SYSAV

Välkommen till Hedeskoga avfallsanläggning och återvinningscentral

Investigation of a landfill leachate treatment plant in southern Sweden

by

Alessandro Sarno

Master Thesis number:

Water and Environmental Engineering

Department of Chemical Engineering

Lund University

June 2014

Supervisor: Associate professor Karin Jönsson

Co-supervisor: PhD Anders Persson (Sysav), Env. Engineer Erika Heander (Sysav), Per Leander (Sysav)

Examiner: Associate professor Per Carlsson

Picture on front page: Hedeskoga landfill and particular of its leachate treatment plant. Photo by Alessandro Sarno.

Postal address **Visiting address** **Telephone**

P.O. Box 124 Getingevägen 60 +46 46-222 82 85

SE-221 00 Lund, Sweden +46 46-222 00 00

Web address **Telefax**

www.vateknik.lth.se +46 46-222 45 26

Preface

Usually, here comes the point in which all the fanciful words are dedicated to those people, without whom, this work would have not been possible. Well, without falling too deep into corniness there is a bunch of people I would like to say “thank you” to: all my gratefulness goes to Lund University intended as the ensemble of human beings, atmosphere, situations that over the last two years played an important role in influencing my thoughts, in giving me the necessary tools to find a niche into this jungle, and in shaping a young scientific self. A special thanks in this sense goes to my supervisors, to the staff working at Sysav and to the people “living” at the Ecology Building and at the department of Water and Environmental Engineering for their terrific example of earnestness and professionalism. It might be taken for granted in Sweden, but, there is so much to learn from the proverbial Nordic coherence and organization!

A big thanks goes also to my roommates and to my friends in Lund, whose companionship fitted the goliardic and international spirit of this young-at-heart city. Special thanks also goes to Kim whose brilliant person was determinant during the writing, and to my old crew back in Italy.

Now, the English reader will excuse me here but…come si può dimenticare di menzionare chi più di tutti attendeva questo “evento” e, più di ogni altro, del medesimo evento ne è il responsabile? Non doveroso, o tecnicamente freddo, ma, spontaneo e sincero è il senso di gratitudine che vorrei esprimere verso la mia famiglia, che da lontano ha seguito sin dall´inizio questa “impresa”, a volte sacrificante, ma comunque entusiasmante e mai priva di stimoli. Con una certa maturità (ad oggi spero acquisita) mi accingo ad affrontare quello che il mondo avrà da offrirmi, sempre armato di buon senso, interesse e dedizione. Per citare la proverbiale umiltà scandinava: *lagom är bäst*, il “giusto” è meglio.

Abstract

Dissolved ammonia is often referred to as one of the major contaminants in landfill leachates. Discharge concentration limits for municipal wastewater treatment plants in Sweden have been tightened in order to meet higher water quality standards. Because of REVAQ, a certification system tailored to ensure better sludge quality, wastewater treatment plants may decide whether to accept leachate from landfills or not. Usually leachate contains potentially harmful compounds and environmental pollutants such as man-made organics, heavy metals, and ammonia. Therefore there is a growing interest in investigating actual capacities of landfills to treat leachate on-site rather than off-site, especially with regard to ammonia which is a potential inhibitor of nitrification. Since the 1980s, lagooning represents among biological treatment methods a versatile, long-term, and low-cost solution for removing organics and ammonia despite yearly climate fluctuations and leachate volume variations. This thesis focuses on the understanding of nitrogen transforming and removal processes that might occur in Hedeskoga, a landfill site provided with a series of basins and a spray irrigation area meant to treat leachate within the facility. A simple water budget and a nitrogen mass balance gave important information on the pathways followed by nitrogen: nitrification and denitrification are the main nitrogen removal processes occurring during summer in the ponds´ system in Hedeskoga; retention times longer than 30 days and temperatures lower than 5°C enhance the possibility for ammonia nitrogen to be removed by sedimentation during winter rather than by active nitrification. Further biological assays could be made in the future to elucidate just as important nitrogen removal pathways within the ponds.

Sammanfattning

Ammoniak anses vanligen som en av de huvudsakliga föroreningarna i lakvatten från avfallsdeponier. Svenskt Vatten försöker att minska flödet av farliga ämnen till reningsverken genom REVAQ, ett certifieringssystem som försäkrar bättre slamkvalitet. Därmed finns det nu ett ökande intresse för att forska vidare på den verkliga kapaciteten för att behandla lakvatten inom deponeringsanläggningarna istället för att skicka lakvattnet till de lokala regningsverken. Luftnings- och sedimenteringsdammarna (en teknologi från 1980-talet) företrädar en långsiktig och billig metod för att behandla lakvatten, med avseende på det organiska materialet och ammoniak. I hanteringsmetoderna används de biologiska processerna som sker i dammarna naturligt; framförallt nitrifikation och denitrifikation. I den här uppsatsen fokuseras det på de kväveförflyttnigsprocesser som kan finnas i Hedeskoga, en deponi bestående av ett antal bassänger och ett bevattningsområde vilka har till uppgift att hantera lakvatten inom området. En enkel vatten- och kvävebalans visade på att den högsta kvävehalten hade tagits bort genom nitrifikation under sommaren (hanteringsperioden 2013) och att det under vinterns lagringsperiod (2013) fanns en stor möjlighet för kvävet att avlägsnas genom sedimentering, då temperaturen inte är lämplig för nitrifikationsprocesser. Ytterligare analyser krävs för att klargöra icke biologiska mekanismer för ammoniakförflyttningar.

Table Of Contents

1 Introduction

The generation of solid waste is a primary consequence of the industrial productive cycle and the household consumption in developed and developing countries. Instead of being perceived as something to reject, solid waste is being gradually considered as an important source of energy and other resources. As every form of energy, the energy in solid waste cannot be destroyed. Rather, according to its constituents, it can be destined to either thermal energy conversion or material recovery. The remaining is generally disposed of in landfills.

As set out by the EU legislation, according to the “waste hierarchy” (Landfill directive 1999/31/EC), landfilling shall be replaced in the long run by (in ascending order of importance) recovery (energy and material), re-use and ultimately by a no-waste condition. But, nowadays, landfilling practices still constitute a major management strategy for many municipalities due to its economic advantages. In spite of any technological upgrade concerning landfill design, the scientific community identifies landfills as a crucial long-term emissions spot of hazardous substances which must be regularly monitored.

Leachate water, whose formation is dependent on a simultaneous action of temperature, precipitation, evapotranspiration and biological activity on the landfilled waste body is an example of potentially hazardous substance (Haarstad and Maehlum, 1999). Unless properly collected and treated, leachate can severely impact the biota by inducing toxic responses or alter the nutrient concentrations in surface waters, ground water tables, marine and freshwater ecosystems. For the aquatic environment leachate water can represent a serious threat as it is often highly concentrated in organic and inorganic contaminants including ammonia nitrogen ($N\text{-}NH_3$), heavy metals and xenobiotics (Wiszniowski *et al.*, 2006; Kurniawan *et al.*, 2010).

Ammonia-related toxic effects such as decreased growth, altered behavior and increased mortality have been detected in aquatic organisms (US EPA, 2013). Additionally, nitrogen is detrimental for leachate treatment methods based on biological activity occurring either on-site, i.e. within the landfill area, or off-site, i.e. in wastewater treatment plants. Particularly, nitrogen in the form of ammonia exhibited inhibitory effects on nitrification and denitrification processes (Kim *et al.*, 2006). With a $N\text{-}NH_3$ concentration higher than 100 mg/L algal growth is stimulated leading to eutrophication (Kurniawan *et al.*, 2010). In several studies conducted in many landfills in the UK, it was shown that a concentration of ammonium in excess of 50 mg/L can significantly inhibit the bacteria carrying out the aerobic treatment and at concentration as high as 80 mg/L (pH values of 7-8) the process ceases completely (EA UK, 2006). Regular effluent quality controls are therefore needed both to determine the entity of the impact caused by leachate water discharge onto the environment and to guarantee a sufficiently good treatment in respect of nitrogen removal.

Since biological methods are versatile, cost-effective and widely spread, the economic interest around leachate treatment is focused on finding the most appropriate technology combination in order to prevent high ammonium discharge and to avoid heavy metals dispersion (Haarstad and Maehlum, 1999; Robinson and Barr, 1999). This is what municipalities and waste management companies within the European community have as a goal. In this respect, a representative case is found in southern Scania, Sweden. Sysav, a company involved in recycling and waste management on account of several municipalities located in this region is responsible for an operational landfill named Hedeskoga after the small country village in which it resides. The facility is situated about 3 km northwards from Ystad city center. The main activities linked to solid waste in this area include: sorting and treatment for recycling, composting, landfilling, treatment of contaminated soil, transfer of combustible household and industrial waste for incineration. The landfill is a sanitary landfill provided with synthetic liners and a leachate collection system, according to the European standards concerning handling of municipal solid waste and leachate water treatment (Landfill directive 1999/31/EC).

Due to REVAQ, a water quality assurance system in force over the whole Swedish territory in recent years, standards are becoming stricter than ever before when it comes to final water discharge into the municipal sewer system (Swedish Water and Wastewater Association, 2013). For this reason, an improvement of the on-site leachate water treatment system in Hedeskoga has been demanded and in 2009-2010 Sysav decided to switch from an off-site to an on-site leachate treatment: the combined treatment with domestic sewage was gradually replaced by a biodegradation aerobic-based system (Environmental report 2009, Environmental report 2010). For self-management and local disposal of leachate there are three storage-aeration basins, one aerated lagoon, one sedimentation basin and a MV irrigation system (where MV in Swedish stands for “mark-växt”, i.e. “soil-plant”).

It is of great relevance to investigate the biological processes and the actual treatment capabilities of an already established system in order to ameliorate its management, especially when stricter environmental standards have to be met. The main outline in this thesis is the understanding of the performance of an on-site treatment system with respect to a major leachate constituent and environmental pollutant: ammonia nitrogen. In particular, nitrogen removal processes related to leachate treatment in aerated lagoons are studied in deep. A water budget and a nitrogen mass balance are calculated for the on-site leachate treatment in Hedeskoga to quantify the amount of nitrogen entering and leaving the system. The relationship between leachate toxicity and potential inhibition of nitrifiers activity in Hedeskoga, formerly thought to be due to a high ammonium level (Environmental report, 2012; Liu, 2013), is also investigated.

1.1 Hypotheses

Ammonium, in equilibrium with ammonia in aqueous solutions, is a dominant fraction of the total nitrogen in leachate water and is therefore reputed to be a major obstacle for nitrification occurring in on-site landfill aerated lagoons; nitrification should occur in those basins loaded with ammonium and nourished with oxygen when aeration and turbulence are provided (Wiszniowski *et al.,* 2006; Renou *et al.,* 2008; Kurniawan *et al.,* 2010). Another biochemical reaction thought to be involved in the removal of nitrogen in Hedeskoga is denitrification;

denitrification occurs when oxygen is unavailable in its molecular form and where nitrate is present as an electron acceptor (Kurniawan *et al.*, 2010; Knowles, 1982). Nonetheless, a consistent fraction of nitrogen could also leave the system either by inorganic nitrogen transformations such as ammonia air stripping or algae biomass uptake (Camargo *et al.*, 2010b; Martins *et al.*, 2013). These four nitrogen removal mechanisms, but mainly nitrification and denitrification, could simultaneously exist in the on-site leachate treatment system in Hedeskoga. Moreover, leachate in Hedeskoga showed inhibitory effects within some treatment ponds (Liu, 2013). Being considered a complex mixture of different compounds it is possible that inhibition occurs because of some toxicants in the leachate.

Seasonal fluctuations of temperature, precipitations, evapotranspiration, leachate characteristics and hydraulic retention times affect biological nitrogen removal processes, particularly in aerated lagoons (Middlebrooks and Pano, 1983; Haarstad and Maehlum, 1999; Frascari *et al.*, 2004). Therefore, the evaluation of the performance of such a system strongly depends on proper hydrological and nitrogen balance calculations that are able to take these variables into account. Hedeskoga leachate treatment system is thought to be affected by precipitation and evapotranspiration which in turn can cause a misinterpretation of the actual quantity of removed nitrogen if not taken into account.

1.2 Aims of the project

The thesis mainly revolves around two main issues:

- To determine what can be expected from an on-site leachate treatment system in terms of nitrogen removal and nitrogen transformation pathways
- To give an evaluation of Hedeskoga´s leachate treatment capacity, mainly in respect of ammonia, and put into context with other known case studies found in the literature.

A secondary objective is to quantify potential nitrification inhibition caused by different leachate qualities.

1.3 Methods

In order to fulfill the aims of the project, the whole work has been split into two parts. One part of the project consists of an extensive literature study focused on the understanding of:

- nitrogen removal processes
- existing technological means by which biological leachate treatment is provided on-site with particular attention to aerated lagoons
- water budget and nitrogen mass balance for Hedeskoga landfill.

Another part, more empirical, comprises:

- an experimental analysis of leachate water and sediment samples collected out of Hedeskoga equalization basins in order to identify any bacterial activity and to quantify nitrification rates
- an experimental analysis of leachate water samples from two different influents at Hedeskoga with regard to potential nitrification inhibition.

The strategy adopted to perform a literature study finds its basis on three main principles:

- data research in published experimental works, case studies, paper reviews and manuals
- appreciation of available data (current and historical) regarding Hedeskoga landfill and its on-site leachate water treatment system
- direct investigation and data acquirement from field experts.

Concerning water budget and nitrogen mass balance, the variables taken into account are:

- weekly and monthly water flow (Almqvist, 2013; Nilsson, T. 2013)
- stored leachate in the different ponds (Almqvist 2013; Nilsson, T. 2013)
- daily precipitation and evapotranspiration measurements (SMHI, 2013)
- basins design characteristics (Almqvist, 2013; Nilsson, T. 2013; Nilsson, P. 2013)
- nitrogen concentrations in different chemical forms (Environmental report, 2013).

The empirical part articulates in both field and laboratory work. Contacts with landfill managers and operators are essential to improve data reliability when it comes to: field sampling, leachate water readings at the different pumping stations and direct environmental measurements such as oxygen content, pH and temperature in the ponds. The analysis of the samples is conducted in respect of: bacterial activity, nitrification rates and potential nitrification inhibition. To accomplish this, the so-called screening method and a modified protocol of the same method are employed. The screening method is a standardized procedure used to quantify inhibition of nitrifiers´ activity due to a variety of substances, most commonly wastewater and leachate water (Jönsson, 2001).

2 Leachate water

Two are the most common ways to define leachate in United States and Europe. Respectively:

“A leachate is a contaminated liquid that results when water collects contaminants as it trickles through wastes, agricultural pesticides, or fertilizers. Leaching may occur in farming areas and landfills and may be a means of the entry of hazardous substances into soil, surface water, or ground water” (US EPA, 2013).

“Liquid that has seeped through solid waste in a landfill and has extracted soluble dissolved or suspended materials in the process” (EEA, 2013).

In the first definition, leachate is intended more generically as a liquid emission coming from different sources and affecting just as many potential sinks; particular regard is also posed to its hazardousness. In the second, its origin is emphasized, by referring specifically to solid waste in landfills. By convention, the European definition will be used in the following text.

2.1 Source

Landfill leachate originates in the discarded refuse as a consequence of rainwater percolation, inherent waste water content, microbial and physical-chemical abatement occurring in the waste body (Renou *et al.*, 2008). Bioreaction (1) represents acetogenesis, i.e. the conversion of carbon dioxide (CO_2) into acetic acid (CH_3COOH) carried out by anaerobic bacteria, while bioreactions (2) and (3) illustrate the two most commonly documented methanogenic reactions detected in landfills:

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \quad (1)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (3)$$

The principal sources of emission are represented by:

- Engineered (or sanitary) landfills; i.e. artificial ditches provided with bottom sealing liners, a leachate drainage system and a pipework to intercept landfill gases.
- Open dumps; i.e. areas of open land in which solid waste is deliberately dumped.

In the first case leachate originates under monitored conditions, while in the second, due to less care in handling the refuse, liquid emissions are not contained.

Landfilling was, and it is still nowadays, a common practice for waste disposal worldwide (Frascari *et al.*, 2004). Even 50 years after closure, landfills may still generate leachate with considerably high ammonia nitrogen concentrations (Kurniawan, 2011). In view of this, it is reasonable to think that landfill liquid emissions are not only widely distributed in space but also continuous in time.

2.2 Law implementations: the Swedish case

In Europe, the way different countries with different legislation systems interpret the concept of leachate quality is strictly dependent on when, how and if the European Landfill directive 1999/31/EC on sanitary landfills has been implemented. In Sweden, one of the most important regulatory documents concerning waste disposal in landfill sites came gradually into force after 2001. Among the norms contained in this document, called SFS 2001: 512, two are particularly important for consequences on leachate quality:

- from January 2002, no unsorted combustible material can be disposed of in landfills.
- from January 2005, landfilling of organic waste was prohibited.

In some exceptional cases the proportion of organic material can be up to 10% of the discarded waste (Avfall Sverige, 2009).

2.3 Factors affecting leachate production in a landfill

Landfill leachate emissions are mainly a function of precipitation and temperature. In (Frascari *et al.*, 2004) yearly leachate amounts were monitored over 10 years in a landfill; an hydrological model was also used to predict yearly leachate production (Q_L). This model included the precipitation rate measured on a daily basis (p); the evapotranspiration rate measured on the basis of average monthly temperatures detected at the landfill (e); the fraction of moisture released by the waste during compaction (I_w); the amount of waste disposed (Q_w); the average effective infiltration area (S_1); and the average waste disposal area (S_2). Equation (4) shows this model in brief:

$$Q_L = p \cdot S_1 - e \cdot S_2 + I_w \cdot Q_w \tag{4}$$

where,

Q_L = yearly leachate production (m^3/y)

p = precipitation rate (m/y)

S_1 = average effective infiltration area (m^2)

e = evapotranspiration rate (m/y)

S_2 = average waste disposal area (m^2)

I_w = moisture released by the waste during compaction (m^3/t)

Q_w = disposed waste (t/y)

Except for S_1 which was a cause of major uncertainty due to its difficult measurability, the model could reasonably be fitted to the actual experimental data.

Nevertheless, some other physical-chemical factors intrinsic to the landfill site are equally determinant for the amount and composition of leachate produced. The following is a list of the most important ones.

