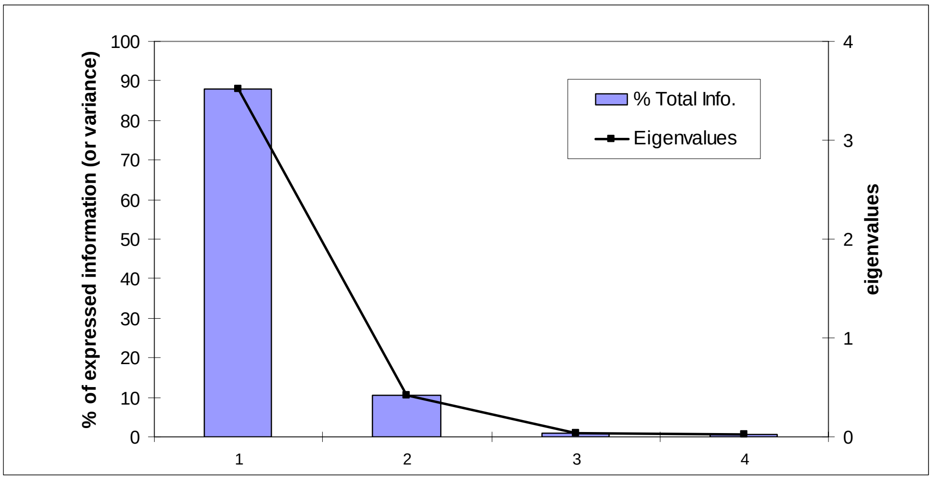
COD (g/l)	Ntotal (mg/l)	NH_4^+ (mg/l)	Conductivity (mS/cm)
-1,54	-1,54	-1,29	-1,42
1,23	-1,48	-1,72	-1,83
-1,38	-2,10	-2,01	-1,86
-2,00	-0,81	-0,59	-0,66
0,42	-0,84	-0,71	-0,86
-1,51	-1,48	-1,26	-1,27
0,01	1,20	1,09	1,21
-0,65	0,50	0,19	0,41
-1,54	-0,89	-0,94	-1,22
-2,14	-2,02	-1,87	-2,03
0,89	1,09	1,40	0,87
0,89	0,72	1,01	0,86
0,69	0,09	0,22	0,25
0,57	-0,06	0,20	0,10
-0,17	0,23	0,07	0,11
0,03	0,27	0,22	0,21
0,33	0,62	-0,34	0,19
0,39	0,34	0,05	0,34
0,19	0,09	0,14	0,37
0,23	0,02	0,09	0,31
0,50	0,45	0,38	0,94
0,81	0,80	1,09	0,86
0,73	0,87	1,04	0,94
0,56	0,62	0,85	0,89
1,45	1,35	1,45	1,37
0,76	1,14	1,21	0,86
0,42	0,58	0,44	0,37
-0,13	0,25	-0,42	-0,30

- Second stage: calculation of the matrix of correlation, its eigenvalues and their respective weights

Table 3 : Matrix of correlation with its eigenvalues and the information percentage given for each eigenvalue

	Axis 1	Axis 2	Axis 3	Axis 4	Variance
COD	0,43	0,90	-0,03	0,03	1
Ntotal	0,52	-0,21	0,71	-0,41	1
NH_4^+	0,52	-0,26	-0,70	-0,42	1
Conductivity	0,52	-0,27	0,01	0,81	1
Eigenvalue	3,51	0,42	0,04	0,02	4
% of tot Info	87,82	10,50	1,07	0,61	

As the percentage of the concentration of information of each axis is given by the eigenvalue, it is possible to establish a hierarchy between the axes. The graph below shows that axis 1 and 2 gather the essence of information. Then a chart representing the variables on these two axes will make it possible to have a reliable analysis.



Graph 1 : Eigenvalues and their respective weights

- Third stage: calculation of the principal factors and chart representing the space of variables

The calculation of the eigenvectors of the matrix of correlation provides the principal factors (cf. table 4).

Table4 : Calculation of the principal factors

	Axis 1	Axis 2	Axis 3	Axis 4
COD	0,81	0,58	-0,01	0,00
NTK	0,98	-0,14	0,15	-0,06
NH4+	0,97	-0,17	-0,14	-0,06
Conductivity	0,98	-0,18	0,00	0,13

Then the space representation of these principal factors according to the selected axes, i.e. axes 1 and 2, makes it possible to represent the space of the variables in a space of dimension 2, and to determine the correlations existing between these variables (see part III - 4)

APPENDIX III : ASSESSMENT MATTER ON THE LAGOON AND ON EXTERIOR CONTRIBUTIONS

The following calculations will use average values of COD and total nitrogen concentration defined in the paragraph bearing on the elaboration of a monitoring protocol of the bioreactor (cf. paragraph III - 3] since the lixiviat going out of the bioreactor comes from the same injection week and that no measurement is available between the 23/09 and 12/10.