2.3.1 Moisture content

Moisture content or water content can be inherent to the discarded materials or be dependent on:

- **Level of rainfall in the area**; periods of heavy rainfall and snowmelt can increase amounts of water trapped in the texture of the refuse (Haarstad and Maehlum, 1999).
- **Surface run-off**; water can leak out the waste cell (i.e. a delimited area in an operative landfill adopted for waste disposal) if this has an increased slope.
- **Percolation of groundwater into the site**; if the site is constructed in an area where the vertical flow from the unsaturated zone is much slower than that of the saturated zone, the bottom of the waste cell might show an increased water content due to groundwater infiltration (EA UK, 2006).
- **Rate of waste biodegradation**; the higher the rate, the higher the moisture content (Kurniawan *et al.*, 2010).

2.3.2 Temperature

The activity of microorganisms responsible for the disintegration of the bulky materials contained in the refuse is strongly dependent on temperature. (Schiopu and Gavrilescu, 2010) reported values between 30 and 35°C in the majority of the waste cells, although, temperature intervals between 80 and 90°C may also occur at an early stage of aerobic degradation (EA, UK 2006). Colder climates are responsible for setting back the biological breakdown, therefore, wide seasonal variations in the entity of dissolved particles such as humic acids can be observed in leachate flows throughout the years (Haarstad and Maehlum, 1999). Temperature also changes in accordance with the waste cell depth causing a layering effect: different temperature ranges affect microbial communities so that these will distribute according to their *optima* (Schiopu and Gavrilescu, 2010). For instance, activity of methanogenic bacteria is strongly reduced at temperature values below 15°C; since the surface temperature is highly dependent on that of the atmosphere, in cold climates there is an high chance that methanogens will occupy spatial microniches deeper down in the waste body (Haarstad and Maehlum, 1999; Hogland, 2002; Kurniawan, 2011).

2.3.3 Site characteristics

Shallower sites tend to develop aerobic environments because of increased air interchange with the closer atmosphere. Conversely, landfill sites exceeding 5 m in depth easily undergo anaerobic conditions (Hogland, 2002; Schiopu and Gavrilescu, 2010).

The high degree of compaction causes a reduction in both number and size of air-filled pores; oxygen becomes less available for the aerobic biodegradation to occur and the temperature within the refuse is subjected to a decrease (Robinson, 2007).

Immediate tipping of the waste cells may act as a barrier for precipitations which cannot reach deeper layers into the waste body; the resulting decreased moisture content is responsible for low biodegradation, especially during the initial stages after closure (Hogland, 2002; Robinson, 2007).

2.3.4 Waste characteristics

Percentage and type of buried waste material can affect the biodegradation pathways occurring in each waste cell as well as the final leachate quality (Schiopu and Gavrilescu, 2010). If the proportion of lignin and cellulose, e.g. contained in wood and paper, are predominant in respect of proteins and short-chain lipids the leachate water will be enriched in recalcitrant substances and less degradable organic matter will be available for biological breakdown.

Generally, procedures such as shredding and pulverization prior to landfilling increase both surface area and homogeneity of the waste making it more bioavailable for enzymatic attack (Schiopu and Gavrilescu, 2010). However, in Hogland (2002) different biodegradation rates and different qualities of liquid emissions were observed even in the same waste cell, due to heterogenic conditions of the waste material (particle size, texture, degree of compaction).

2.3.5 Acidity

The pH of leachate solutions depends on the degree of carbon dioxide, water, and organic acids produced during the breakdown of organic matter (Schiopu and Gavrilescu, 2010). At the very beginning of its life cycle a landfill maintains a neutral pH; as the waste cell conditions shift from aerobic to anaerobic, changes towards more neutral or slightly alkaline solutions are observed in the long-run.

Heavy precipitations, i.e. between 300 and 600 mm/y have shown to decrease pH in Norwegian landfill sites and a peculiar sensitiveness to rainfall patterns, particularly in operative waste cells, was observed at an early stage in British landfills (Haarstad and Maehlum, 1999; Robinson, 2007).

2.3.6 Landfill age

Leachate can assume different physical-chemical characteristics in agreement with the landfill life cycle (Renou *et al.*, 2008). Particularly, what makes a certain leachate distinguishable on a time basis is the degree of decomposition and biological activity within the discarded refuse although advanced or delayed decomposition stages might be observed simultaneously in the same waste body (EA UK, 2006). In the classical view, during its life cycle, a waste cell can typically undergo five decomposition phases:

- **Aerobic**; in this period, known to last only few days or weeks, carbon dioxide and water are the main products and leachate is near neutral pH (EA UK, 2006).
- **Acidogenic**; carbon dioxide, hydrogen and easily degradable organic acids are found in high concentrations causing the leachate solutions to become more acidic. As pH decreases, metals and ammonium become also more soluble (Kurniawan, 2011).
- **Acetogenic**; waste becomes more anaerobic and increased concentrations of acetic acid and derivatives are observed (Schiopu and Gavrilescu, 2010).
- **Methanogenic**; after several months or years, predominant anaerobiosis offers the right conditions for the establishment of methanogenic communities (Robinson, 2007). Leachate solutions during this phase are usually neutral or slightly alkaline (EA UK, 2006).
- **Aerobic**; progressively, anaerobic biodegradation approaches completion and aerobic condition may return, although this phase is rarely observed in closed landfill sites (EA UK, 2006).

The type of leachate produced during the aerobic phase is classically referred to as “young”; the one coming from either the acidogenic or acetogenic phase is called “intermediate”; the leachate originating from either methanogenic or aerobic phase is defined as “old” or “stabilized”. However, depending on the variables and leachate characteristics taken into account and the different ways to implement landfilling regulations this conventional classification might differ from landfill to landfill (Robinson, 2007; Kurniawan, 2011). An example is found in Fläskebo, the first Swedish landfill constructed after the ordinance mentioned in section 2.2 (Avfall Sverige, 2009). Already from the first year of use (2003), organic carbon content and nutrients (nitrogen and phosphorus) were comparatively low in leachate samples in relation to other six landfills. This is due to the low-organic waste deposited in the waste cells. In addition, nitrogen patterns suggested a less reducing environment in Fläskebo than in other landfills which were designed prior to the new legislation. Therefore, engineered landfills do not undergo the decomposition phases mentioned earlier.

2.4 Characteristics

Leachate characteristics are mainly a resultant of the physical and biochemical processes occurring in the waste body (Renou *et al.*, 2008). The physical-chemical composition of leachates, although showing wide variations from landfill to landfill, can be determined at the effluent by quantifying:

colour, which encompasses different shades of brown and green (Kurniawan, 2011)

odor, which can be faint, earthy, and slightly ammoniacal (Knox, 1985)

pH, typically between 5.5 and 8.5 because of biological activity inside the waste (Renou *et al.*, 2008)

total organic carbon (TOC), which in large landfills encompasses values between 10 mg/L to a maximum of 20 000 mg/L (Robinson, 2007)

chemical oxygen demand (COD), which in Renou *et al.* (2008) is reported to vary considerably from very high (~60 000 mg/L), high (~1 000 mg/L), low (~500 mg/L) to very low (less than 100 mg/L)

biochemical oxygen demand (BOD), which ranges from less than 10 to 26 000 mg/L (Renou *et al.*, 2008)

BOD/COD ratio, which can range from more than 0.5 in young leachate, between 0.5 and 0.1 in intermediate leachate, and less than 0.1 in stabilized leachate (Kurniawan, 2011)

total nitrogen (as TKN), which can enlarge from values as low as 5 mg/L to values as high as 10 000 mg/L (Robinson, 2007)

ammoniacal nitrogen ($N-NH_3$), which is typically distinguished either in low strength (concentration between 100 and 400 mg/L) or high strength (concentration between 2 000 and 5 000 mg/L) (Kurniawan, 2011)

alkalinity ($CaCO_3$), reported in large landfills to vary between concentrations as high as 30 000 mg/L and as low as 2 000 mg/L (Robinson, 2007)

suspended solids (SS), which can vary between values lower than 100 mg/L to higher than 2 000 mg/L (Renou *et al.*, 2008)

fatty acids (FAs), which typically constitute a higher percentage in old leachate than in intermediate ones (Robinson, 2007)

heavy metals (Fe, Cr, Cu, Mo, Mn, Zn, As, Cd, Pb and Hg), generally highly variable in concentrations depending on waste pH and type of discarded material (Renou *et al.*, 2008)

conductivity (Cond), typically in the range of 12 000 mg/L in intermediate leachate and lower than 1 mg/L in stabilized leachate (Robinson, 2007)

chlorides (Chlor), typically in concentration of ~1500 mg/L and ~3000 mg/L in young and stabilized leachate, respectively (Robinson, 2007)

phosphates ($P\text{-}PO_4$), typically ~10 mg/L in intermediate leachate and ~2 000 mg/L in old leachate (Robinson, 2007)

sulphates (SO_4^{2-}), typically ~500 mg/L in intermediate leachate and ~20 mg/L in old leachate (Robinson, 2007)

nitrates ($N\text{-}NO_3$), typically lower than 1 mg/L in intermediate leachate and lower than 0.1 mg/L in old leachate (Robinson, 2007)

nitrites ($N\text{-}NO_2$), typically lower than 0.1 mg/L in intermediate leachate and ~50 mg/L in old leachate (Robinson, 2007)

xenobiotic organic compounds, which encompass a wide array of chemicals depending on the material disposed of in the waste cell and their relative degree of biodegradability (Kurniawan, 2011)

pathogens, which are mainly represented by thermo-tolerant bacteria, fecal *Streptococcus, Salmonella*, various protozoa and nematodes (Haarstad and Maehlum, 1999)

Undoubtedly, all of these characteristics constitute relevant information about the quality of every leachate; but, pH, COD, BOD/COD ratio, FAs, $N\text{-}NH_3$, TKN, and heavy metals which are respectively indicative of waste decomposition stage, recalcitrant molecules, landfill and leachate age, organic matter, leachate strength, organic and ammonium nitrogen, and degree of heavy metals pollution in leachate effluents could provide an overall picture about the ongoing processes within the waste body (Schiopu and Gavrilescu, 2010). Table 2.1 summarizes these characteristics with their typical values detected in the majority of both intermediate and stabilized landfill leachates.

Table 2.1. *Most important physical-chemical characteristics regrouped according to leachate type in a worldwide perspective. Apart from pH, all the measure units are given in mg/L.*

	Young	Intermediate	Stabilized	Reference
pH	4.5 – 6.5	6.5 – 7.5	> 7.5	Kurniawan *et al.*, 2010 Kurniawan, 2011
COD	6 000 – 60 000	4 000 – 10 000	< 4 000	Renou *et al.*, 2008 Kurniawan *et al.*, 2010
BOD/COD ratio	> 0.5	0.1 – 0.5	< 0.1	Kurniawan *et al.*, 2010 Kurniawan, 2011
FAs	NA	6 000	9 000	Robinson, 2007
N-NH_3	500	1 250	2 000 – 5 000	Robinson, 2007 Kurniawan, 2011
TKN	100 – 2 000	NA	NA	Schiopu and Gavrilescu, 2010
Heavy metals	>2	< 2	< 2	Kurniawan, 2011

2.5 Toxicity

Toxicity is not automatically synonym of danger: a wide range of compounds contained in leachate water may induce a toxic response in aquatic organisms at different extents without posing any risk for neither human health nor biota (US EPA, 2013). Examples of detected toxicants in landfill leachates can be: ammonia, phenols, polyaromatic hydrocarbons (PAH), dioxins, polychlorinated biphenyl´s (PCB) and heavy metals (Haarstad and Maehlum, 1999). However, among these, ammonia nitrogen has been recognized as one major long-term source of pollution and toxicity in landfill leachates (Kurniawan, 2011) and one big obstacle for leachate treatment technologies based on nitrification-denitrification processes (Kim *et al.*, 2006). One way for ammonia nitrogen to be released in solution is after the biological breakdown of organic matter present in the refuse. In methanogenic environments this molecule is very persistent and not easily biodegraded (Kurniawan, 2011). What happens in sanitary landfills in a long-term perspective where the amount of organic matter is intentionally reduced? In Fläskebo, the ratio between ammonium nitrogen and total nitrogen was found to be lower than in other landfills (Avfall Sverige, 2009). This may indicate either that the waste cell is in reducing conditions or that ammonium releasing is not enhanced by organic matter breakdown due to low TOC and low nutrient content. It could be argued that another way for ammonia to be dissolved in leachate is caused by dilution of residual surfactants. Unless properly treated, ammonia could represent a direct source of toxicity for aquatic biota living in groundwater and surface waters in the vicinity of a landfill site (EA UK, 2006). In addition, since ammonia stimulates algal growth and consecutively oxygen depletion, toxicity on higher biological organizational level (eutrophication) may be detected in the long run (Craggs, 2005).

Because of the wide array of compounds and the expensiveness of some analytical methods, it is quite difficult nowadays to relate leachate toxicity to one or few specific chemicals. Therefore, it is more convenient to safely assume leachate to be a complex mixture of toxicants that is able to induce a toxic response as a whole. For this purpose, the most common practice today is to evaluate landfill leachate potential hazard by using species tests; these tests aim at different endpoints (i.e. arbitrary characteristic for which toxicity is investigated and quantified such as decreased growth rate, activity inhibition, acute toxicity) and investigate various organisms representing all trophic levels (bacteria, algae, plants, invertebrates and vertebrates).

Standard aquatic organisms such as zebrafish (*Danio rerio*), and small crustaceans (*Daphnia magna*) were reported as indicators of toxicity due to ammonia in Kurniawan *et al.* (2010). However, differing toxic effects might be observed depending on the type of toxic test and endpoint chosen. For instance, if standard single species tests are preferred to community tests and mortality is chosen as an endpoint in place of decreased growth rate, the resulting toxic response may give high mortality in one species at very high concentrations of tested substance; whereas, for the same substance and at the same concentration, the community might respond with no altered decreased growth rate. Eventually, results interpretation greatly depends on which test, endpoint or biological level is used to represent toxicity in relation to a chemical.

2.6 Leachate management options

In landfill management three ways are possible to handle leachate water: self-management at the landfill facility, disposal to local sewerage systems, and transport for treatment elsewhere (EA UK, 2006). The first is referred to as “on-site” or “in-situ” treatment while the second and the third are referred to as “off-site” treatment. On-site treatment is nowadays strongly demanded within the European Community because leachate can seriously reduce treatment efficiency in common wastewater treatment plants posing a potential threat for the aquatic ecosystems, e.g. wetlands, freshwater, and coastal water, nearby the discharge area (Renou *et al.* 2008).

Within the Swedish water regulatory framework there are two main driving forces that push private and public institutions to reduce the amount of pollutants reaching the environmental compartment at the municipal level; one of them is a certification system that strictly regards the quality of the sludge obtained as byproduct in wastewater treatment processes and goes, since its creation in 2002, under the name of REVAQ (Swedish Water and Wastewater Association, 2013). The main target is to produce a high-quality sludge by reducing the amounts of heavy metals and nutrients reaching the wastewater treatment plant upstream. The other important driving force comes from the environmental administration in the form of local regulations and general conditions regarding the type of wastewater that can be accepted at the sewage treatment plant. This ensemble of regulations is called ABVA (in Swedish, “Allmänna Bestämmelser för brukande av Allmänna Vatten- och Avloppsanläggningar”, i.e. ”General decisions for the usage of public water and sewage facilities”). In Ystad, municipality responsible for Hedeskoga landfill, the local wastewater treatment plant has the obligation to take care of household wastewater (Ystad Kommun, 2013). However, according to the regulations declared in the ABVA for the area concerning Simrishamn, Sjöbo, Skurup, Tomelilla, and Ystad, the local sewage treatment facility connected to Hedeskoga landfill can express its denial towards the acceptance of leachate water. Eventually, both REVAQ and ABVA constitute a strong motivation for waste management companies like Sysav to handle leachate treatment on-site.

In order to reduce the risk of pollution by landfill liquid emissions various options are possible to treat leachate on-site. By convention, they can be regrouped into five big categories:

- recirculation within the pumping systems
- biological treatment
- physical-chemical treatment
- microfiltration
- ultrafiltration

Each of those is obtained by means of different technological implements whose detailed description is out of the scope of this text. However, a specific remark is given to biological treatment in respect of both nitrogen removal and one of the most widespread technology used to achieve it: aerated lagoons.

3 Processes for nitrogen removal

Nitrogen is fairly ubiquitous. The organic fraction is mainly represented by amino-groups bound to carbon-skeletons of various molecular size whereas inorganic nitrogen is mainly under the form of free ammonia (unionized NH_3 or simply NH_3), ammonium (NH_4^+), dinitrogen gas (N_2), nitrous oxide (N_2O), nitric oxide (NO), nitrite (NO_2^-), nitrate (NO_3^-). Many human activities can contribute to displace the ecosystemic nitrogen balance with potential negative consequences. The main sources are associated with agriculture, aquaculture, urbanization and industry. Most commonly, four are the transport pathways directly involved in the nitrogen input increase: stormwater runoff, leakage into groundwater sources, atmospheric emissions and deposition, or direct effluent discharges (US, EPA 2013).

Biological nitrogen removal (BNR) is a widely adopted strategy to control unwanted and potentially harmful effects of nitrogen emissions from industrial and domestic wastewater to the environment. It is effective and economically convenient. For this reason, it is also applied to on-site landfill leachate treatment to remove nitrogen originating from the breakdown of residual organic matter contained in the municipal solid waste. The main principle is to exploit the reactions participating to the biogeochemical cycle of nitrogen (figure 3.1).

Two of the most important and well-studied bioreactions are without any doubt nitrification and denitrification. Both of them are intimately connected one to each other: ammonia nitrogen, derived from microbial decomposition of organic matter, fertilization of agricultural lands (natural and chemical), deposition of atmospheric nitrogen compounds, fixation of dinitrogen gas, is oxidized to nitrate during nitrification; in turn, nitrate is used as substrate for denitrification. In optimal conditions these two processes, catalyzed by bacteria, are usually found in sequence in biological treatment of sewage and leachate (Jokela *et al.,* 2002; Xie *et al.,* 2003; Zimmo *et al.,* 2004; Sundberg *et al.,* 2007b). Bacterial activity is usually dependent on substrate availability, pH, oxygen level and temperature; these factors can negatively or positively determine the establishment of a community in a variety of ecosystems, either natural and artificial. It can be argued that one of these parameters can solely “govern” the development and the activity of a given community at a given time when the degree of change of that parameter is dominating with respect to the others. For instance, this can happen in cold climates where the seasonal temperature variations are known to drastically reduce nitrifiers growth rate and activity. Such is the temperature effect that the other parameters fluctuations can be neglected when it comes to evaluations of potential nitrification. However, in the case of large microscale variations in natural or semi-natural systems this might not be true and divergent or synergistic effects can be observed within the same environment. In Sundberg *et al.* (2007a), during a growing season (May-August-November), nitrifiers were able to survive and remain active at lower temperatures in compacted constructed wetlands (CCWs); the unexpected lack of effects due to temperature drops was confirmed by an unchanged ammonia-oxidizing bacteria community composition. This can possibly be explained by a fundamental metabolic versatility of nitrifiers and their capacity to occupy different ecological niches. It is worthy of note that on a microscale, an individual effect is not as determinant as on a larger scale. Therefore, depending on the scale considered, bacteria respond to environmental changes at different extents.

Another relevant step within the nitrogen cycle (figure 3.1) is the biological immobilization (or assimilation) of NH_3 or NO_3^- carried out by plants and microflora. In shallow waste stabilization ponds or in aerated lagoons this process can represent a predominant way by which nitrogen is removed, given suitable conditions for algal photosynthesis such as sufficient light and high temperature (Takamizawa *et al.,* 1991; Camargo *et al.,* 2010b; Martins *et al.,* 2013).

Other mechanisms of nitrogen removal include inorganic nitrogen transformations such as ammonia air stripping (or volatilization) or nitrite reduction by iron (Parkes *et al.,* 2007; Leite *et al.,* 2011).

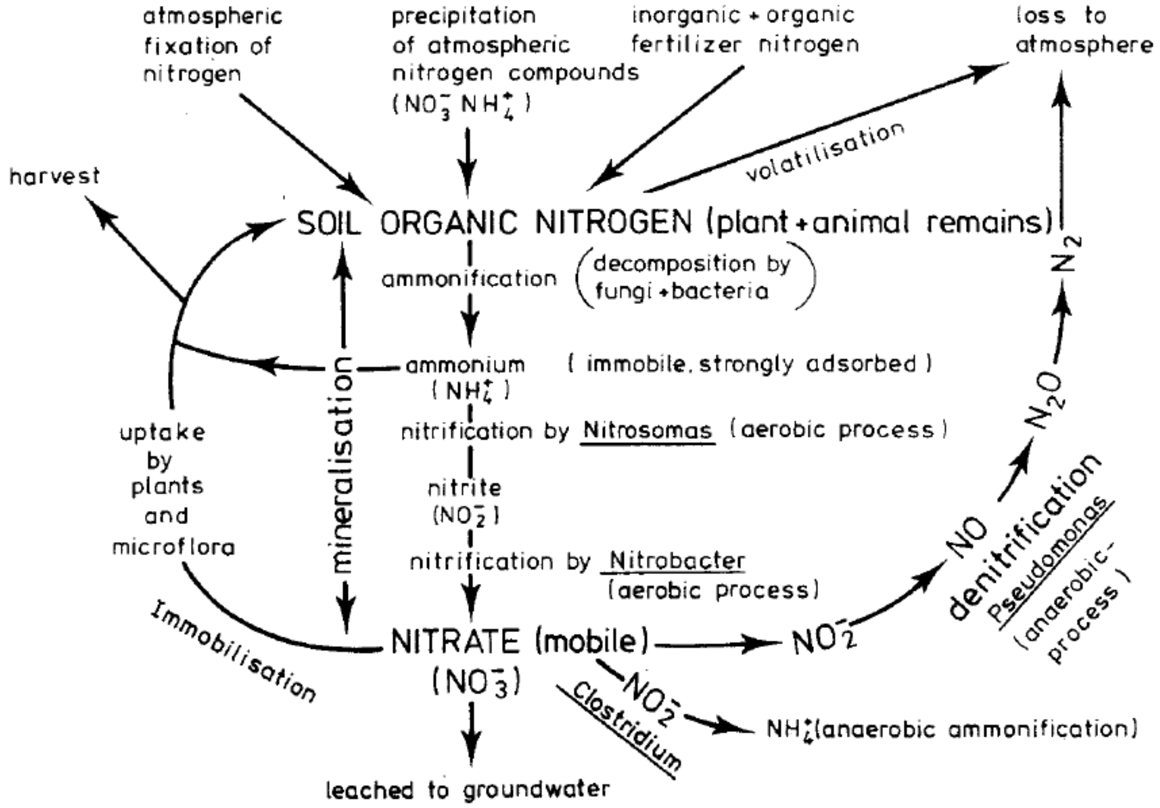


Figure 3.1. *Main reaction pathways in the nitrogen cycle from Hiscock et al. (1991). With permission of the author.*

The following sections describe in detail: autotrophic nitrification, heterotrophic and autotrophic denitrification, algae nitrogen assimilation and ammonia air stripping. Their *optimum* conditions and limitations mostly occurring in lab-scale, pilot-scale and large-scale engineered or semi-natural environments where an adequate variables control is fundamental to obtain a desired nitrogen removal are also investigated.

3.1 Bacterial autotrophic nitrification

In this section nitrification or, more properly, bacterial autotrophic nitrification is described in deep. The following paragraphs discuss in order: a general understanding of the process, the energy source used by bacteria, the environmental factors affecting the course of the reaction (pH, oxygen availability, and temperature), and the factors limiting nitrification (inhibitory compounds and substrate inhibition).

3.1.1 Main principle

The autotrophic oxidation of NH_4^+ to NO_3^-, defined as nitrification, is divided into two irreversible reaction steps:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad [\Delta G_0= -275 \text{ kJ/mol}] \qquad (5)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \qquad [\Delta G_0= -75 \text{ kJ/mol}] \qquad (6)$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad [\Delta G_0= -350 \text{ kJ/mol}] \qquad (7)$$

Nitrification is usually performed by two distinctive groups of chemo-lithotrophic bacteria (i.e. using inorganic carbon as a food source) which act sequentially. The first group, mainly represented by members of the genus *Nitrosomonas*, oxidize NH_4^+ to NO_2^- (5) while the second group, represented by members of the genus *Nitrobacter,* further oxidize NO_2^- to NO_3^- (6). Reactions (5) and (6) are however a simplistic view of the more complex biochemical pathway which involves a set of different enzymes, accumulation of by-products (NO and N_2O), and biomass synthesis (Sutka *et al.,* 2003; Parkes *et al.,* 2007)

It must be addressed that bacteria take up ammonia by passive diffusion. In aqueous solution, NH_3 is in equilibrium with its ionic form NH_4^+ (Emerson *et al.,* 1975). This detail assumes greater importance when the synergistic effect of temperature and pH on the course of the reaction is taken into consideration.

A great variety of bacterial species are able to perform nitrification; up to date, based on ultrastructural properties and biomolecular techniques, ammonia-oxidizing bacteria (AOB) are classified in five genera: *Nitrosomonas*, *Nitrosococcus*, *Nitrosospira*, *Nitrosolobus* and *Nitrosovibrio*; whereas nitrite-oxidizing bacteria (NOB) cover four genera: *Nitrobacter, Nitrococcus*, *Nitrospira* and *Nitrospina*. The reason why *Nitrosomonas* and *Nitrobacter* are referred to as the main nitrifying microorganisms is twofold: most physiological studies have been carried out on *Nitrosomonas europea* and *Nitrobacter winogradskyi* strains which are easy to isolate from available bacterial culture collections (Juretschko *et al.,* 1998); *Nitrosonomonas*- and *Nitrobacter*-like bacteria outcompete other bacterial species during standard enrichment and isolation procedures or in artificial high-ammonia load ecosystems such as sewages and wastewater treatment plants. The second aspect, however, it is only partially true and it has been substantially debated in many studies. In Juretschko *et al.* (1998)

the nitrifying consortium present in the activated sludge from an industrial sewage treatment plant was investigated by means of molecular and cultivation-based techniques. Surprisingly, *Nitrosococcus mobilis* cells were of the numerically dominant AOB type and *Nitrospira*-like bacteria were the dominant population of NOB compared to the non-detectable *Nitrobacter* cells. Although a single predominance of *N. europea* was expected, Sundberg *et al.* (2007a) found more *Nitrosospira* populations in a CCW receiving leachate water with high ammonium nitrogen load. Moreover, only *Nitrosospira*-like populations were detected in the ammonia-rich environment of a similar CCW treating leachate water in Sundberg *et al.* (2007b). Different species of AOB and NOB, as further emphasized by Juretschko *et al.* (1998), most likely differ in their *in situ* growth kinetics, their NH_4^+ and NO_3^- oxidation rates, their substrate and oxygen affinities and their sensitivities to environmental perturbations. Therefore, establishment, composition, species diversity and nitrification performance of a nitrifying community will depend on its ability to adapt to site-specific conditions.

3.1.2 Energy sources

The main food source for nitrifying bacteria is represented by carbon dioxide (CO_2) (Wiszniowski *et al.,* 2006). Stoichiometrically:

$$55NH_4^+ + 76O_2 + 5CO_2 \rightarrow 54NO_2^- + 109H^+ + 52H_2O + C_5H_7O_2N \tag{8}$$

$$115NO_2^- + 52.5O_2 + 5CO_2 + NH_4^+ + H_2O \rightarrow C_5H_7O_2N + H^+ + 115NO_3^- \tag{9}$$

According to equations (8) and (9), for 1 Kg of NH_3 that is nitrified:

- 4.27 Kg of dissolved O_2 are consumed
- 7.14 Kg of alkalinity, as $CaCO_3$, are destroyed
- 0.22 Kg of new cells are synthesized (i.e. $C_5H_7O_2N$).

The redox potential of the NO_2^-/NH_4^+ couple is +340 mV and the one for the NO_3^-/NO_2^- couple is +430 mV. This positive potential is destined to generate reducing power for the CO_2 fixation, which imposes a high energy demand (Prosser, 1989). Although the energy released by the oxidation process is relatively low, the adaptive response of nitrifiers is to increase the number of membrane invaginations which in turn enhances the number of ammonia mono-oxygenase (enzyme responsible of the NH_4^+ oxidation step) and respiratory enzymatic sites. Membrane proliferation is responsible of the increase of energy-generating cell material and, potentially, the actual rate of biomass production (Prosser, 1989).

3.1.3 Environmental factors controlling nitrification

Several environmental factors must be taken into account to optimize nitrification in artificial or semi-natural treatment systems. Here optimal and detrimental conditions are reported and put in contrast for different lab-scale and full-scale treatment systems to address the importance of three parameters: pH, oxygen availability and temperature.

pH

Both NH_4^+ and NO_2^- oxidation are optimal at neutral-basic pH values (Prosser, 1989). Nitrifiers can grow at pH values between 5.5 and 9.0 (Wiszniowski *et al.,* 2006). Nevertheless, reported *optima* pH values for nitrification and simultaneous cell growth range between 7.5 and 8.0 (EA UK, 2006; Kurniawan *et al.*, 2010). Nitrifying bacteria are frequently isolated from acid soils in which nitrification takes place and they can adapt to acid environments, but rarely operate efficiently within them (Prosser, 1989). Below the *optimum* pH value, in fact, specific growth rate falls off sharply. As can be observed in (10), among the reaction products there are hydrogen ions:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad (10)$$

the biological ammonium oxidation is an acidifying process. Acid production during nitrification may result in pH drops in poorly buffered wastewater and lead to loss of process stability (Wiszniowski *et al.*, 2006); low pH coupled to elevated degree of aeration are the main cause for CO_2 air stripping. In turn, this can reduce the carbonates used as alkalinity and decrease ammonium oxidation rates (Parkes *et al.*, 2007). Therefore, unless the leachate water being treated in full-scale treatment plants contains sufficient alkalinity, the nitrification will ultimately prove to be self-inhibitory (EA UK, 2006). The nitrification process can be self-inhibitory for another reason which will be clearer after having considered the dynamic equilibrium (11) between the two chemical forms of ammonia existing in aqueous solutions:

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \leftrightarrow NH_{3(g)}\uparrow + H_2O \qquad (11)$$

arising pH values displace this equilibrium to the right in favor of a higher fraction of gaseous ammonia ($NH_{3(g)}$); in combination with a substantial temperature rise, $NH_{3(g)}$ volatilization rates increase and consequent substrate depletion for nitrification will eventually occur (Leite *et al.*, 2011; Martins *et al.*, 2013). Both ways, large pH variations are detrimental for a good reaction course.

Oxygen availability

The free energy Gibbs for nitrification, ΔG_0= -350 kJ/mol, is negative which indicates that the biochemical process occurs spontaneously in presence of an electron acceptor, in this case molecular oxygen (O_2). Dissolved oxygen (DO) is a critical parameter for nitrification (Xie *et al.*, 2003), particularly in wastewater treatment plants because it seems to exert a significant selective pressure on the community of autotrophic nitrifying bacteria (Park and Noguera, 2004).

A widely accepted engineering design recommendation to achieve adequate ammonium oxidation is to maintain the DO values above 2 mg/L (Knox, 1985). This is also to ensure the establishment of stable population of both AOB and NOB, since there is a marked difference between the two nitrifying groups when it comes to oxygen affinity: as clearly showed by Hanaki *et al.* (1990), the nitrite oxidation step was strongly inhibited by low DO values, whereas ammonium oxidation was not affected in a laboratory suspended-growth reactor.

Generally, a DO value of 0.5 mg/L is reputed to be a critical threshold where accumulation of NO_2^- can largely occur (Hanaki *et al.*, 1990; Xie *et al.*, 2003; Zimmo *et al.*, 2004). In Park and Noguera (2004), a nitrification efficiency of 91% without significant accumulation of NO_2^- was reached in a highly oxygenated environment at a DO value of 8.5 mg/L. In contrast, complete nitrification was not achieved at DO values of 0.24 mg/L due to a non-active sludge AOB community; successively in the same experiment, a decrease of oxygen level (DO values down to 0.12 mg/L) was imposed as additional selective pressure and a re-establishment of full nitrification was observed. However, this was due to an acclimation phenomenon which will be discussed further down. Similar recommended DO values are also reported for leachate treatment: a DO concentration of 1 mg/L is the lowest limit for nitrifiers growth (Wiszniowski *et al.*, 2006). Below a DO value of 2 mg/L, oxygen content is already considered insufficient for nitrification in full-scale treatment plants (EA UK, 2006).

At either too high or too low concentration, oxygen can hamper nitrification and nitrifiers growth rates (Prosser, 1989). It is important to address, however, that sudden and drastic changes in oxygen concentrations are rather the cause for a reduced nitrification performance. Park and Noguera (2004) compared two AOB enrichments in respect of growth kinetics; although having a high oxygen affinity under oxygen-limited conditions, the low-DO enrichment (0.12 to 0.24 mg/L) exhibited a lower growth in comparison with that of the high-DO enrichment (8.5 mg/L) when exposed to sudden conditions of oxygen saturation. In the same study it has been exceptionally demonstrated that acclimation can also occur at low-oxygen conditions and that stable nitrification can be accomplished at DO concentrations as low as 0.12 mg/L. In both the enrichments, members of the lineage *Nitrosomonas europea* were detected.

In low-oxygen environments, it is has been observed that autotrophic nitrifiers are poor competitors since their oxygen saturation constant is higher in comparison with that of heterotrophic bacteria, especially when organic carbon is in ample supply (Sundberg *et al.*, 2007a; Sundberg *et al.*, 2007b). Nevertheless, an interesting phenomenon can occur in conditions of oxygen limitation: both AOB and NOB are capable of reducing NO_2^- to N_2O and NO_3^- to NO_2^-. During nitrification, nitrous oxide is produced by two mechanisms: in the first, N_2O is a by-product of the oxidation of hydroxylamine (NH_2OH) to NO_2^- ; in the second, NO_2^- is reduced to N_2O by the enzyme nitrite reductase (Prosser, 1989; Sutka *et al.*, 2003). This pathway, firstly documented in *N. europea*, but also in *Nitrosolobus*, *Nitrosospira* and *Nitrosocystis* is referred to as “nitrifiers denitrification” or “dissimilatory nitrite reduction” and it must not be confused with “heterotrophic denitrification” (Sutka *et al.*, 2003). An oxido-reductase, mostly found in the bacterial genus *Nitrobacter* (Parkes *et al.*, 2007), is the key enzyme responsible for both the oxidation of NO_2^- to NO_3^- and the reduction of NO_3^- to NO_2^- in presence of an electron donor such as NADH (Prosser, 1989).

Temperature

Like other biochemical reactions, microbial nitrification activity is affected by temperature. Optimal nitrification occurs between 5 and 35°C (EA UK, 2006). It is commonly known that nitrification rate significantly decreases at low temperature and that both NH_4^+ and NO_2^- oxidation increase continuously with the increase in temperature (Xie *et al.*, 2003; Kim *et al.*, 2008). Nonetheless, the way the nitrification proceeds when temperature value rises from low (~5°C) to high temperatures (~30°C) needs a further explanation.

At high temperatures AOB have superior growth rates than NOB. This is a direct consequence of the two specific NH_4^+ and NO_2^- oxidation rates taking part in the overall nitrification rate. In Kim *et al.* (2008), for instance, with the increase in temperature from 10 to 30°C, the specific NH_4^+ utilization increased by about 5 times. Instead, the specific NO_2^- oxidation rate increased only by a factor of 2.6 within the same temperature range. By contrast, at low temperature the NO_2^- oxidation rate is greater than the NH_4^+ oxidation rate. Figure 3.2 illustrates the specific oxidation rates.