To calculate the volume of recovered rainwater by the lagoon, the following formula has been used: $V_{rain} = rain \times S_{lagoon}$ with rain, the daily precipitation and $S_{lagoon} = 450\ m^2$, the surface of the surface of the lagoon.

Table 4 : calculation of entering volumes into the lagoon

	precipitation (mm)	Input of rainwater in the lagoon (m^3)	Input of leachate coming from the bioreactor (m^3)
2/10/04	0	0,0	7
3/10/04	0	0,0	6
4/10/04	0	0,0	4
5/10/04	14	6,3	4
6/10/04	0	0,0	5
7/10/04	1	0,5	4
8/10/04	8	3,6	4
9/10/04			
10/10/04			
11/10/04	47	21,2	12
cumulated volume of liquid arrived in the lagoon		31,5	46

Assessment matter on the lagoon between the le 1st et le 12th of October

Table 5 : Assesment of the COD of the leachate from the lagoon on the 12/10/04 calculated with the different inputs

Average COD (g/L)	CODav	5,5
cumulated quantity of COD brought by the bioreactor (kg)	$m_{CODinput} = COD_{av} * V_{exit\ bioreact}$	253
volume of lagoon on the 1st October, after injection (m^3)	V_{init}	20
$COD_{lagoon\ 12/10}$(g/L)	$(COD_{lagoon01/10} * V_{init} + m_{CODinputt}) / (V_{init} + V_{rain} + V_{exit\ bioreact})$	2,60*

* measured COD: 2,52 g/L

Table 6 : Assesment of the total nitrogen concentration (Ntotal) of the leachate of the lagoon on the 12/10/04 calculated with the different inputs

average concentration in N_{total} (mg/L)	$N_{total\ av}$	1578
cumulated quantity of N_{total} brought by the bioreactor (g)	$N_{total\ input} = N_{total\ av} * V_{exit\ bioreact}$	72588
volume of the lagoon after the injection of the 1st of October (m^3)	V_{init}	20
$N_{total\ lagoon\ 12/10}$ (mg/L)	$(N_{tot\ lagoon01/10} * V_{init} + N_{total\ input}) / (V_{init} + V_{rain} + V_{exit\ bioreact})$	745*

* N_{total} measured: 790 mg/L

with:

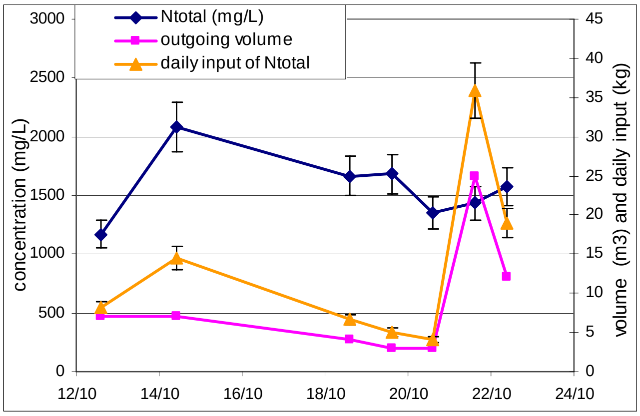
- V_{init} : volume of the lagoon after the injection on the 1st of October,
- V_{rain} : cumulated volume of rainwater recuperated by the lagoon between the 2nd and the 11th of October
- $V_{exit\ bioreact}$: cumulated volume of leachate that had left the bioreactor between the 2nd and the 11th of October
- COD_{input}: cumulated quantity of COD brought to the lagoon between the 2nd and the 11th of October
- $COD_{lagoon\ 01/10}$: COD of the leachate of the lagoon on the 01/10, estimated to 3,1 g/L
- $COD_{lagoon\ 12/10}$: COD of the leachate of the lagoon on the 12/10 obtained by calculation
- $N_{total\ input}$: cumulated quantity of total nitrogen brought to the lagoon between the 2nd and the 11th of October
- $N_{total\ lagoon\ 01/10}$: total nitrogen concentration of the leachate of the lagoon on the 01/10, estimated to 1000 mg/L
- $N_{total\ lagoon\ 12/10}$: total nitrogen concentration of the leachate of the lagoon on the 12/10 obtained by calculation

Finally, the various parameters of the lagoon (COD, total nitrogen, volume) could have been recomputed thanks to this assessment on the entering quantities (the PET is negligible at this period of the year). This part has also shown that the reduction in COD and in the total nitrogen concentration in the lagoon were not due to an important fall of their values at exit of bioreactor, since calculation with the average values gives results close to reality.

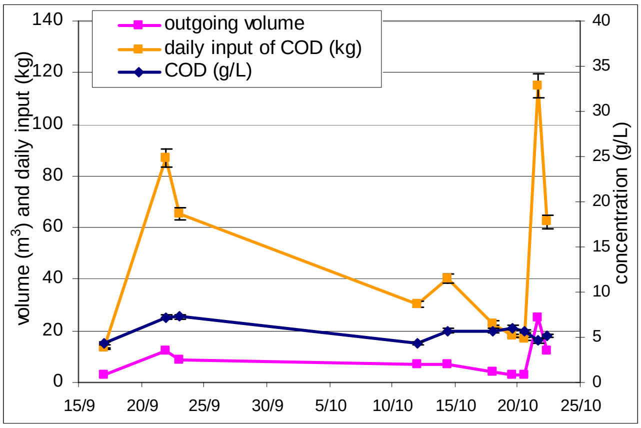
Then the reduction in COD and total nitrogen in the lagoon is caused by the arrival of liquids coming at the same time from the exit of the bioreactor and from the rain, as well as by the very low volume of the lagoon after the injection on the 01/10/04.

Contributions in the lagoon: volume or concentration effect?

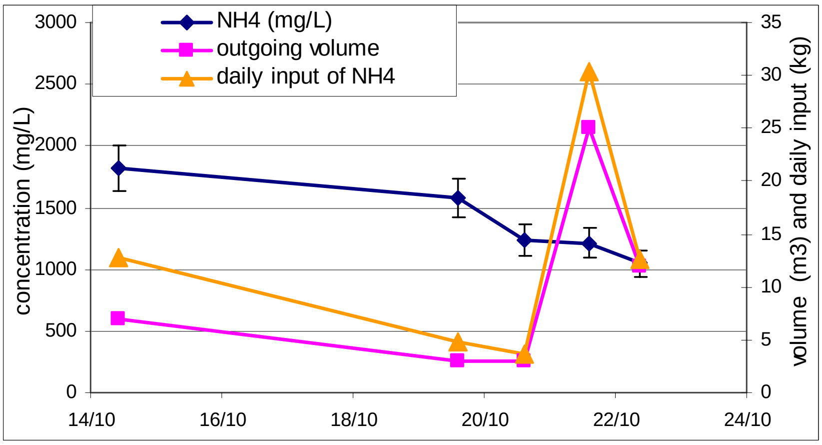
To see which effect is prevalent, the concentration, volume at exit and the daily mass contribution were gathered on the same graph. Graphs 14, 15 and 16 show that this daily mass contribution varies in an important way and seems to follow more volume variations than the concentration ones.



Graph 14 : Comparison between COD, the quantity brought to the lagoon and the volume going out of the bioreactor

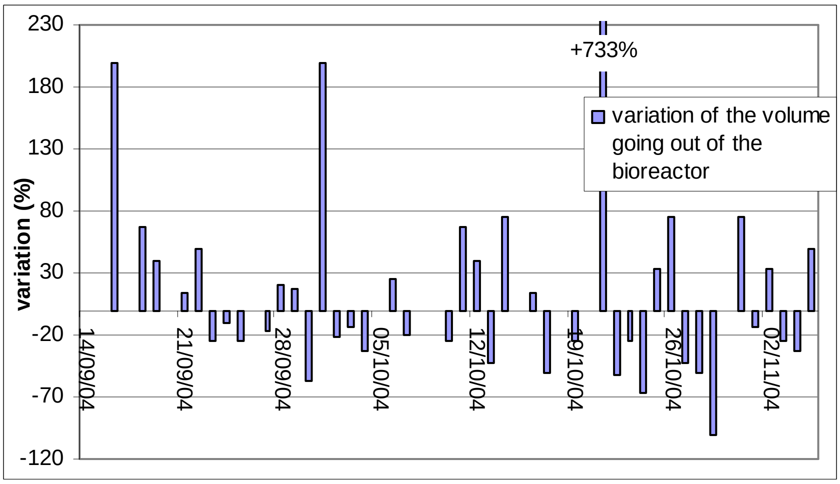


Graph 15 : Comparison between the total nitrogen concentration, the quantity brought to the lagoon and the volume going out of the bioreactor



Graph 16 : Comparison between the ammonia concentration, the quantity brought to the lagoon and the volume going out of the bioreactor