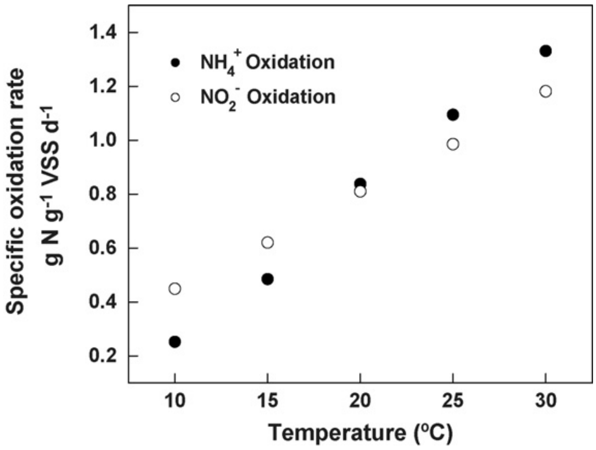


Figure 3.2. *Specific NH_4^+ and NO_2^- oxidation rates obtained between 10 and 30°C from Kim et al. (2008). With permission of the author.*

The difference in oxidation rates (*k*) is due to differences in activation energies (E_a) and temperature regimes (*T*) at which the reaction kinetics proceeds (Kim *et al.*, 2008). According to the Arrhenius equation:

$$k = A_0 exp^{-\frac{E_a}{R \cdot T}} \tag{12}$$

where,

k = specific oxidation rate (g N/g VSS · d)

A_0 = is a frequency factor

E_a = activation energy (kJ/mol)

R = 8.31 (J/mol · K), universal gas constant

T = temperature (K)

As can be observed in table 3.1, two distinct temperature regimes exist for NH_4^+ oxidation and only one for NO_2^- oxidation. Between 10 and 30°C, NO_2^- oxidation is thermodynamically promoted with respect to the specific NH_4^+ oxidation because of the lower E_a. Above 20°C the difference in E_a values becomes less relevant and both the reaction steps are ensured. In wastewater and leachate treatment, if stable nitrification is required, temperature values should be above 20°C.

Table 3.1. *Arrhenius parameters for ammonium and nitrite oxidation.*

	T (°C)	E_a (kJ/mol)
NH_4^+ oxidation	10 – 20	87.1
	20 – 30	38.6
NO_2^- oxidation	10 – 30	34.2

By using nitrification as a treatment process other issues come along when temperature rises. Temperature influences nitrification performances in coordination with other factors such as DO and substrate concentrations. The DO saturation value in water decreases with an increase in temperature (Bartsch and Randall, 1971); being less soluble, oxygen becomes also less bioavailable. The concentration of NH_3 increases with increasing temperature (and pH), i.e. doubling for every 10°C rise in temperature (Emerson *et al.*, 1975). This is beneficial for substrate uptake until a certain limit; in fact, it has been noted in leachate stabilization ponds (Leite *et al.*, 2011; Martins *et al.*, 2013) that $NH_{3(g)}$ can take routes other than nitrification once water temperature is above 25°C causing the substrate to be depleted (see section *pH*).

Although temperature seems to play a primary role, it is hard to say whether its individual effect prevails on the other environmental factors in limiting nitrification efficiency. In a semi-pilot scale study, Kim *et al.* (2006) jointly investigated the effects of temperature and free ammonia in a nitrifying municipal landfill leachate treatment plant in Korea characterized by seasonal nitrification failure. Results indicated that the low winter temperature (11°C) was the initial factor limiting nitrification efficiency; roughly above 15°C the temperature did not constitute a limit for the course of the nitrification, whereas at the same temperature the NH_4^+ load determined its inhibition. Another example is a suspended-carrier biofilm technology operated at temperature as low as 5°C by Welander *et al.* (1997): instead of the low temperature that slows down the enzymatic reactions, oxygen diffusion into the biofilm was the factor limiting nitrification.

3.1.4 Limitations in the nitrification process

Apart from the environmental parameters formerly discussed, direct limitation of the nitrification reaction may be due to either inhibitory compounds or excess of substrate.

Inhibitory compounds

Nitrifying bacteria are sensitive to heavy metals, organic and inorganic pollutants. The chelation of metal components of the ammonia mono-oxygenase is the main mechanism of inhibition that has been proposed (Prosser, 1989).

Substrate inhibition

Free ammonia, which is the chemical form of nitrogen taken up by bacteria, is also known to inhibit nitrifiers (Prosser, 1989; Kim *et al.,* 2006; Kim *et al.,* 2008). Reported values for inhibition occur around 7 mg NH_3/L for *Nitrosomonas* and from 1 to 5 mg NH_3/L for *Nitrosobacter* (Zimmo *et al.*, 2004). Other authors, however, claim that AOB are inhibited by NH_3 in a concentration range between 10 and 150 mg NH_3/L while NOB already between 0.1 and 1.0 mg NH_3/L (Kim *et al.,* 2006; Martins *et al.*, 2013). An important consequence of this major sensitiveness shown by NOB is the resulting NO_2^- accumulation, which was detrimental for nitrification in some experiments (Knox, 1985; Kim *et al.*, 2006).

The potential effect of initial high NH_4^+ load in lab-scale and full-scale bioreactors is of prime concern since NH_3 concentration will depend on the amount of NH_4^+ released in solution (ammonium salts), pH and temperature (Emerson *et al.*, 1975). In Kim *et al.* (2006) high NH_3 concentration inhibited both AOB and NOB activity, although during winter (~5°C) only NOB remained completely inhibited. The main cause for inhibition in the nitrifying landfill leachate treatment plant was attributed to high NH_4^+ load and to a substantial failure to lower its concentration in a pre-treatment oxidation basin. The higher the NH_4^+ load, the higher the NH_3; especially when a concomitant role of increasing pH promotes the conversion of NH_4^+ to NH_3. Nonetheless, a strong resistance to substrate inhibition was observed in Kim *et al.* (2008) after acclimation to highly NH_4^+ concentrated waste streams, indicating that adaptation of nitrifying communities to substrate-rich conditions may occur to a certain degree.

3.2 Heterotrophic and autotrophic denitrification

In this section both heterotrophic and autotrophic denitrification are described in deep. In order, the following paragraphs deal with: a general understanding of the process, the energy source used by bacteria, the environmental factors affecting the course of the reaction (pH, oxygen level, temperature, and carbon to nitrogen ratio), and the factors limiting the reaction.

3.2.1 Main principle

Denitrification or dissimilatory denitrification is a process by which nitrate (NO_3^-) functions as an electron acceptor and it is converted to dinitrogen gas (N_2) (Gayle *et al.*, 1989; Kurniawan, 2011). The overall redox reaction (13) it can be expressed as in (Hiscock *et al.*, 1991):

$$NO_3^- + 6H^+ + 5e^- \leftrightarrow \tfrac{1}{2}N_{2(g)} + 3H_2O \qquad (13)$$

The reduction of NO_3^- to N_2 includes several steps (14):

$$NO_3^- \xrightarrow[\text{reductase}]{\text{Nitrate}} NO_2^- \xrightarrow[\text{reductase}]{\text{Nitrite}} NO \xrightarrow[\text{reductase}]{\text{Nitric oxide}} N_2O \xrightarrow[\text{oxide reductase}]{\text{Nitrous}} N_2 \qquad (14)$$

Many bacteria are only able to perform one or two of these steps (Gayle *et al.*, 1989). Thus, the denitrifying consortium must be considered as a group of complementary microorganisms able to convert NO_3^- to N_2 (Hiscock *et al.*, 1991).

Biological denitrification can be catalyzed by either heterotrophic or autotrophic bacteria. *Pseudomonas*, *Micrococcus*, *Archromobacter*, *Bacillus*, *Flavobacterium* and *Alcaligenes* are the most important groups of heterotrophs (Hiscock *et al.*, 1991; Kurniawan, 2011); while *Paracoccus denitrificans* and *Thiobacillus denitrificans* are the main representative of the autotrophs (Gayle *et al.*, 1989; Hiscock *et al.*, 1991; Koenig and Liu, 1996). Denitrifying bacteria are classified as facultative aerobes; they can thrive either in aerobic conditions where O_2 is used as electron acceptor or in anoxic conditions where O_2 is absent and NO_3^- is utilized as electron acceptor. By contrast, they are not considered facultative anaerobs because they cannot use organic compounds as terminal electron acceptors or obtain energy by means of fermentation (Wiszniowski *et al.*, 2006; Kurniawan, 2011).

3.2.2 Energy sources

Sugars, organic acids and amino-acids are commonly utilized as organic carbon source during heterotrophic denitrification (Hiscock *et al.*, 1991). In the biological nitrogen removal processes occurring in wastewater and leachate treatment plants, the electron donor is typically represented by one of the following three sources: the COD in the influent wastewater, the COD produced by endogenous decay and an external source of carbon such as methanol or acetate (Kurniawan, 2011). In order to derive their reducing potential, heterotrophic denitrifiers generally make use of carbohydrates or methanol (Hiscock *et al.*, 1991). Respectively:

$$5CH_2O + 4NO_3^- + 4H^+ \leftrightarrow 2N_2 + 5CO_2 + 7H_2O \qquad (15)$$

$$NO_3^- + 1.08CH_3OH + 0.24H_2CO_3 \rightarrow 0.06C_5H_7O_2N + 0.47N_2 + 1.68H_2O + HCO_3^- \qquad (16)$$

According to equilibrium (16) for 1 Kg of NO_3^- that is denitrified:

- 2.47 Kg of methanol are used
- 0.45 Kg of new cells are synthesized (i.e. $C_5H_7O_2N$)
- 3.57 Kg of alkalinity are formed.

When a low proportion of readily degradable carbon is present, denitrification as a nitrate removal process in leachate treatment does not occur to any significant extent (Knox, 1985). To compensate the lack of carbon, an external supply must be added. Alternatively, autotrophic denitrification can be exploited.

The feasibility of autotrophic denitrification in leachate has been well demonstrated by Koenig and Liu (1996). Autotrophic denitrifiers oxidize inorganic material such as elemental sulphur (S) to reduce NO_3^- and to contemporarily produce sulphate (SO_4^{2-}):

$$NO_3^- + 1.10S + 0.40CO_2 + 0.76H_2 + 0.08NH_4^+ \rightarrow 0.5N_2 + 1.10SO_4^{2-} + 1.28H^+ + 0.08C_5H_7O_2 \quad (17)$$

Either carbon dioxide or bicarbonate is used as a carbon source for cell synthesis, represented by $C_5H_7O_2$ (Gayle *et al.*, 1989).

3.2.3 Environmental factors controlling denitrification

Optimal conditions are reported and put in contrast mostly by taking examples from different experiments of lab-scale and full-scale wastewater and leachate water treatment systems. The influence of four parameters is addressed: pH, oxygen level, temperature, and carbon to nitrogen ratio (C/N ratio).

pH

Denitrification is positively related to pH with an *optimum* in the range 7.0 to 8.0 (Gayle *et al.*, 1989). A narrower optimal range between 7.0 and 7.5, maintained by addiction of sulphuric acid is recommended to ensure a denitrification step after nitrification in leachate treatment systems (EA UK, 2006).

Oxygen level

Experimental evidences demonstrated that NO_3^- reduction is not observed at dissolved oxygen concentrations above 0.2 mg/L while in biological reactors DO levels should be maintained below 0.5 mg/L (Knowles, 1982). In a study conducted by Zimmo *et al.* (2004) on main nitrogen removal processes in wastewater treatment pond systems nitrogen losses by denitrification accounted for ~15 – 25% of total influent nitrogen; higher denitrification rates occurred in the sediment fraction rather than in the water column due to higher concentration of DO in the top layers in all the tested ponds. It must be addressed that pond samples were analyzed in a controlled laboratory environment and the results were used to predict field conditions. However, microaerophilic (semi-anaerobic) environments offered by sediments and roots are known to stimulate denitrification in vegetation based constructed wetlands which are used for further leachate water polishing in on-site treatment plants (Sundberg *et al.*, 2007b).

Temperature

Denitrification can markedly decrease between 0 and 5°C whereas a doubling of denitrification rate is seen with every 10°C increase in temperature (Knowles, 1982).

A synergistic effect of temperature and oxygen levels can be noted: at high temperature, the oxygen saturation constant decreases; the reduced solubility leads to a gradual oxygen depletion which, in turn, favor denitrification rates. This is also the reason why high temperature values are beneficial up to a limit of 40 or 60°C (Wiszniowski *et al.*, 2006).

C/N ratio

A C/N ratio of 1 is required to approximately reach 80 – 90% denitrification (Gayle *et al.*, 1989). Under an *optimum* condition, the anoxic biological denitrification process converts more than 95% of nitrate and nitrite into the inert nitrogen gas.

The C/N ratio explains two fundamental conditions occurring in a denitrifying environment: availability of an appropriate electron donor (biodegradable material) and availability of NO_3^- as electron acceptor (Wiszniowski *et al.*, 2006). The optimal C/N ratio for biological denitrification varies however from system to system and it must be determined experimentally (Chiu and Chung, 2003). In general, if C/N ratios and pH are low and oxygen is present incomplete denitrification may occur with consequent N_2O and NO_2^- accumulation (Craggs, 2005).

3.2.4 Limitations in the denitrification process

Substrate inhibition may limit denitrification: NO_3^- is able to suppress the enzymatic activity in the reductase which converts NO to N_2O (Hiscock *et al.*, 1991). In Koenig and Liu (1996), at a concentration value of 100 mg NO_3^-/L, nitrate removal efficiency decreased in both synthetic and already-nitrified leachate undergoing denitrification. Furthermore, when nitrate removal is incomplete, NO_2^- appears in the effluent indicating that nitrite reduction is the limiting step in the denitrification process (Koenig and Liu, 1996).

Sulphur compounds can hinder N_2 production, but stimulate the reduction of NO_3^- to $NH4^+$. Acetylene is a well-known inhibitor of the last reduction step (N_2O to N_2).

3.3 Algae nitrogen assimilation

In the following section algae nitrogen assimilation is described in deep. In order, a general understanding of the process, the energy source used by algae, the environmental factors affecting the course of the reaction (pH, temperature and sunlight), and the factors limiting the reaction (ammonia toxicity and hydrogen sulphide toxicity) are discussed.

3.3.1 Main principle

Algae can incorporate inorganic nitrogen species such as ammonia or urea. This process is defined as biological assimilation or algal biomass nitrogen uptake (Craggs, 2005). During the conversion of ammonia, production of new algal biomass is possible if solar radiation, carbon and phosphorus are also supplied as algae are photosynthetic organisms.

As part of the eukaryotic domain, algae constitute a great variety of species within the phytoplankton; key taxonomic groups identified so far in waste stabilization ponds (WSP) are *Euglenophyta*, *Clorophyta*, *Chrysophysta* and *Cyanobacteria*. Tough, the latter belongs to the prokaryotic domain (Craggs, 2005).

Algae thrive in different ecosystems such as freshwater, brackish water and seawater. Biosynthesis is intensified whenever light and nutrients are abundant. This eutrophic condition can lead to diminished oxygen content by increasing the activity of decomposers. In turn, negative effects on aquatic life such as fish death can manifest (Martins *et al.*, 2013).

Being a simulation of highly polluted natural aquatic ecosystems, WSP can offer the right environment in which algal growth is promoted in order to remove nitrogen. Ammonia assimilation into algal biomass depends upon the biological activity in the system and it is affected by several factors such as temperature, organic load, detention time and wastewater characteristics (Craggs, 2005). It is known that to a long retention time corresponds a greater algae diversity, although, in pond treatment technology, *Chlamydomonas* seems to dominate the algae population when high organic loads are provided (Craggs, 2005). In both Leite *et al.* (2011) and Martins *et al.* (2013), a monoculture of this flagellate micro-algae dominated the series of leachate stabilization ponds for hydraulic retention times (HRT) longer than 1 month. Conversely, in Takamizawa *et al.* (1991) *Chlamydomonas* populations underwent a rapid increase followed by a drastic decline only in short times during a three-year study. *Thalassiosira* sp. and *Oocystis* sp., widespread in brackish and seawater, tolerated the saline environment (Cl^- ion concentration ranged between 12 400 and 16 400 mg/L) occurring in a leachate treatment system combining facultative ponds and aerated lagoons.

A fundamental mutualism between algae and bacteria is observed in WSP: new bacterial biomass is produced from metabolization of organic waste; the nutrients and the CO_2 released are utilized by the algae through photosynthesis which increases oxygenation in the ponds, mostly in proximity of the surface. Aerobic bacteria are eventually favored by the increased oxygen content (Craggs, 2005). In addition, when light conditions are not limiting, algal biomass function as an attachment surface for bacteria such as nitrifiers. Combined algae and bacteria biofilms increased nitrogen removal in algae-based treatment ponds (Zimmo *et al.*, 2004).

Along with ammonia nitrogen assimilation there is another important mechanism of nitrogen removal which occurs in eutrophic lakes and artificial aquatic ecosystems: sedimentation of dead (or inert) biomass (Craggs, 2005). Once bacteria and micro-algae are dead, the organically bound nitrogen may undergo bottom deposition. In several studies (Camargo and Mara, 2007; Camargo *et al.,* 2010b; Martins *et al.*, 2013), sedimentation of inert biomass accounts for the majority of removed nitrogen in shallow waste stabilization ponds with long HRT (maturation ponds). However, there are few exceptions: in condition of low phytoplanktonic activity or well-established nitrifying-denitrifying bacterial communities, this process can be reduced or totally replaced by nitrification-denitrification (Mehmood *et al.*, 2009; Valero *et al.*, 2010). In addition, certain algal genera such as *Chlorella sp*., *Euglena* sp. and *Oscillatoria* sp., due to their size, motility or floatation cannot easily deposit on the bottom causing less biomass settle (Craggs, 2005).

3.3.2 Energy sources

A N:P ratio of roughly 15:1 classically characterize both bacteria and algae chemical composition, meaning that nitrogen removal is higher in comparison with that of phosphorus (Craggs, 2005). Algae can only assimilate reduced forms of nitrogen such as free ammonia and urea in preference of other oxidized forms because of the great energy requirement for nitrate reduction. In order to synthesize new biomass, algae use phosphates, ammonium, carbon dioxide and water as food source in the following proportion (18):

$$106CO_2 + 16NH_4^+ + HPO_4^{2-} + 236H_2O \xrightarrow{\substack{light \\ + \\ algae}} C_{106}H_{181}O_{45}N_{16}P + 118O_2 + 171H_2O + 14H^+ \quad (18)$$

3.3.3 Environmental factors controlling algae nitrogen assimilation

Three are the main factors ruling algae nitrogen assimilation: pH, temperature and sunlight. Carbon dioxide level is also important, although difficult to control in aerobic based treatment plants.

pH

As can be observed in (18) algal photosynthesis directly affect the sources of CO_2 and free ammonia (in equilibrium with NH_4^+). In pond water, carbon dioxide depletion can cause a raise in pH up to 11 while free ammonia assimilation by algae populations can lead to pH decrease (Craggs, 2005).