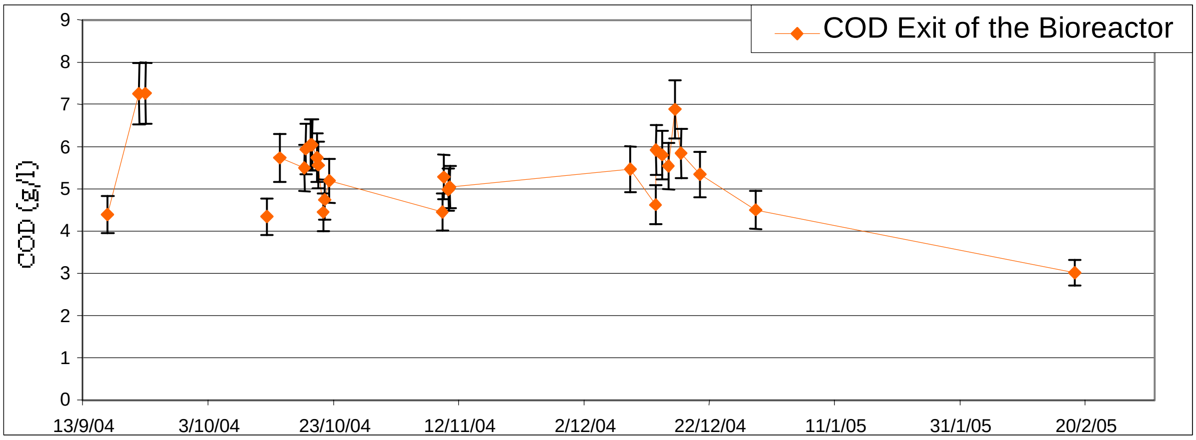
To confirm this last point, the variations of the outgoing volume of the bioreactor have been studied between the 14/09/04 and the 05/11/04. The variations between consecutive two days are represented on graph 17.

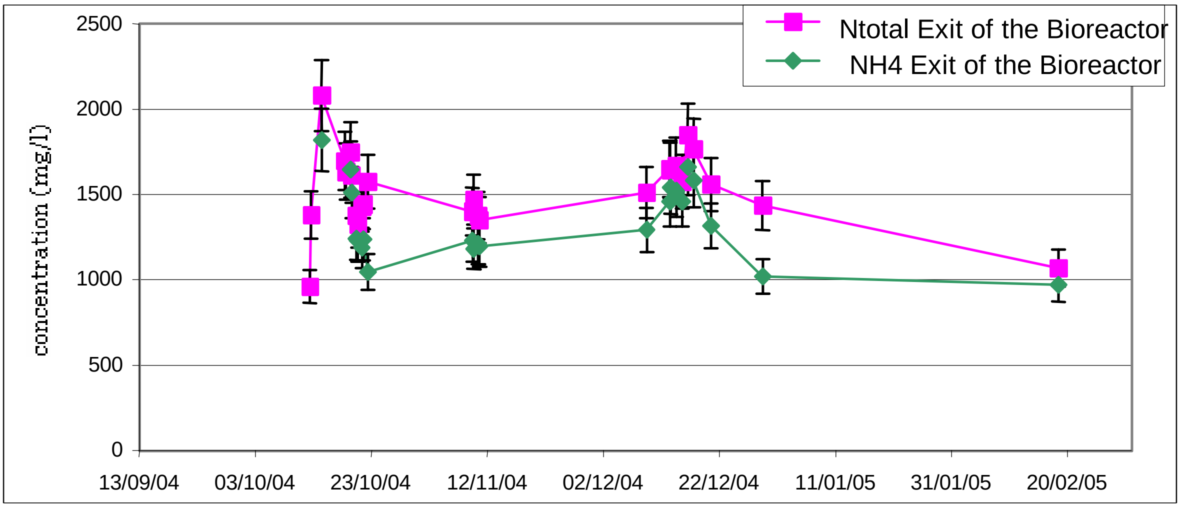


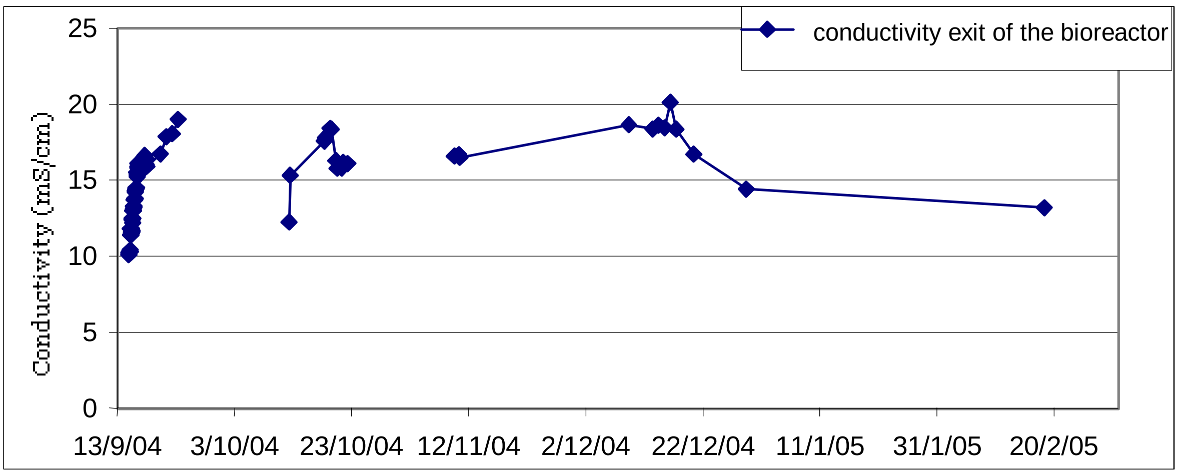
Graph 17 : Monitoring of variations of the volume going out of the bioreactor bteween 2 consecutive days in September, October 2004

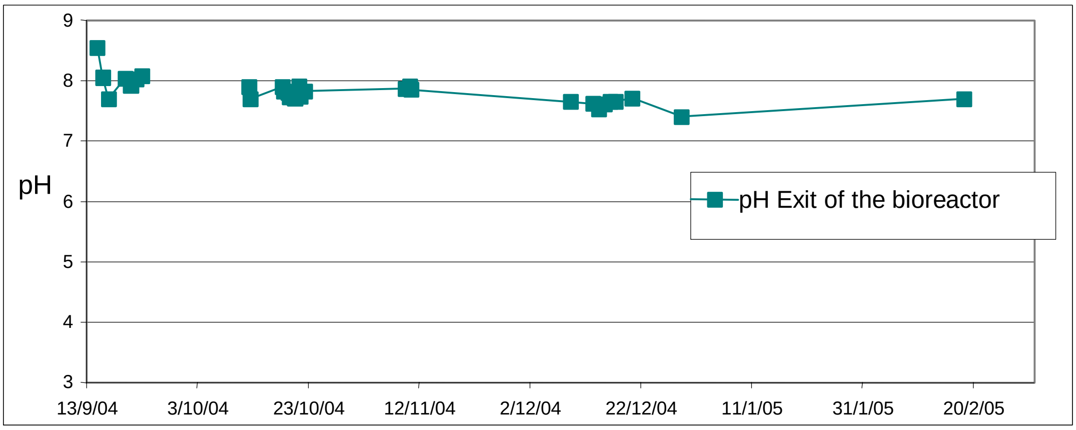
Graph 17 shows that the volume leaving the bioreactor presents strong variations, generally higher than 20 %. But, according to the paragraph III.3.b), the variations between two days of the various parameters are generally lower than 10% and can reach 20 % or more in some specific cases. This difference in the variation scales of the variables used to calculate the daily contributions thus explains why the mass contribution varies according to the volume and not to the concentration.

APPENDIX IV: MONIORING OF THE LEACHATE QUALITY OF THE LAGOON AND OF THE ONE GOING OUT OF THE BIOREACTOR FROM SEPTEMBER 2004 TO FEBRUARY 2005