When pH is elevated carbon dioxide becomes less bioavailable for the algal uptake because it is converted into carbonate and bicarbonate as can be seen in (19):

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow CO_3^{2-} + 2H^+ \quad (19)$$

Equilibrium (19) is also known as "pH – carbon dioxide – bicarbonate system" and it is of primary importance in all aquatic environments since it can buffer drastic pH changes due to biological activity such as photosynthesis and microbial respiration (Craggs, 2005).

Temperature and sunlight

Phytoplanktonic activity, measured through photosynthesis-associated parameters such as chlorophyll *a* concentration (chl*a*), DO and pH, is enhanced during early-spring and summer rather than in winter because of the remarkable variation in water temperature and photoperiod (Craggs, 2005). In Valero *et al.* (2010) at water temperature between 3.1 and 6.4°C and sunlight of 2.4 hours per day (winter), chl*a* values barely reached 46 µg/L; pH values did remain between 6.1 and 7.6. On the contrary, at water temperature between 5 and 12°C and at mean sun hours of 5.3 (late winter-early spring), chl*a* reached 250 µg/L in the studied ponds system; pH values ranged between 6.8 and 8.2 and DO levels increased up to 5.3 g/L.

Intense algal blooming is commonly observed in the upper-most layer of a stabilization pond and in correspondence of summer temperatures (Takamizawa *et al.,* 1991; Martins *et al.*, 2013).

In parallel to an augmented nitrogen assimilation by algae biomass due to favored phytoplanktonic activity at higher temperature, improved sedimentation rates can be observed in correspondence of summer periods as clearly shown in Camargo *et al.* (2010b).

3.3.4 Limitations in the nitrogen algae assimilation process

The responsible for slowing down the process of nitrogen incorporation by algal biomass are two: free ammonia and hydrogen sulphide. But the first is of primary importance for biological treatment of wastewater and leachate water, since it is strictly connected to the amount of ammonia load received by the treatment plant.

Ammonia toxicity

Free ammonia has an inhibitory effect on the photosynthetic activity since it disrupts algal cell chloroplast function (US EPA, 2013). At pH values higher than 9.0 and temperatures between 20 and 25°C, ammonia concentrations of 54 mg/L can inhibit algal photosynthesis by 90% and cause a serious slowdown of algal growth and oxygen production (Craggs, 2005). Slightly different inhibitive concentration values are however reported in the literature, meaning that sensitivity to ammonia can be community dependent. Interestingly, in fact, healthy populations of *Chlamydomonas* (capable of elevating pond pH) tolerated leachate toxicity due to NH_3 concentrations as high as 175 mg/L (Leite *et al.*, 2011). Values ranging from 5.6 to 56 mg/L were inhibitive for *Bacillariophyceae* in Takamizawa *et al.* (1991).

pH and temperature exert a combined effect either on the increase and on the decrease of free ammonia concentration. Elevated pH and temperature are known to increase the fraction of

NH_3 in solution (see section 3.1.3). But, the pH-carbon dioxide-bicarbonate system sets in to bring back pH values into balance: pH and DO levels increase as a consequence of active algae biosynthesis which is favored during warmer seasons; at high pH carbon dioxide is less available for algae carbon fixation and algal growth is reduced. On the other hand, highly oxygenated water stimulates microbial catabolism resulting in increasingly high amounts of CO_2. In turn, pH is lowered and free ammonia concentration returns below inhibitory levels (Craggs, 2005).

Hydrogen sulphide toxicity

Dissolved hydrogen sulphide (H_2S) can inhibit algal growth at concentrations above 1 g S/m^3 (Craggs, 2005). The total sulphide concentration is dependent on pH: at pH value lower than 6 almost all sulphide is present as $H_2S_{(g)}$, while at pH higher than 9 anionic forms (HS^- and S^-) predominate.

3.4 Ammonia air stripping

The following section deals with the abiological ammonia air stripping. In order, a general understanding of the process, the environmental factors affecting the course of the reaction (pH, temperature, ammonia concentration, turbulence and mixing), and the factors limiting it are discussed.

3.4.1 Main principle

At constant temperature, volatility of a substance in equilibrium at the gas-water interface can be described by the inverse of the Henry´s constant (20):

$$\frac{1}{H} = \frac{P}{C_w} \tag{20}$$

where,

P = partial pressure of the substance in the gaseous form (Pa)

C_w = substance concentration or molarity in the water phase (mol/m^3)

That phenomenon by which free ammonia is transferred from the water phase to the air is known under the name of ammonia air stripping, ammonia volatilization or ammonia desorption (Middlebrooks and Pano, 1983; Smith and Arab, 1988; Camargo and Mara, 2010a). The rate at which ammonia volatilize at certain given conditions of temperature and atmospheric pressure can be expressed as first derivative of the mass transfer in time (21):

$$\frac{dm}{dt} = V_l \cdot \frac{dC_l}{dt} \tag{21}$$

where,

m = mass of NH_3 (mg)

V_l = volume of the liquid (L)

C_l = concentration of NH_3 (mg/L)

t = time (sec or min)

This volatilization process is not catalyzed by any biological organism and it is primarily affected by the chemical equilibrium between two ammonia species: unionized ammonia and ammonium ion, whose sum is defined as total ammonia (or tot-NH_3) (Emerson *et al.*, 1975). Equilibrium (11) already showed this process as a way of hampering nitrification by depleting ammonia substrate supply. A more detailed chemical expression is illustrated in equilibrium (22):

$$NH_{3(g)} + nH_2O \leftrightarrow NH_3 \cdot nH_2O \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)} + (n-1)H_2O \qquad (22)$$

where,

n = number of moles

NH_3 = unionized ammonia

$NH_4^+{}_{(aq)}$ = ammonium ion or ionized ammonia

Ammonia air stripping has been reported in the past years as a principal mechanism of nitrogen removal in a variety of artificial aquatic ecosystems used to treat wastewater and leachate, especially in condition of high temperature, high pH, and high water turbulence (Middlebrooks and Pano, 1983). Nowadays, however, the theory that ammonia volatilization may offer the main nitrogen removal mechanisms in pond technology is profoundly discussed because of the more advanced investigation techniques, such as radio-labeled nitrogen tracers, biomolecular essays, and mathematical modeling capable of give another view of the routes followed by ammonia nitrogen in field and laboratory experimental systems (Camargo and Mara, 2007; Mehmood *et al.*, 2009; Camargo and Mara, 2010a; Martins *et al.*, 2013).

3.4.2 Environmental factors controlling ammonia air stripping

Among the environmental factors ruling the natural process of ammonia volatilization, pH, temperature, unionized ammonia concentration, surface turbulence and mixing are the most controllable in artificial ecosystems designed to remove ammonia by air stripping.

pH and temperature

$NH_4^+{}_{(aq)}$ predominates below pH 7.2 and $NH_{3(g)}$ concentration increases proportionally as the dynamic equilibrium (22) is displaced to the left consequently to a build-up in alkalinity until at pH 9.2 $NH_{3(g)}$ accounts for 50% of the total ammonia (Leite *et al.,* 2011). These numbers given here are however derived from direct field measurements using different initial concentration of free ammonia. In fact, different percentages of ammonium ion and unionized ammonia depend on the model developed and at which temperature range the ammonium ion acid dissociation constant (pK_a) has been calculated (Emerson *et al.,* 1975). However, as a rule-of-thumb, *optima* pH values for ammonia volatilization in waste stabilization ponds range between 8.9 and 10.2 at mean summer temperature between 15.2 and 18.2°C (Camargo and Mara, 2010a). A synergistic effect with temperature is therefore observed for ammonia air stripping.

Generally, the higher the temperature (and the pH) the higher the degree of volatilized ammonia fraction (Emerson *et al.,* 1975). As concluded by Leite *et al.* (2011), high surface pH values (above 9) coupled to high water temperatures (between 22 and 28°C) and solar intensities would favor ammonia volatilization as an important route of nitrogen removal from shallow leachate treatment ponds (between 0.45 and 0.60 m). Ammonia volatilization was proposed by Middlebrooks and Pano (1983) to be feasible in aerated lagoons even at winter temperature between 1 and 5°C, provided complete mixing condition, low biological activity and pH above 11. However, two main arguments were received against this conclusion: the predictive model was developed in steady-state flow conditions and continuous mixing often difficult to ensure in full-scale treatment ponds systems (Camargo and Mara, 2010a); and the high pH in pond technology is usually reached as a consequence of algal synthesis (see section 3.3.3, *pH*), which is in contradiction with the assumption regarding low biological activity (Camargo and Mara, 2010a).

Unionized ammonia concentration, surface turbulence and mixing

The mass transfer process of ammonia (21) from an aqueous solution into the atmosphere depends not only on Henry´s constant (20), pH, and temperature, but also on other factors such as water surface turbulence, air velocity above the water surface (that would correspond to wind velocity in stabilization ponds), and mixing properties of the liquid (Camargo and Mara, 2010a).

In a stabilization ponds system treating domestic wastewater, ammonia volatilization rates were found to be linearly correlated to NH_3 concentrations by Zimmo *et al.* (2003). Their ammonia volatilization rates (λ_{NH3}) were obtained multiplying the concentration of unionized ammonia ($[NH_3]$) by a mass transfer coefficient (K_l) as can be seen in equation (23):

$$\lambda_{NH3} = -K_l \cdot [NH_3] \cdot \frac{V}{A} \qquad (23)$$

where,

λ_{NH3} = mass transfer rate (g $NH_3/m^2 \cdot d$)

K_l = mass transfer coefficient in the liquid phase (d^{-1})

$[NH_3]$ = concentration of ammonia in the liquid phase (mg/L)

V = pond volume (m^3)

A = pond area (m^2)

temperature, pH and ammonium nitrogen concentrations were also taken into account in the calculation of $[NH_3]$. The same model, with some adaptation concerning area and volume of the system, was applied to a batch-scale reactor and similar results were obtained by Martins *et al.* (2013).

In a batch-scale reactor study by Smith and Arab (1988), to an increased air flow rate corresponded increased ammonia desorption; aeration was provided by means of either bottom stirring blades or air injectors. Moreover, in comparison with the stirring blades, air injectors resulted in improved bubbling which in turn caused both increased water surface turbulence, mixing and ammonia volatilization rates. The enhanced NH_3 removal by volatilization was thought to be caused by a larger surface area available for gaseous exchanges, particularly in the upper surface of the reactor where better surface turbulence is created by the bubbles.

3.4.3 Limitations in the ammonia air stripping process

Occurrence of ammonia air stripping has virtually no limitations because the necessary and sufficient condition is that constant supply of NH_3 and alkaline pH occur in the same environment. However, as described in the previous section, the degree at which gaseous ammonia is transferred from an aqueous phase to a gaseous phase can simultaneously depend on different variables which in turn make hard to predict nitrogen removal rates by means of volatilization. In the particular case of waste stabilization ponds, first-order kinetic models based on mass transfer coefficients as seen in Middlebrooks and Pano (1983), Smith and Arab (1988) or in Zimmo *et al.* (2003) may lead to overestimation of ammonia losses to the atmosphere unless other mechanisms of nitrogen removal are considered to happen simultaneously as demonstrated in Parkes *et al.* (2007), Camargo and Mara (2007) and in Martins *et al.* (2013).

4 Technological implementation

A quick look on biological treatment anticipates the section about aerated lagoons, a technology designed to treat domestic and industrial wastewater by means of aerobic biodegradation. The third and last section will deal with few case studies taken from the literature in order to provide a basis for further comparison with Hedeskoga landfill.

4.1 A brief overview

Several are the options for handling leachate emissions on-site and improve their quality before either direct discharge into the natural recipient or into the sewage system; some of the management strategies have been listed in section 2.6. Among those, biological treatment is largely carried out on-site. Biological treatment processes have been successfully applied for domestic and industrial wastewater and the technologies used nowadays for treating leachate on-site mainly derive from the experiences obtained in wastewater management. An increasingly high number of technological devices is at disposition for contaminants removal in leachate, given the wide variations in physical-chemical characteristics proper to this heterogeneous solution. The use of a certain technology (or combination of these) in respect to another is strictly dependent on the environmental requirements that must be fulfilled in accordance with the law, the peculiar characteristics of the leachate emitted from a specific landfill, the spatial conformation of the landfill site, and ultimately, operational costs and level of staff preparation (Robinson and Barr, 1999).

Biological treatment is classically divided into four main categories: aerobic, anaerobic, natural (or semi-natural) systems, and combined biological and physical-chemical methods (Kurniawan *et al.,* 2010). The principle behind all four categories is the same: exploit microbial reactions to obtain contaminants breakdown with consequent biomass synthesis. The description of the entire range of technological means designed to recreate favorable conditions for these bioreactions to occur is not part of this project. Nevertheless, particular attention will be given to one of the most widely-spread and easy-to-maintain devices designed to aerobically treat leachate water in respect of various contaminants, among others, ammonia nitrogen.

4.2 Aerated lagoons

“Lagooning” is a general term used in wastewater science to indicate that kind of treatment technology based on the use of a simple artificial pond provided with aeration. An “aerated lagoon” is generally defined as a basin, usually 1.8 to 4.6 m deep in which oxygenation is accomplished by mechanical or diffused aeration units (bottom aerators) and by induced surface aeration (Bartsch and Randall, 1971). In pond technology the terms “stabilization” or “equalization” are often used as synonyms for lagooning by some authors (Kurniawan *et al.*, 2010). The main difference between stabilization ponds and aerated lagoons is the hydraulic retention time, which is longer in stabilization and equalization ponds (greater than 30 days) than in aerated lagoons (between 10 and 20 days). Despite any definitions, from a process viewpoint, aerated lagoons can be distinguished into two types: aerobic lagoons and aerobic-anaerobic lagoons (or facultative ponds). In the first, solids are maintained in suspension by means of high turbulence; the advantage is that continuous oxygenation is provided so that suspended biomass (mainly free swimming bacteria) can more efficiently react with the substrate. In the second, oxygenation and solids suspension do not occur uniformly because of less power input and various mixing conditions in the same basin. This situation creates an heterogeneous environment in which particles resuspension, aerobic biodegradation (e.g. nitrification) as well as solids settlement and anaerobic processes (e.g. denitrification) may occur at the same time.

Typical aerated lagoons for leachate treatment look like the ones in figure 4.1: in one basin (background), aeration is provided from the surface; in the other, diffused aeration is provided by a bottom air injector (foreground). The entity of turbulence is higher in the close vicinity whereas some particles settlement might occur in less turbulent more distant areas.

Figure 4.1. *Example of aerated lagoons in Hedeskoga landfill: a bottom aerator (b) and a surface aerator (a). Pictures taken with permission of Sysav. Author: Alessandro Sarno, Lund University.*

It has been shown since the 1980s in UK that aerated lagoons can offer an interesting solution for treating leachate water in spite of various degree of contamination or climate fluctuations (Robinson, 1987; Robinson and Grantham, 1988). Although the allowed limit concentrations values for discharge are nowadays lower, aerated lagoons still provide a long-term cheap solution for either pre-treatment or complete treatment of landfill leachate (Mehmood *et al.*, 2009). The only potential economic drawback could come from running costs, i.e. electricity for aeration (Bartsch and Randall, 1971; Robinson and Grantham, 1988).

The bioreactions occurring in an aerated lagoon are determined on the simultaneous actions of temperature (air and water), pH, oxygenation level, flow regime, mixing regime, organic load, and wastewater characteristics (Narasiah and Larue, 1982; Middlebrooks and Pano, 1983; Robinson and Grantham, 1988; Narasiah *et al.,* 1990). Depending on the degree of treatment that must be fulfilled, these parameters can be controlled to achieve a high removal of both organics (COD, TOC, BOD, SS) and ammonia nitrogen: in this respect, aerated lagoons showed ability to resist fluctuations in climate and leachate quality during time (i.e. robustness) with minimal maintenance (Robinson and Grantham, 1988; Narasiah *et al.*, 1990; Haarstad and Maehlum, 1999; Frascari *et al.*, 2004).

As clearly stated in Middlebrooks and Pano (1983), the main biochemical pathways for nitrogen removal, reputed to simultaneously occur in aerated lagoons (and more generally in treatment ponds), are:

- Nitrification
- Denitrification
- Algae nitrogen assimilation and consequent biomass sedimentation
- Ammonia air stripping

Typical winter-summer variations in nitrogen form and type of microorganisms, which give evidence of biological activity, are observed in aerated lagoons. In Takamizawa *et al.* (1991), from June to November, to a high temperature corresponded a decrease in ammonium concentrations simultaneously to an increase in nitrate concentrations. Algae also increased and nitrate reducing bacteria decreased. During a low temperature season (December-May) the opposite situation is observed.

4.3 Case studies

This section is the result of the literature study performed to give a solid theoretical basis for the most common management strategies and issues encountered when lagooning is applied as a main treatment technology in on-site landfill leachate treatment plant. Among those analyzed, the case studies described below were found to be the most representative according to the criteria specified in section 6.1.2.

4.3.1 Bryn Posteg, UK (Robinson and Grantham, 1988)

The landfill site, opened in 1982, received 50 tons per day of both domestic and commercial solid waste and was located close to the catchment area of the River Severn (near a public water supply) with an average annual rainfall of more than 1 200 mm. The refuse was tipped in small clay-lined waste cells and the leachate was collected in a drainage pipes system. The landfill leachate treatment plant consisted of a an aerated lagoon with two surface aerators whose effluent was sent to a small rural municipal sewage treatment plant. The treatment results showed in table 4.1 represented a total period of 30 months study. During this time a total leachate volume of 26 000 m^3 was treated at flow rates varying around 150 m^3/d. The HRT was kept to approximately 10 days. Lagoon temperature oscillated regularly between 2 – 4°C in winter (February) and 10°C during the treatment period (October-November). At the beginning of the commissioning, the lagoon was filled with diluted leachate with a COD less than 3 000 mg/L and phosphorus was added to give a P:COD ratio of 1:100; the lagoon was aerated continuously, with subsequent additions of leachate, until a population of microorganisms had become established. No addition of activated sludge was required.