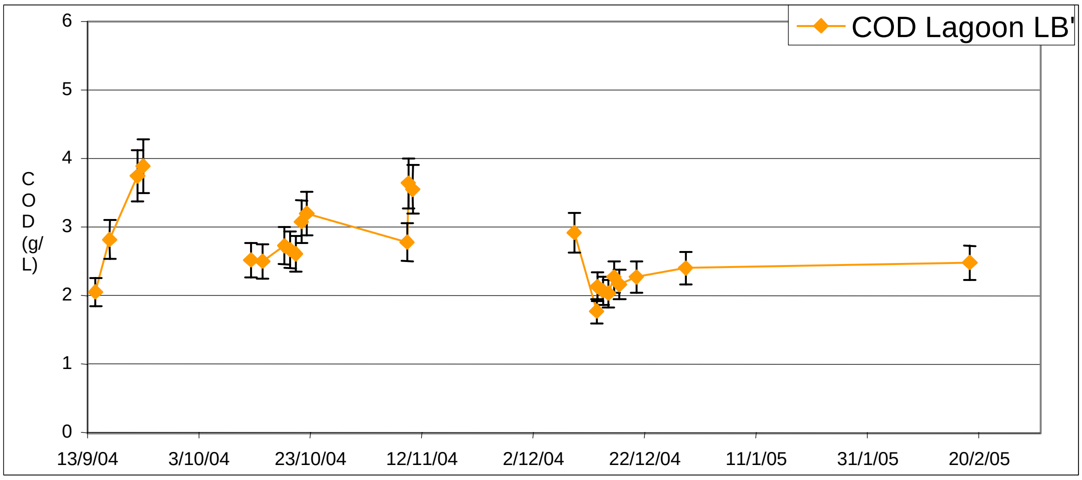




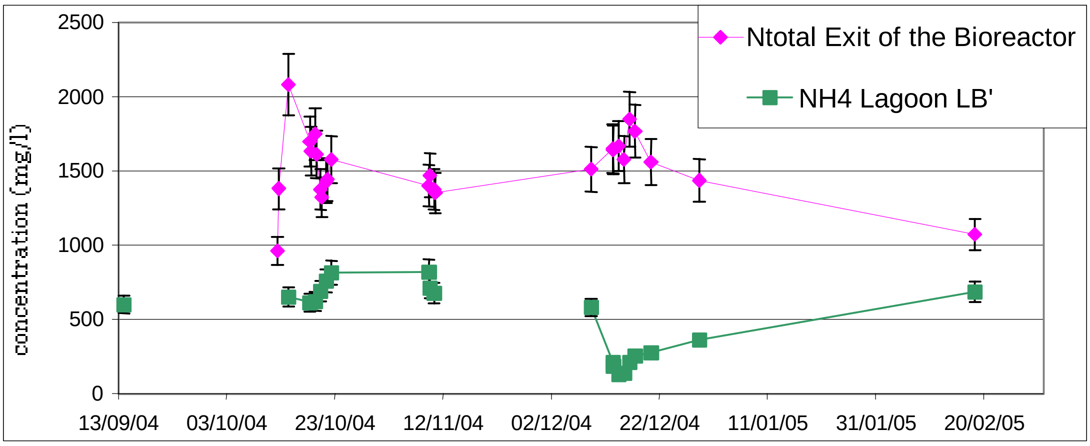




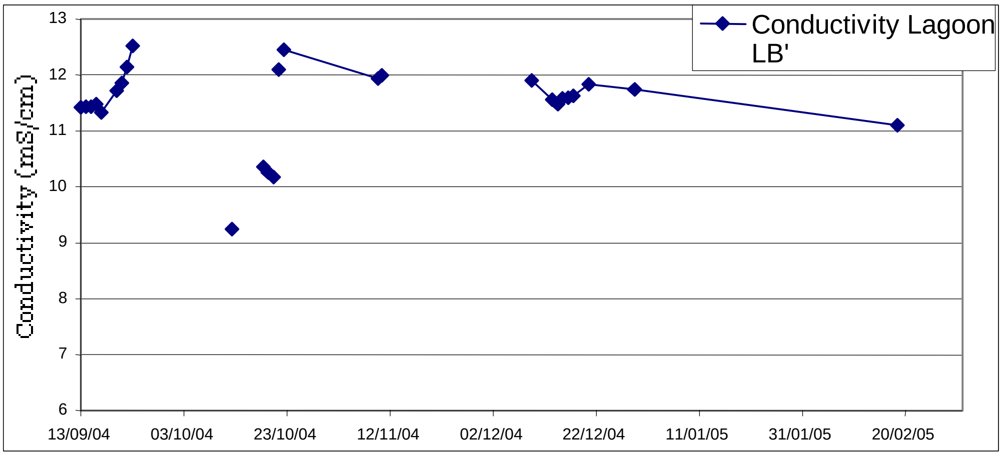
pH
9
8
7
6
5
4
3
13/9/04
3/10/04
23/10/04
12/11/04
2/12/04
22/12/04
11/1/05
31/1/05
20/2/05
pH Exit of the bioreactor

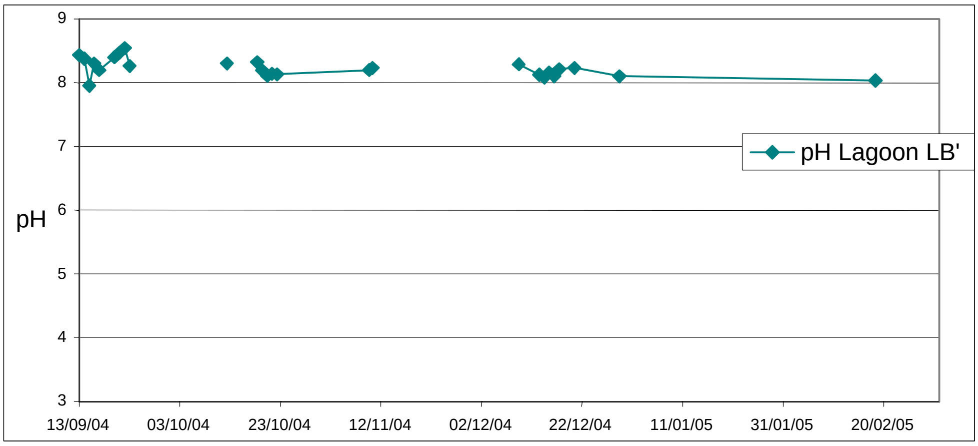


COD (g/L)
6
5
4
3
2
1
0
13/9/04
3/10/04
23/10/04
12/11/04
2/12/04
22/12/04
11/1/05
31/1/05
20/2/05
COD Lagoon LB'



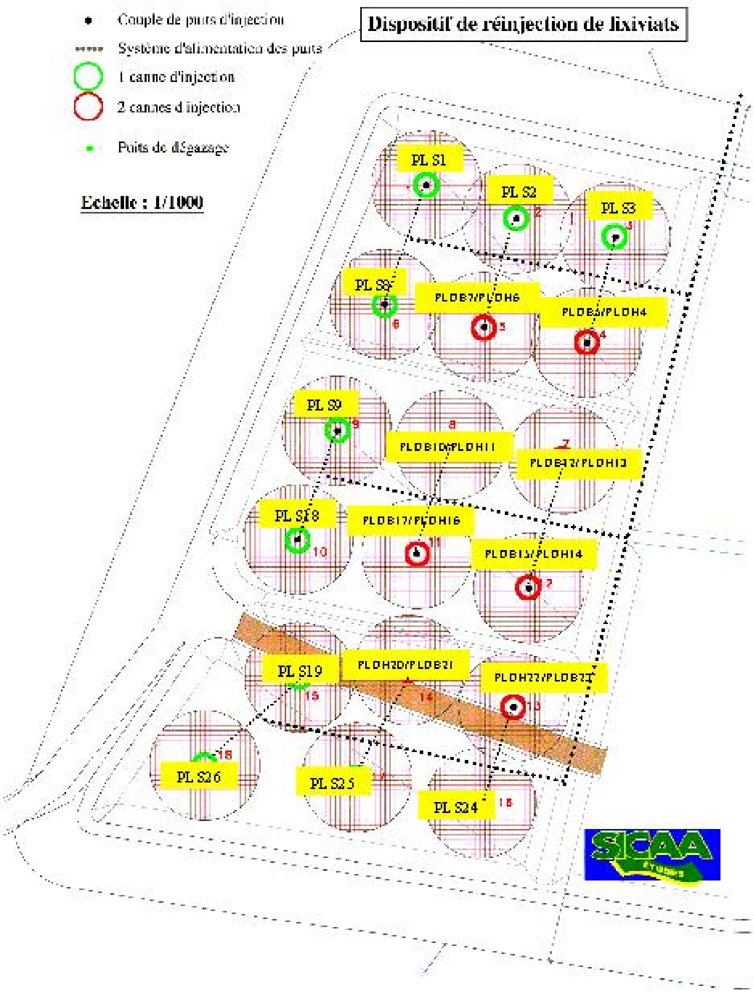
concentration (mg/l)
2500
2000
1500
1000
500
0
13/09/04
03/10/04
23/10/04
12/11/04
02/12/04
22/12/04
11/01/05
31/01/05
20/02/05
Ntotal Exit of the Bioreactor
NH4 Lagoon LB'


Conductivity Lagoon LB'
Conductivity (mS/cm)
13
12
11
10
9
8
7
6
13/09/04
03/10/04
23/10/04
12/11/04
02/12/04
22/12/04
11/01/05
31/01/05
20/02/05