Concerning ammonia removal, the plant was not designed to achieve this by nitrification-denitrification but through nitrogen incorporation by microbial biomass (bacteria and algae) and consequent sludge removal. The sludge contained in the aerated lagoon constituted 3% solids dry weight and was occasionally pumped out or handled using a tanker; organic content in the sludge was 50% and, when disposed of onto the landfilled waste, 1.2 g/Kg of organic nitrogen were found. According to the authors of this study, leachate might ultimately be discharged in a watercourse and nitrification of ammonia in the range of hundreds (see table 4.1) could not be acceptable in view of the nitrate levels in drinking water supplies.

Table 4.1. *Overall summary of leachate composition and treatment performance of the aerated lagoon-based system at Bryn Posteg landfill, UK.*

	Concentration (mg/L except pH)		
parameter	influent	effluent	overall removal (%)
pH	5.8	8.0	-
COD	5 518	153	97.2
BOD_5	3 670	18	99.5
$N\text{-}NH_3$	130	9.4	92.8
organic-N	27	11	59.3
Chlor	1 522	1 300	14.6
SS	184	39	78.8
VSS	110	20	81.8

4.3.2 Bell House, UK (Mehmood *et al.*, 2009)

Located north-west of Colchester, Bell House landfill had a on-site leachate treatment plant commissioned in 1995 comprised of four aerated lagoons with volumes varying from 60 to 80 m^3. The lagoons base and sides were lined with polyethylene material. Mixing and aeration were provided by means of compressed air flowing through diffuser pipes from the bottom of each lagoon. The aeration system was operated 4 to 6 h per day. This set up enabled the development of a facultative environment in which both aerobic and anaerobic degradation could occur. Some settlement occurred in the fourth lagoon. The lagoons were in series and two pumps recorded the flow rates of both influent (raw leachate) and effluent (pre-treated) directed to a sewer.

Leachate mean temperature and pH were respectively 16.7 ± 1.0°C and 7.2 at the influent; lagoon leachate temperatures followed air temperatures (mean value 13.5 ± 1.0°C) and lagoon mean pH was 8.5. COD concentration was initially higher in the raw leachate (mean value 1 740 mg/L) than in the fourth lagoon (mean value 426 mg/L), resulting in high COD removal mostly after the first lagoon (64%). However, starting COD values were not as high as in other leachates containing higher amount of organics. The authors claimed that sufficient treatment in respect of organics could have been achieved with only two lagoons and longer retention times.

Ammonia caused some concern in Bell House landfill: quantified as $N\text{-}NH_4$, the mean concentration value detected in raw leachate samples was as high as 965 mg/L. Already after the first lagoon in which nitrification was proved to be the main biological pathway for nitrogen removal, ammonium concentrations gradually decreased (mean value 185 mg/L); 99% ammonium removal occurred after the fourth lagoon since $N\text{-}NH_4$ concentrations as low as 9 mg/L were measured at the effluent. However, at 15°C and pH 8.5, 9 mg/L of $N\text{-}NH_4$ is equivalent to 0.23 mg/L of $N\text{-}NH_3$, which is toxic to fish.

Nitrification accounted for 67% of ammonium removal in the four-lagoons system. The highest nitrate concentration was found in the first lagoon and considered to be a direct consequence of active nitrification. Established microbial communities were detected using DNA assays in all four lagoons, but the highest diversity among gene fragments was found in the first. Despite evidences for nitrification might be supported by looking at both leachate quality and genetic analysis, neither volatilization nor assimilation by microorganisms were excluded as other mechanisms of nitrogen removal. Concentration values for the four nitrogen species measured within each lagoon are reported in table 4.2.

Table 4.2. *Concentration values for four nitrogen species measured in Bell House aerated lagoons based leachate treatment system (UK). "Raw leachate" indicates the input and "lagoon 4" represent the output of the system.*

	Concentration (mg/L)			
	$N\text{-}NH_4$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	N-tot
raw leachate	965	1.2	7.4	974
Lagoon 1	185	14.6	102	302
Lagoon 2	25	4.4	181	212
Lagoon 3	4	2.2	208	215
Lagoon 4	9	0.3	183	193

5 Hedeskoga

This chapter is a full insight on the site characteristics, treatment system components, functioning, technical data, and history of Hedeskoga´s aerobic-based landfill leachate treatment plant. For the method adopted to write the following, reference is made to section 6.1.1.

5.1 Site characteristics

Hedeskoga is a small village situated in the municipality of Ystad, southern Scania, Sweden. The facility is surrounded by agricultural lands to the north, east and south. To the west there is a reserve of pure deciduous forest and small occasional marshy ponds. A confined aquifer is found at 10 m below the ground level, beneath a layer of boulder clay (Thorneby *et al.*, 2003).

The total facility area is 41 000 m^2 of which ca 21 000 are destined to landfilling. Sysav is the company responsible for this area where urban and industrial non-hazardous solid waste, generated in the municipalities of Ystad, Skurup and Sjöbo (ca 62 000 inhabitants) is processed and ultimately landfilled. A maximum amount of 30 000 tons per year of waste can virtually be landfilled even though its actual value rarely reached this amount from 1994 to 2013.

In 1972-73 waste started to be landfilled in the southernmost part, area that is now occupied by a salix plantation (Nilsson, T. 2013); then, from 1985 up to date, the expansion of new waste cells continued northwards (Nilsson, P. 2013). As stated in Thorneby *et al.* (2003), the BOD/COD ratio calculated in the early 1990s was slightly above 0.1 with a declining trend, indicating that Hedeskoga landfill was mainly heading for its methanogenic stage. However, attempts to classify leachate quality in accordance with the conventional landfill age system (see section 2.3.6) are not always valid for every landfill and sometimes not even for the same site: depending on the type of waste and the latest legislation implemented, the classical view "young *vs.* old" leachate cannot be applied for leachate generated from more modern engineered waste cells.

Hedeskoga landfill area can be divided into three main parts: a closed area mainly asphalted or covered by soil and vegetation destined to spray irrigation prior to 2001, a closed asphalted area designed after 2001 according to the criteria contained in the Swedish ordinance on landfilling (see section 2.2) and a new operative partly covered engineered section with active waste cells (figure 5.1).

Topography of the area reveals (Thorneby *et al.*, 2003; see also Appendix Hedeskoga) that the highest and the lowest points in the northern area are respectively 60 and 53 m above the sea level; while in the eastern area, 72 m is the highest and 52 m the lowest. Two declivities are resulting from this difference in elevation. Thus, the formation of two main drainage basins in both the northern and eastern parts is favored. Accordingly, a ramified underground pipe system was constructed to collect liquid and intercept gaseous emissions from the buried waste. The leachate is ultimately converged towards two wells provided with their respective pumping systems, whereas methane gas is extracted from the landfill and used for district heating (Nilsson, T. 2013).

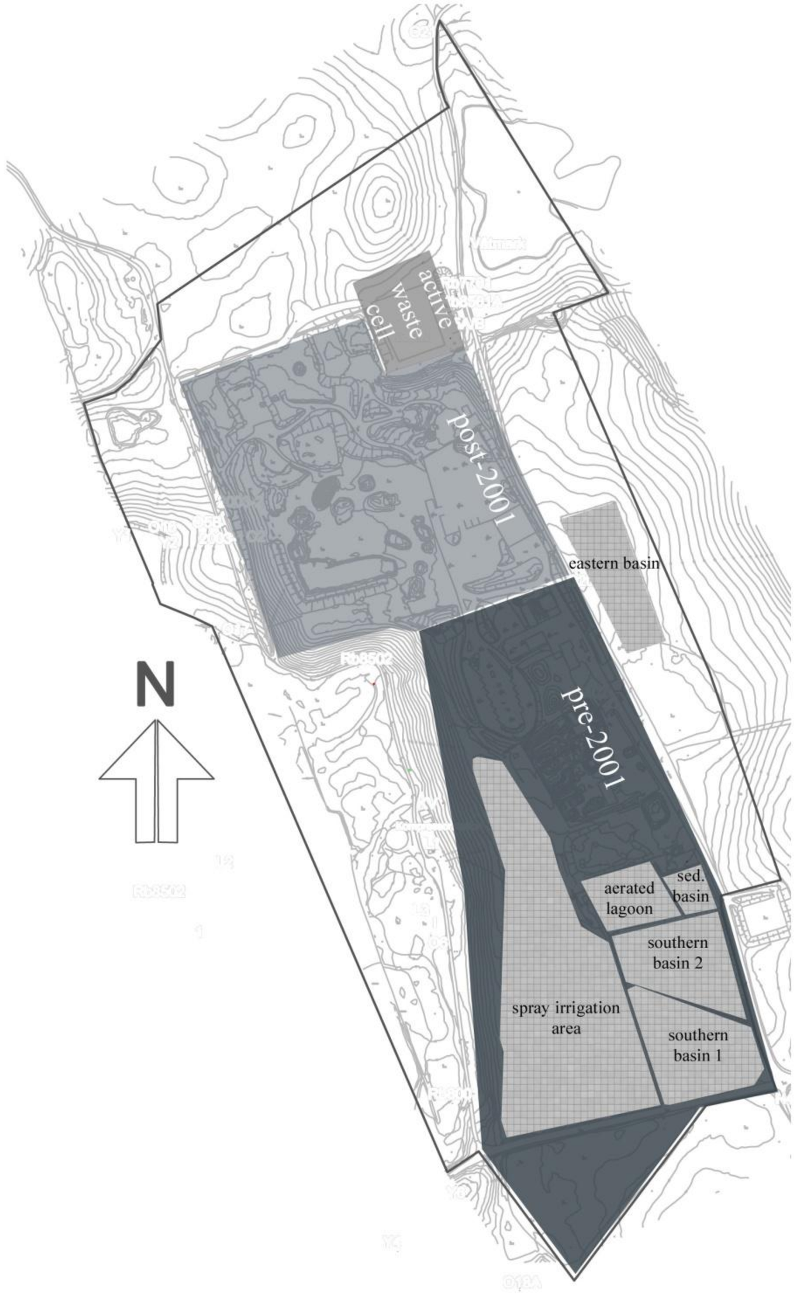


Figure 5.1. *Hedeskoga landfill area. In the south-north direction the landfill is divided in three main parts according to the different leachate quality generated before (“pre-2001”) and after (“post-2001” and “active waste cell”) the ordinance SFS 2001: 512. The patchwork area indicates the on-site leachate treatment components: eastern basin, southern basins 1 and 2, aerated lagoon, sedimentation basin (“sed. basin”) and spray irrigation area. Picture elaborated with permission of Sysav.*

5.2 The on-site leachate treatment system

The leachate produced in Hedeskoga landfill can undergo two main treatment routes: one consists of an on-site biological treatment step followed by combined treatment with domestic sewage in a local wastewater treatment plant; the other is entirely carried out on-site and comprises an aerobic-based biodegradation phase, a sedimentation step followed by land spray irrigation. Figure 5.1 schematically shows the area (indicated by a patchwork) destined to the on-site leachate treatment. Which strategy is followed year by year is entirely dependent on the landfill managers and operators who can decide how much and where the leachate flow can be directed; in 2009-2010, however, in view of stricter environmental water quality standards demanded by Swedish authorities, the off-site treatment combined with the local wastewater treatment plant was nearly replaced. The main components of the on-site treatment system are a series of treatment ponds and an irrigation area divided into salix plantations and grassland (together defined as "energy crops" or MV irrigation system where MV in Swedish stands for "mark-växt", i.e. "soil-plant"). Currently, two pilot-scale plants are present in the landfill site for further water polishing: one small active-carbon fibers pond and an artificial reed bed (or constructed wetland); since they have not yet been fully implemented, they will not be considered as part of the system in this paper.

5.2.1 The ponds system: description and treatment strategy

A total of five ponds are included in the system: three are designed for simultaneous storage, equalization and pre-treatment, one is an aerated lagoon meant to aerobically treat leachate and one is a sedimentation basin. Two pumps provide the leachate input from two separated wells: one is called P5B and pumps in leachate originating in the operative partly covered landfill area to the north ("post-2001" and "active waste cells" in figure 5.1). The second goes under the name of P0 and gets into the ponds system stabilized leachate originating from the older closed landfill area to the east ("pre-2001" and part of "post-2001" in figure 5.1). The output is represented by P4, a well situated immediately after the sedimentation basin (Sed) which is connected to a pumping station used for spray irrigation onto the MV-system. Surface aerators are installed one each in the two basins to the south (LVD 1 and LVD 2). One bottom aerator is placed in the aerated lagoon (IL 3) and another one in the eastern basin to the east (LD Öst). Figure 5.2 gives a clearer view of the system.

The main principle behind the leachate treatment in Hedeskoga is to store in the winter and to treat during late spring/summer in correspondence of the growing season (Leander, 2013; Nilsson, P. and Nilsson, T. 2013). This is because leachate formation occurs mostly from late autumn to spring after precipitation events while aerobic biological treatment is favored at higher temperatures (Robinson and Grantham, 1988). Moreover, better light and temperature conditions stimulate evapotranspiration and plant growth in the energy crops. Using this rule-of-thumb, the southern equalization basins function as a reserve of leachate while the aerated lagoon together with the sedimentation basin constitute the actual treatment. *De facto,* aerobic pre-treatment is ensured all year-round in all the storage-equalization basins (LD Öst, LVD 1 and LVD 2) since aerators are able to provide turbulence and oxygenation. Although, for this purpose, surface aerators are less efficient than bottom aerators (Middlebrooks and Pano, 1983; Nilsson, T. 2013).

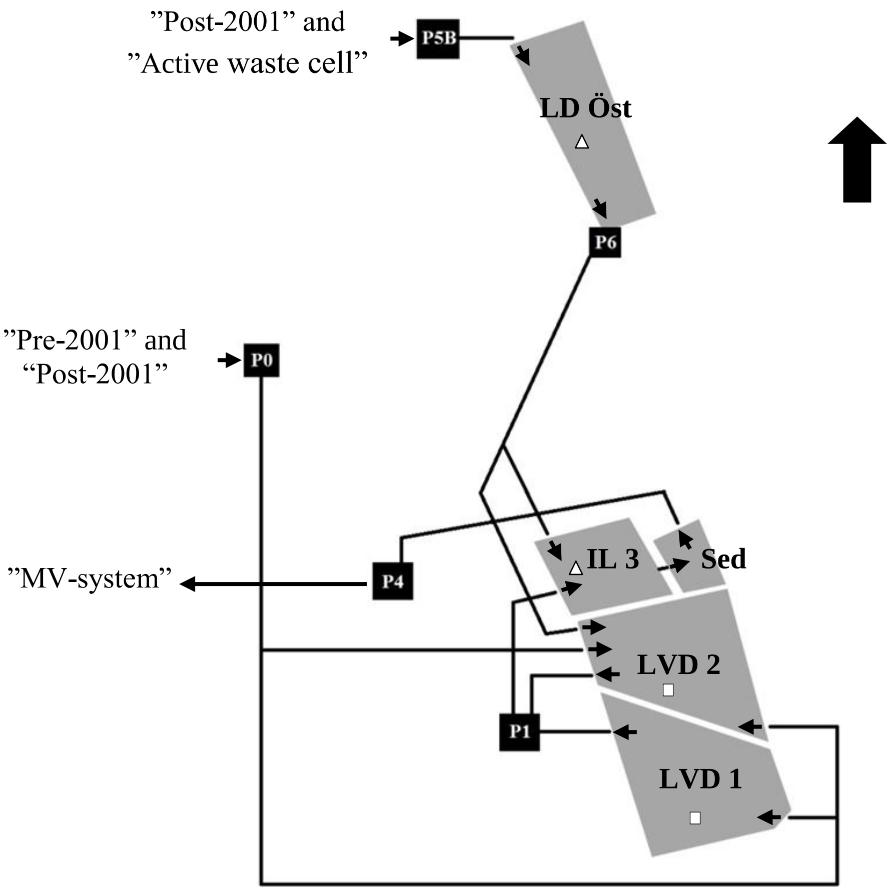


Figure 5.2. *Hedeskoga´s ponds system. The core system is composed of a storage, equalization and pre-treatment basin to the east (LD Öst), two storage, equalization and pre-treatment basins to the south (LVD 1 and LVD 2), an aerated lagoon (IL3), a sedimentation basin (Sed), and a spray irrigation area (“MV-system”). The black squares indicate the wells and their respective pumps: P0= leachate input from the area “pre-2001”and part of “post-2001”; P1= equalized leachate pumped in to IL3; P5B= leachate input from both the area “post-2001” and “active waste cell”; P6= pretreated leachate that can be pumped either in IL 3 or in LVD 2. The white triangles and squares indicate bottom aerators and surface aerators, respectively. Every pump is provided with a flow-meter except that in P1. The tiny black arrows indicate the leachate flow direction, while the big one to the right indicates the north.*

Despite the site temperature and the yearly amount of leachate may affect the operations, the procedure adopted by the landfill staff can be summarized as follows:

- **Pre-treatment of leachate east**: the leachate generated in the northern landfill area is pumped in to, stored and aerated in the eastern equalization-aeration basin from January to December (P5B → LD Öst).
- **Pre-treatment of leachate**: the leachate generated in the old landfill area is pumped in to, stored and aerated in the two equalization basins to the south from January to December (P0 → LVD1 or LVD 2).
- **Beginning of aerobic treatment and irrigation**: in March the leachate formerly treated in the aerated lagoon and sedimentation basin goes into the irrigation pipe system (IL 3 → Sed →P4). At the same time, the content of the southern storage ponds is transferred into the aerated lagoon to begin the actual treatment (LVD 1 and LVD 2 → IL3 via P1 well).
- **Mixing**: from the end of March (or beginning of April) to late September the leachate contained in the eastern equalization basin is transferred to the southern equalization basins to provide some mixing (P6 → LVD 2).
- **Aerobic treatment**: during the all treatment period, the idea is to maintain a constant water level in both aerated lagoon and sedimentation basin (communicating vessels) so that enough biological breakdown is provided. To do this, leachate is pumped in from the southern equalization-pre-treatment basins to the aerated lagoon and to the sedimentation basin (LVD 1 and LVD 2 → IL 3 → Sed).
- **End of the treatment**: in October all the storage-equalization ponds (LD Öst, LVD 1 and LVD 2) are ready to receive leachate again. A low volume of leachate is harbored in the aerated lagoon and in the sedimentation basin. The irrigation system is suspended until the beginning of the new growing season.

5.2.2 System technical data

Technical data, collected according to the methods stated in section 6.1, are presented in a tabular form with regard to:

- Landfill site characteristics (table 5.1)
- Precipitation and evapotranspiration data for years 2009 to 2013 (table 5.2)
- Ponds´ design characteristics in 2013 (table 5.3)
- Ponds´ environment in 2013 (table 5.4)
- Leachate quality measured in P0, P5B and P4 in 2013 (table 5.5)
- Monthly leachate volumes measurements and leachate water flow values expressed on a daily basis for 2013 (table 5.6 and 5.7, respectively)
- Nitrogen balance for 2013 (table 5.8 and 5.9).

Table 5.1. *Landfill site characteristics.*

Hedeskoga landfill	
Total facility area (m^2)	Landfill area (m^2)
41000	21000

Year	Landfilled waste (ton/y)	Leachate production (m^3/y)	Reference
1994 – 2002	~30 000	50 000 – 70 000	Thorneby *et al.*, 2003
2003	20 744	46 800	Env. report (2003)
2004	5 189	58 050	Env. report (2004)
2005	1 218	74 300	Env. report (2005)
2006	6 950	88 356	Env. report (2006)
2007	27 611	99 508	Env. report (2007)
2008	23 829	86 408	Env. report (2008)
2009	16 102	82 655	Env. report (2009)
2010	16 645	97 900	Env. report (2010)
2011	13 013	135 000	Env. report (2011)
2012	9 487	106 000	Env. report (2012)
2013	9069	111 304	Almqvist; Nilsson, T. (2013)

Table 5.2. *Annual precipitation (P) and Evapotranspiration (E) in Hedeskoga´s catchment area. Measurements for 2013 were also taken on a daily basis and expressed as average values ($\bar{y}$).*

Year	P (mm)	E (mm)	Reference
2009	491	-	Env. report (2009)
2010	566	-	Env. report (2010)
2011	738	-	Env. report (2011)
2012	630	-	Env. report (2012)
2013	659	504	SMHI (2013)

$\bar{y}$	P (mm/d)	E (mm/d)
Jan	1.9	0.5
Feb	1.3	0.1
Mar	0.5	0.2
Apr	0.7	1.8
May	1.5	2.4
Jun	2.7	2.4
July	0.8	1.5
Aug	1.1	1.4
Sept	2.1	1.8
Oct	3.3	1.3
Nov	3.0	1.4
Dec	2.6	1.4

***Table 5.3.** Ponds´ design characteristics. V= maximum design capacity, d_{max}= maximum depth, S= pond surface area based on V and max depth (see section 6.1.3), HRT_{th}= theoretical hydraulic retention time calculated as the ratio between maximum design capacity of each pond and flow rates expressed in m^3/d. Leachate volume measurements were taken on a monthly basis (see table 5.6).*

Pond	V (m^3)	d_{max} (m)	S (m^2)	HRT_{th} (d)
LD Öst	16 000	3.5	4 571	29
LVD 1	10 000	4.25	2 353	33
LVD 2	10 000	2.5	4 000	31
IL 3	5 000	2.8	1 786	17
Sed	1 000	NA	350	NA
Tot	42 000		13 060	

***Table 5.4.** Ponds´ environment. T_{win}= temperature interval Jan-Feb, T_{spr}= temperature interval Apr-May, T_{sum}= temperature interval June-July; dissolved oxygen (DO) depth intervals are taken from the water surface level. All measurements were done on a monthly basis.*

	DO (%)					
Well/pond	0-1 m	1-2 m	pH	T_{win}(°C)	T_{spr}(°C)	T_{sum}(°C)
P0	35	29	7.6	0 – 5	-	-
P5B	-	-	7.4	-	-	-
P6/LD Öst	44	47	8.0	0 – 4.7	10 – 16	17 – 20
LVD 1	73	77	8.0	0 – 4.5	10 – 16	17 – 20
LVD 2	87	87	8.0	0 – 4.5	10 – 16	17 – 20
P4/IL 3	87	84	8.1	0 – 4.5	10 – 16	17 – 20
P4/Sed	67	61	8.1	0 – 4.5	10 – 16	17 – 20

Table 5.5. *Leachate quality in Hedeskoga for 2013. Concentrations were measured at the input wells (P5B, P0), the pre-treatment output (P6), the two equalization basins (LVD 1, LVD 2) and at the final output (P4). Sampling was done in 2013 on a monthly basis except in March, where the samples froze. Negative values may indicate either a measurement under range ("less than") or an experimental error;* $\bar{\boldsymbol{y}}$ *indicates the annual average value for each parameter. Figures for the nitrogen species in italics are based on estimates (see section 6.1.3, nitrogen mass balance).*

P5B	pH	Cond (mS/m)	BOD_7 (mg/L)	COD (mg/L)	TOC (mg/L)	Chlor (mg/L)	SS (mg/L)	Alkalinity (mg HCO_3/L)	N-tot (mg/L)	$N\text{-}NH_4$ (mg/L)	$N\text{-}NO_2$ (mg/L)	$N\text{-}NO_3$ (mg/L)	P-tot (mg/L)	$P\text{-}PO_4$ (mg/L)
Jan	7.5	924	58	680	160	940	60	2 800	260	260	0.9	2.2	130.0	4.1
Feb	-	-	-	-	-	-	-	-	*260*	*267*	0.6	*1.4*	-	-
Mar	-	-	-	-	-	-	-	-	*260*	*274*	0.3	*0.6*	-	-
Apr	7.5	878	67	730	220	930	58	2 500	260	240	0.0	-0.2	3.5	-5.0
May	-	-	-	-	-	-	-	-	*296*	273	0.0	-0.2	-	-
June	-	-	-	-	-	-	-	-	*332*	306	0.0	-0.2	-	-
July	7.3	970	86	810	200	1 000	28	3 500	370	340	0.0	-0.2	6.9	5.0
Aug	-	-	-	-	-	-	-	-	*313*	*300*	0.0	*-0.1*	-	-
Sept	-	-	-	-	-	-	-	-	*256*	*260*	0.0	*0.0*	-	-
Oct	7.2	832	73	680	180	870	35	2 600	200	220	0.0	0.1	7.9	4.0
Nov	-	-	-	-	-	-	-	-	*224*	*235*	0.0	*0.2*	-	-
Dec	-	-	-	-	-	-	-	-	*248*	*250*	0.1	*0.3*	-	-
$\bar{y}$	7.3	901	71	725	190	935	45	2 850	273	269	0.2	0.3	37.1	2.0

P0	pH	Cond (mS/m)	BOD$_7$ (mg/L)	COD (mg/L)	TOC (mg/L)	Chlor (mg/L)	SS (mg/L)	Alkalinity (mg HCO$_3$/L)	N-tot (mg/L)	N-NH$_4$ (mg/L)	N-NO$_2$ (mg/L)	N-NO$_3$ (mg/L)	P-tot (mg/L)	P-PO$_4$ (mg/L)
Jan	8.5	337	14	200	58	370	94	1 300	130	120	0.1	5.2	1.1	0.1
Feb	8.1	390	16	230	71	410	73	1 900	160	160	0.0	1.0	1.0	0.0
Mar	-	-	-	-	-	-	-	-	*150*	*145*	*0.1*	*1.0*	-	-
Apr	7.2	357	13	220	72	370	39	1 500	140	130	0.2	1.0	1.4	0.5
May	7.6	353	10	260	40	430	98	1 800	170	160	0.1	1.8	0.9	0.1
June	7.2	352	12	210	61	400	61	1 400	110	100	0.3	4.6	0.7	0.2
July	7.7	187	13	360	86	300	280	640	40	24	0.4	8.1	2.2	0.5
Aug	7.0	354	15	210	34	460	55	1 200	98	82	0.3	7.2	0.5	0.4
Sept	7.3	384	14	250	69	470	79	1 400	120	120	0.2	3.5	3.2	1.9
Oct	7.6	349	11	220	63	430	90	1 300	97	84	0.1	7.9	0.6	0.2
Nov	7.9	304	5	160	55	360	42	1 000	81	68	0.1	6.9	1.0	0.5
Dec	7.8	298	7	180	66	370	50	1 000	91	71	0.2	11.0	0.9	0.1
$\bar{y}$	7.6	333	12	227	61	397	87	1 313	116	105	0.2	4.9	1.2	0.4

P6	pH	Cond	BOD_7	COD	TOC	Chlor	SS	Alkalinity	N-tot	$N\text{-}NH_4$	$N\text{-}NO_2$	$N\text{-}NO_3$	P-tot	$P\text{-}PO_4$
		(mS/m)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg HCO_3/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Jan	8.0	555	33	450	110	580	78	1 400	130	110	0.1	0.6	7.3	4.4
Feb	7.9	518	20	380	110	550	54	1 400	130	100	0.0	0.8	5.1	4.2
Mar	-	-	-	-	-	-	-	-	*135*	*110*	*0.1*	*1.4*	-	-
Apr	8.2	521	21	410	120	590	56	1 300	140	120	0.1	1.9	4.8	3.7
May	7.6	465	24	430	120	590	83	1 200	120	72	4.6	21.0	4.9	3.9
June	8.0	511	57	460	140	620	100	780	76	4	2.3	47.0	3.9	2.9
July	7.3	480	14	390	110	700	25	1 100	54	17	0.7	20.0	3.7	3.0
Aug	8.2	539	16	400	97	710	38	1 000	23	3	0.1	5.1	1.8	1.1
Sept	8.4	534	18	500	110	720	90	820	28	1	0.0	2.6	2.2	0.9
Oct	8	471	34	350	110	630	16	1 100	24	12	0.0	0.5	4.4	3.7
Nov	8.3	464	23	440	110	600	110	740	33	0	0.0	15.0	2.1	1.1
Dec	8.1	458	11	330	120	620	14	950	19	8	0.0	0.0	2.6	1.0
$\bar{y}$	8.0	501	25	413	114	628	60	1 072	76	46	0.7	9.7	3.9	2.7

LVD 1	pH	Cond	BOD$_7$	COD	TOC	Chlor	SS	Alkalinity	N-tot	N-NH$_4$	N-NO$_2$	N-NO$_3$	P-tot	P-PO$_4$
		(mS/m)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg HCO$_3$/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Jan	7.8	344	11	280	60	380	160	1 400	130	120	0.0	4.0	3.6	0.1
Feb	8.0	284	6	200	52	350	210	1 100	100	97	0.0	5.1	0.2	0.0
Mar	-	-	-	-	-	-	-	-	*110*	*104*	*0.1*	*4.9*	-	-
Apr	8.2	279	8	210	59	380	99	920	120	110	0.1	4.7	0.3	0.6
May	8.1	244	11	200	50	390	48	760	110	82	3.8	16.0	0.2	0.0
June	8.2	302	6	220	62	410	83	850	94	75	1.9	11.0	0.4	0.2
July	7.8	316	10	260	61	470	57	700	65	42	2.7	16.0	0.3	0.2
Aug	8.1	285	17	390	98	430	360	740	75	34	0.9	10.0	0.7	0.1
Sept	7.8	326	20	240	63	460	63	830	75	41	9,7	15.0	1.0	0.5
Oct	7.9	265	13	220	58	390	68	510	65	12	0.4	42.0	0.3	0.0
Nov	8.1	262	7	160	48	360	40	660	63	26	5.1	25.0	0.3	0.0
Dec	8.1	250	7	170	61	350	91	620	67	30	2.6	22.0	0.3	0.0
$\bar{y}$	8.0	287	11	232	61	397	116	826	90	64	2.3	14.6	0.7	0.2

LVD 2	pH	Cond (mS/m)	BOD$_7$ (mg/L)	COD (mg/L)	TOC (mg/L)	Chlor (mg/L)	SS (mg/L)	Alkalinity (mg HCO$_3$/L)	N-tot (mg/L)	N-NH$_4$ (mg/L)	N-NO$_2$ (mg/L)	N-NO$_3$ (mg/L)	P-tot (mg/L)	P-PO$_4$ (mg/L)
Jan	7.7	325	13	550	50	400	440	1 500	140	130	0.0	4.3	17.0	0.2
Feb	7.8	332	9	190	60	380	130	1 500	130	120	0.0	3.1	0.2	0.0
Mar	-	-	-	-	-	-	-	-	*140*	*130*	*0.1*	*2.5*	-	-
Apr	8.1	367	11	260	78	450	120	1 300	150	140	0.2	1.9	1.2	0.4
May	8.1	251	9	180	50	390	43	780	110	83	3.6	16.0	0.2	0.0
June	8.0	344	8	230	69	430	55	1 100	99	79	1.9	10.0	0.6	0.2
July	8.1	293	18	250	72	440	520	1 000	96	77	1.1	4.6	1.7	0.3
Aug	8.2	292	25	250	54	440	84	850	80	64	1.1	2.5	1.0	0.4
Sept	7.8	344	19	320	68	460	260	1 200	95	92	0.8	0.0	2.0	0.4
Oct	8.1	300	8	190	58	410	53	910	72	55	0.4	7.8	0.6	0.2
Nov	8.0	293	4	170	53	350	100	960	84	62	0.3	9.0	1.1	0.3
Dec	8.0	287	6	180	59	360	74	1 000	91	63	0.2	11.0	0.7	0.0
$\bar{y}$	8.0	312	12	252	61	410	171	1 100	107	91	0.8	6.1	2.4	0.2

P4	pH	Cond (mS/m)	BOD_7 (mg/L)	COD (mg/L)	TOC (mg/L)	Chlor (mg/L)	SS (mg/L)	Alkalinity (mg HCO_3/L)	N-tot (mg/L)	$N\text{-}NH_4$ (mg/L)	$N\text{-}NO_2$ (mg/L)	$N\text{-}NO_3$ (mg/L)	P-tot (mg/L)	$P\text{-}PO_4$ (mg/L)
Jan	8.1	278	8	170	52	360	32	830	100	80	0.1	11.0	1.8	0.1
Feb	8.2	256	11	170	50	330	26	770	96	75	0.1	11.0	0.2	0.0
Mar	-	-	-	-	-	-	-	-	*97*	*78*	*0.2*	*11.0*	-	-
Apr	8.2	250	7	220	61	350	61	710	98	80	0.3	11.0	0.2	0.0
May	8.1	228	7	180	47	370	27	690	95	72	1.0	16.0	0.2	0.0
June	8.2	278	6	190	56	400	30	670	89	61	2.5	19.0	0.2	0.1
July	7.4	287	9	240	74	460	34	630	68	38	1.5	18.0	0.6	0.3
Aug	8.0	278	15	230	55	440	43	590	43	14	1.8	16.0	0.4	0.1
Sept	8.1	315	11	270	66	490	53	520	30	0	0.1	19.0	0.6	0.0
Oct	8.0	296	15	220	62	450	110	530	55	1	0.2	28.0	0.8	0.1
Nov	8.3	269	3	180	53	420	10	480	38	2	0.4	27.0	0.3	0.1
Dec	8.1	252	5	160	59	380	54	500	40	1	0.1	27.0	0.3	0.1
$\bar{y}$	8.1	272	9	203	58	405	44	629	71	42	0.7	18.0	0.5	0.1

Table 5.6. *Monthly leachate volumes measurements (V_m) for 2013 obtained according to the methods explained in section 6.1.1. P5B, P0 and p= input; P4 and e= output; ΔV=stored leachate calculated as the difference between input and output; PE_{eff}= net contribution of both precipitation and evapotranspiration to the ponds system (unitless). For major details about the PE_{eff} coefficient see equation (25) in section 6.1.3, water budget.*

	V_m (m^3/month)						
	input			*output*		*stored*	
	P5B	**P0**	**p**	**P4**	**e**	**ΔV**	**PE_{eff}**
Jan	1 558	11 443	778	0	202	13 577	1.04
Feb	759	6 614	483	0	37	7 820	1.06
Mar	794	10 189	219	2 010	72	9 121	1.02
Apr	664	0	289	0	686	267	0.40
May	493	7 377	615	7 480	991	14	0.04
Jun	526	9 551	1 049	12 354	923	-2 152	0.94
July	734	9 355	304	14 832	640	-5 080	1.07
Aug	826	9 355	454	14 832	614	-4 811	1.03
Sept	665	10 116	823	6 149	496	4 959	1.07
Oct	615	8 452	1 341	447	444	9 517	1.10
Nov	789	9 193	1 190	0	562	10 611	1.06
Dec	725	10 512	1 057	793	731	10 769	1.03
Tot	9 148	102 156	8 602	58 897	6 398		

Table 5.7. *Leachate water flow values expressed on a daily basis for 2013 (ϕ_d). P5B and P0= input; P4= output. The original measurements correspond to monthly volume records. For more details on the method see section 6.1.3, water budget; $\bar{y}$ indicates the average value.*

	ϕ_d (m^3/d)		
	input		*output*
	P5B	**P0**	**P4**
Jan	50	369	0
Feb	27	236	0
Mar	26	329	65
Apr	22	0	0
May	16	238	241
Jun	18	318	412
July	24	302	478
Aug	27	302	478
Sept	22	337	205
Oct	20	273	14
Nov	26	306	0
Dec	23	339	26
$\bar{y}$	25	279	160

Table 5.8. *Monthly nitrogen balance “N” (given in Kg/month). N-tot= total nitrogen; N-NH_4= ammonium nitrogen; N-NO_2 + N-NO_3= oxidized nitrogen. P5B and P0= input; P4= output. In section 6.1.3 it can be seen how these values has been calculated.*

	N-tot			*N-NH_4*			*N-NO_2 + N-NO_3*		
	P5B	**P0**	**P4**	**P5B**	**P0**	**P4**	**P5B**	**P0**	**P4**
Jan	405	1 488	0	405	1 373	0	5	61	0
Feb	197	1 058	0	203	1 058	0	2	7	0
Mar	206	1 528	195	218	1 477	157	1	11	23
Apr	173	0	0	159	0	0	0	0	0
May	146	1 254	711	135	1 180	539	0	14	127
Jun	175	1 051	1 100	161	955	754	0	46	272
July	272	374	1 009	250	225	564	0	80	297
Aug	259	917	638	248	767	208	0	70	267
Sept	170	1 214	184	173	1 214	1	0	37	117
Oct	123	820	25	135	710	0	0	68	13
Nov	177	745	0	185	625	0	0	64	0
Dec	180	957	32	181	746	1	0	116	21

Table 5.9. *Daily nitrogen balance "n" (given in Kg/d). N-tot= total nitrogen; N-NH_4= ammonium nitrogen; N-NO_2 + N-NO_3= oxidized nitrogen. P5B and P0= input; P4= output. In section 6.1.3 it can be seen how these values has been calculated.*