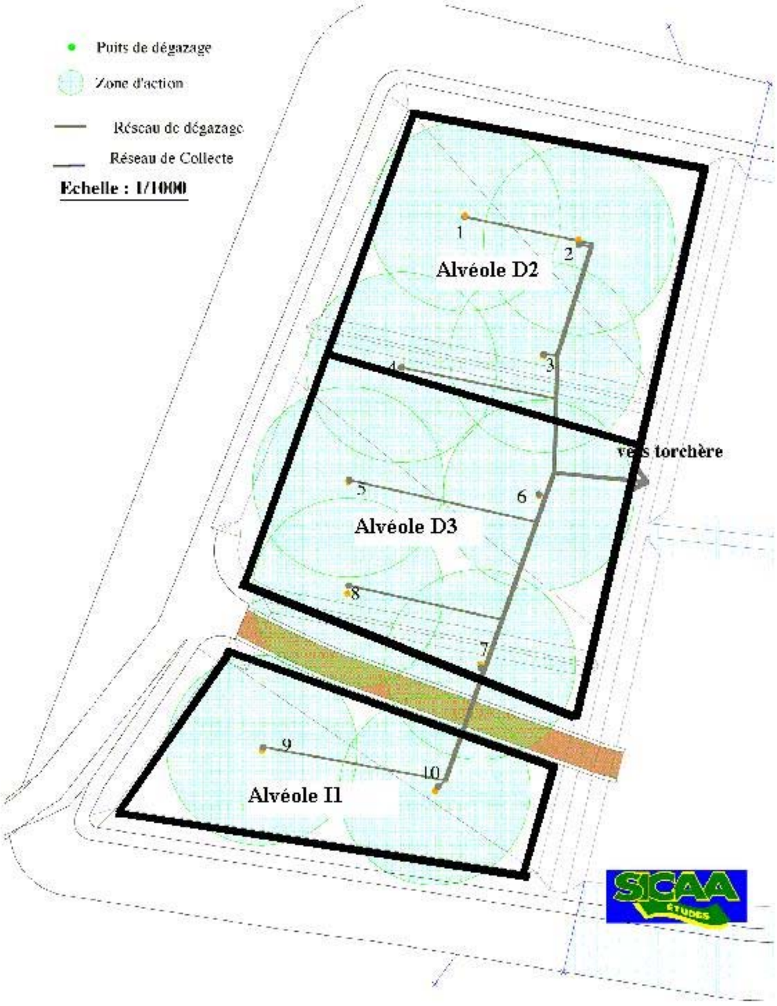

pH Lagoon LB'
pH
9
8
7
6
5
4
3
13/09/04
03/10/04
23/10/04
12/11/04
02/12/04
22/12/04
11/01/05
31/01/05
20/02/05

APPENDIX V: THE BIOREACTOR CELL OF THE MSW LANDFILL OF LA VERGNE

Distribution of the injection wells on the bioreactor cell with their theoretical operating ranges



Distribution of the wells of biogas collection on the bioreactor cell with their theoretical operating ranges



APPENDIX VI : ARRETE DU 9 SEPTEMBRE 1997

Minimal applicable criteria to the rejections of liquid effluents in the natural environment [ARRETE DU 9 SEPTEMBRE 1997, France]

Total Suspension Matter	<100 mg/l if the daily flow is max < 15 kg/j < 35 mg/l beyond
Total Organic Carbon	< 70 mg/l
Chemical Oxygen Demand (C.O.D)	< 300 mg/l if the daily flow is max < 100 kg/j < 125 mg/l beyond
Biological Oxygen Demand (B.O.D.5)	< 100 mg/l if the daily flow is max < 30 kg/j < 30 mg/l beyond
Total nitrogen	Monthly average concentration < 30 mg/l if the daily flow is max > 50 kg/j
Total phosphorus	Monthly average concentration < 10 mg/l if the daily flow is max > 15 kg/j
Phenols	< 0,1 mg/l if the rejection exceed 1 g/j
Total Metals : Cr 6+ Cd Pb Hg	< 15 mg/l < 0,1 mg/l if the rejection exceed 1 g/j < 0,2 mg/l < 0,5 mg/l if the rejection exceed 5 g/j < 0.05 mg/l
As	< 0,1 mg/l
Fluorine and derivative (in F)	< 15 mg/l if the rejection exceed 150 g/j
Free CN	< 0,1 mg/l if the rejection exceed 1 g/j
Total Hydrocarbures	< 10 mg/l if the rejection exceed 100 g/j
Halogeneous Organic Components (in AOX ou EOX)	< 1 mg/l if the rejection exceed 30 g/j

N.B.: Total metals are the sum of the concentration in mass per liter of the following elements: Pb, Cu, Cr, Ni, Zn, Mn, Sn, Cd, Hg, Fe, Al.

SHORT DICTIONARY

Active Life : the period of operation beginning with the initial receipt of solid waste and ending at the completion of closure activities.

Biogas : gas coming from the waste fermentation.

Cell : subdivision of the exploited zone delimited by a stable and sealed dam and hydraulically independent.

Geomembrane Liners : geosynthetic hydraulic barriers manufactured in sheets and installed by field seaming techniques.

Leachate : a liquid that has passed through or emerged from solid waste and that contains soluble, suspended, or miscible materials removed from the waste.

Municipal Solid Waste Landfill : a discrete area of land or an excavation that receives household waste.

Post-closure : this period begins after the active life. It is characterized by a significant production of biogas or leachate or other phenomena likely to harm the interests mentioned in article 1 of the law of July 19, 1976.