	N-tot			*N-NH_4*			*N-NO_2 + N-NO_3*		
	P5B	**P0**	**P4**	**P5B**	**P0**	**P4**	**P5B**	**P0**	**P4**
Jan	13.6	50.1	0.0	13.6	46.3	0.0	0.2	2.0	0.0
Feb	7.5	40.1	0.0	7.7	40.1	0.0	0.1	0.3	0.0
Mar	6.8	50.1	6.4	7.1	48.4	5.1	0.0	0.4	0.7
Apr	2.3	0.0	0.0	2.1	0.0	0.0	0.0	0.0	0.0
May	0.2	1.4	0.8	0.2	1.4	0.6	0.0	0.0	0.1
Jun	5.5	33.1	34.6	5.1	30.1	23.7	0.0	1.4	8.6
July	9.4	12.9	34.8	8.6	7.8	19.5	0.0	2.7	10.2
Aug	8.6	30.6	21.3	8.3	25.6	6.9	0.0	2.3	8.9
Sept	6.1	43.3	6.6	6.2	43.3	0.0	0.0	1.3	4.2
Oct	4.4	29.2	0.9	4.8	25.3	0.0	0.0	2.4	0.4
Nov	6.3	26.4	0.0	6.6	22.1	0.0	0.0	2.3	0.0
Dec	6.0	31.8	1.1	6.0	24.8	0.0	0.0	3.8	0.7

5.2.3 Evolution of the on-site treatment: a brief historical insight

- **1972-73**: municipal solid waste begun to be landfilled in the southern part of the landfill site. The area is now occupied by a salix plantation.
- **1985-2005**: the expansion of new waste cells continued northwards.
- **1989-1991**: three equalization basins were designed in the southern part of the site to store leachate water during winter months. An aerated lagoon and a sedimentation basin were built to provide an aerobic-based treatment during summer. A satisfactory 60-80% of the total annual average leachate flow could be treated on-site and the remaining 20% sent to the local municipal wastewater treatment plant (Nilsson, P. 2013).
- **1996-2003**: a pilot-scale reverse osmosis plant was tested and its performance evaluated. The technology was considered neither cost-effective nor easy-to-maintain in relation to the quality of leachate generated. Hence, its full-scale implementation was cancelled (Thorneby *et al.,* 2003).
- **2002**: consequently to the European Landfill directive 1999/31/EC on sanitary landfills and to the Swedish ordinance SFS 2001: 512, combustible waste could not be landfilled any longer. Contemporarily, a proposal for a new equalization pond in the eastern part was suggested and evaluated.
- **2005**: in view of the Swedish ordinance SFS 2001: 512, also organic waste disposal was prohibited.
- **2006**: a new pre-treatment equalization pond was constructed to compensate the extra leachate production from the newest northern landfill part designed according to more modern engineering criteria.

As primarily designed in 1988 the on-site leachate water treatment system consisted of: a tripartite equalization pond with a total volume of 20 000 m^3, an aerated lagoon of 5 000 m^3 (with approximately 10 days HRT_{th}) and a 1 000 m^3 sedimentation basin (Nilsson, P. 2013). The equalization ponds were designed to store an expected yearly leachate amount of about 50 000 – 70 000 m^3 (Nilsson, P. 2013). Annual fluctuations of this value, mostly depending on precipitations and temperatures, were also taken into account. The actual biological treatment occurred exclusively within the aerated lagoon during the summer months. According to the first results the system performed well showing efficiency and robustness despite seasonal leachate and ammonia nitrogen fluctuations (Nilsson, P. 2013).

6 Material and Methods

The whole chapter has been split into two parts which reflect the outline of the thesis: an extensive literature study and an empirical part describing two experiments.

6.1 Literature study

Data collection about Hedeskoga and other case studies was based on three main principles:

- data research in published experimental works, paper reviews and manuals
- appreciation of available data (current and historical) regarding Hedeskoga landfill and its on-site leachate water treatment system
- direct investigation and data acquirement from field experts.

6.1.1 On-site leachate treatment in Hedeskoga

A deep understanding of the ponds, pumping and well systems was initially obtained by going through protocols and other available material provided by Sysav. In order to clarify the operational characteristics such as robustness, functioning, and capacity, field experts were also consulted. Yearly available data regarding landfill site characteristics, precipitation and evapotranspiration data, ponds´ design characteristics, ponds´ environment, leachate water quality, monthly leachate volumes measurements were also reviewed and compiled in section 5.2.2.

6.1.2 Case studies

The main criteria used to look for comparable case studies were:

- Landfill site and waste characteristics
- Leachate characteristics
- Type of technology used to obtain biological nitrogen removal
- Removal efficiency for different leachate parameters as a determinant of system performance.

6.1.3 Ponds´ performance

A simple model for the on-site treatment plant in Hedeskoga (figure 6.1) was constructed based on the following assumptions:

- All the five basins are considered altogether as a closed system in which steady-state and complete mixing conditions occur and where *P5B*, *P0* and precipitation (*p)* are the input and *P4* and evapotranspiration (*e*) are the output
- Biological breakdown of inorganic nitrogen species occurs throughout the year in all the pre-treatment and treatment basins provided with aerators (see figure 5.2)
- The main treatment step occurs in the aerated lagoon-sedimentation pond system by means of combined nitrification-denitrification
- Ammonia air stripping was neither quantified nor taken into account
- Maximum design capacity *(V)* and maximum mean depths (d_{max}) for each pond were estimated based on best available data (see table 5.3). Subsequently, surface areas (*S*) were calculated by rounding off each basin to a parallelepiped:

$$S = \frac{V}{d_{max}} \tag{24}$$

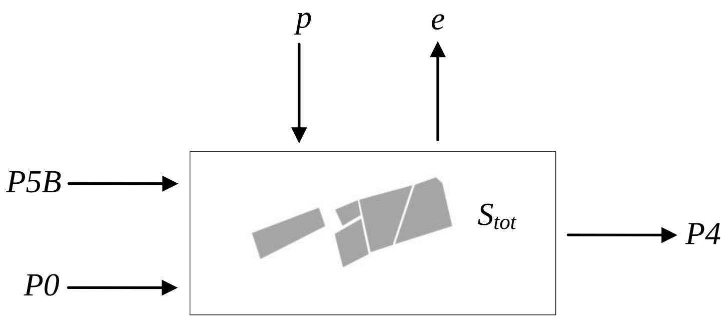


Figure 6.1. *Schematic model of the ponds system used to evaluate ponds´ performance. Parameters taken into account: P5B, P0 and precipitation (p) are the input and P4 and evapotranspiration (e) are the output of the system;* S_{tot} *is the sum of all the ponds´ areas (see table 5.3). Depending on the purpose, all the parameters may represent either volumes (see section "water budget" below) or quantities of nitrogen entering and leaving the system (see section "nitrogen mass balance" below).*

Water budget

The yearly hydrological balance was determined using monthly leachate volumes measurements (V_m) at three different pumping stations: P5B, P0 and P4. Amounts of leachate stored by the system in the time span of one month (ΔV) was calculated as the difference between input and output leachate volume records. Then, for each month, the net contribution of precipitation and evapotranspiration (PE_{eff}) to the final water volume of the ponds was calculated through equation (25):

$$PE_{eff} = \frac{P5B + P0 + p - P4 - e}{P5B + P0 - P4} \tag{25}$$

where,

PE_{eff} = net contribution of both precipitation and evapotranspiration to the ponds system (unitless coefficient)

$P5B$ and $P0$ = volume of leachate entering the system on a monthly basis (m^3)

$P4$ = volume of leachate leaving the system on a monthly basis (m^3)

p = volume of precipitation relatively to the total surface area (A_{tot}) occupied by the ponds (m^3)

e = volume of evapotranspirated water relatively to the total surface area (S_{tot}) occupied by the ponds (m^3)

The obtained values for equation (25) can be found in table 5.6. Leachate water records detected in P5B, P0 and P4 together with the stored volume ΔV were also expressed on a daily basis (see ϕ_d in table 5.7) in order to be used for further calculations in the nitrogen mass balance.

Nitrogen mass balance

To determine the proportion of nitrogen input and output in Hedeskoga, three nitrogen species were taken into consideration: total nitrogen ($N\text{-}tot$), ammonium nitrogen ($N\text{-}NH_4$) and oxidized nitrogen ($N\text{-}NO_2$ + $N\text{-}NO_3$). Concentration values (C) were obtained from monthly based leachate quality analysis conducted by an accredited laboratory on account of Sysav (see table 5.5). For the nitrogen species in P5B the samples were taken only every quarter of the year. Lacking data (represented in italics in table 5.5) were interpolated by dividing the difference between two known concentrations values by the number of intervals between two known sampling points. The estimate is based on the assumption that the unknown concentration values gradually increase or decrease between two sampling points if the first is less than the second, or, if the first is higher than the second, respectively. The amount of nitrogen (N) was calculated adopting both monthly leachate volume measurements (see table 5.6) and leachate water flow records expressed on a daily basis (see ϕ_d in table 5.7) as in equation (26) and (27). Respectively:

$$\mathrm{N} = \mathrm{V_m} \cdot \mathrm{C} \tag{26}$$

where,

N = amount of nitrogen (Kg/month)

V_m = monthly leachate volumes (m^3/month)

C = concentration values for the different chemical species (mg/L)

and,

$$\mathrm{n} = \phi_\mathrm{d} \cdot \mathrm{C} \cdot \mathrm{PE}_{eff} \tag{27}$$

where,

n = amount of nitrogen (Kg/d)

ϕ_d = leachate water flow records (m^3/d)

PE_{eff} = net contribution of both precipitation and evapotranspiration to the ponds system (unitless coefficient)

The difference between equation (26) and (27) is the addition of a coefficient (PE_{eff}) in (27) that quantifies the effect of precipitation and evapotranspiration in the closed system, and, the use in (27) of leachate water flow records transformed into m^3/d (ϕ_d) instead of leachate monthly readings detected in the pumping stations (V_m).

Nitrification Efficiency

Nitrification efficiency of the system has been estimated as the ratio between the amount of Kg nitrogen leaving *P4* under the form of oxidized nitrogen ($N\text{-}NO_2$ + $N\text{-}NO_3$), and the amount of Kg nitrogen entering both *P5B* and *P0* under the form of ammonium nitrogen ($N\text{-}NH_4$).

Removal Efficiency

The ponds system performance in respect of different nitrogen species removal (*N-tot*, $N\text{-}NH_4$, and $N\text{-}NO_2$ + $N\text{-}NO_3$) is expressed as:

$$removal = \frac{KgN\ in - KgNout}{KgN\ in} \cdot 100 \tag{28}$$

where,

Kg N in = daily input of nitrogen measured as the sum of *N*- (in different form) in *P5B* and *P0* (Kg)

Kg N out = daily output of nitrogen measured as *N*- (in different form) in *P4* (Kg)

6.2 Field and laboratory work

An experimental analysis, called “biotest”, was conducted on leachate water and sediment samples collected out of Hedeskoga equalization basins, in order to identify any bacterial activity and to quantify nitrification rates of the suspended cultures. Leachate water samples from two different influents at Hedeskoga with regard to potential nitrification inhibition where also analyzed through a standardized procedure: the so-called screening method.

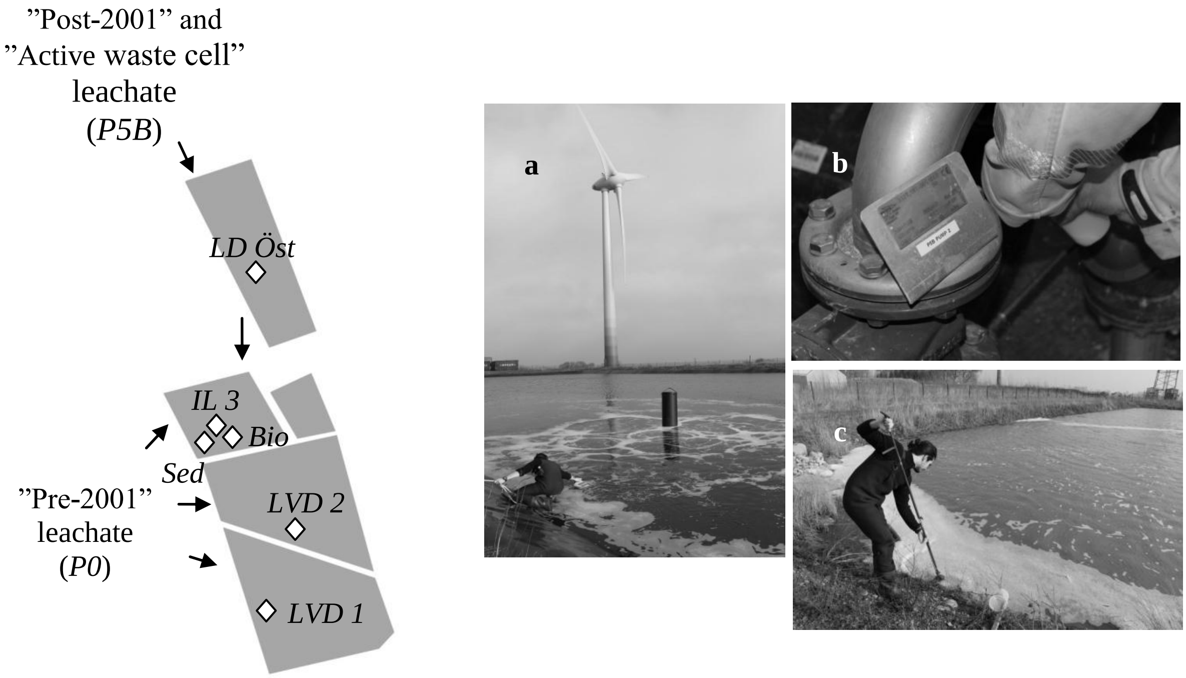


Figure 6.2. *Sampling area and strategy. To the left, the scheme indicates where the leachate for both "biotest" (white squares) and "nitrification inhibition" (P0 and P5B) has been taken; the black arrows represent the connection between the two wells collecting leachate from three landfill parts ("post-2001", "active waste cell" and "pre-2001") and the basins; compare also with figure 5.2. To the right, (a) and (b) illustrate the technique adopted for the "biotest" sampling (see section 6.2.1); insert (c) shows how leachate has been collected for the "nitrification inhibition" analysis (see section 6.2.1). Pictures taken with permission of Sysav. Author: Alessandro Sarno, Lund University.*

6.2.1 Biotest

Sampling

Three leachate water samples were taken from the aerated lagoon (*IL3*, *Bio* and *Sed*), one from the eastern basin (*LDÖst*) and two from the southern basins (*LVD1* and *LVD2*) with 5 L plastic containers; *IL3*, *LDÖst*, *LVD1* and *LVD2* represented suspended cultures and were collected in proximity of the aerators at depth between 20 and 50 cm below the water surface (see figure 6.2). *Bio* represented the biofilm adhering on the surface of the gravel laying on the edge of *IL3* which was accurately scraped off with a laboratory spatula, while *Sed* was mainly composed of bottom pebbles (~7 – 10 mm) grabbed with a wading rod endowed with a claw-like tip at one end. The samples were soon after transported and stored in cold room at 4°C.

Execution

1. **Sample pre-characterization**; once taken out from the cold room and left to reach room temperature (T= 20.3°C), all the six samples were concentrated by removing about 3 L of supernatant from the plastic containers and characterized with respect to pH, temperature, DO, SS and VSS (see Appendix Biotest). At the same time, already available data on N-NH_4 concentration were examined and a preliminary leachate analysis was performed with regard to N-NH_4 in order to calculate possible concentration adjustments. A spectrophotometer *Dr. Lange*™ and standardized *Lange*™ test cuvettes were used.
2. **Suspension preparation**; the final non-inhibitory N-NH_4 concentration in each 30 mL test tube was set to 50 mg/L (see Appendix Screening Method). Accordingly, a suspension containing ammonium sulphate $(NH_4)_2SO_4$, sodium hydrogen carbonate $NaHCO_3$, potassium dihydrogen phosphate KH_2PO_4, and sample was prepared in six different 500 mL flasks. Gentle mixing was provided to keep particles in suspension by means of magnetic stirring plates.
3. **Run**; one at a time, with one minute interval, 10 mL of suspension were pipetted into their respective 30 mL test tubes which were immediately capped and put onto a shaker with spring-clips at 238 rpm. The controls were represented by filtration of the first replicate of each series of samples at t= 0.
4. **Sample post-characterization**; after incubation times (see Appendix Biotest), the samples were sequentially filtered into glass tubes to stop the reactions and then analyzed with regard to N-NH_4.

Assumed to be due to nitrifying communities inhabiting the suspended sludge, ammonium consumption rates were quantified as g N/g VSS · h where N is ammonium nitrogen (N-NH_4).

6.2.2 Potential nitrification inhibition: the screening method

Sampling

A total of six leachate samples were collected in 0.5 L plastic bottles every third week starting at end of February: of these samples, *P0-Feb*, *-Mar*, *-Apr* represented mostly “pre-2001” leachate and *P5B-Feb*, *-Mar*, *-Apr* represented “post-2001” and “active waste cell” area (see figure 6.2 and, for further comparison, also section 5.2.1).

Execution

1. **Sludge pre-characterization and sludge suspension preparation**; in this preliminary phase, measurements of DO, SS and VSS of an already established activated sludge coming from a treatment plant in Klagshamn (Sweden) were

carried out in order to calculate the exact amounts of activated sludge and tap water to be used in the sludge suspension preparation. The final non-inhibitory N-NH_4 concentration in each 30 mL test tube was set to 50 mg/L; according to this value, 220 mL of sludge, 770 mL of tap water and 10 mL of stock solution were mixed in a flask to make 1 L of sludge suspension. Tap water was characterized for N-NO_2 and N-NO_3.

2. **Sludge suspension characterization**; the suspension was analyzed with respect to pH, temperature, SS, VSS, N-NO_2 and N-NO_3. No pH adjustments were required.
3. **Sample pre-characterization**; original samples were poured in six 75 mL beakers in order to determine their initial quality in respect of temperature and pH. Dilutions 1:5 (2 mL original sample + 8 mL deionized water) were prepared in small glass tubes for determination of COD, N-NH_4, N-NO_2 and N-NO_3. No pH adjustments were required.
4. **Run**; sample and control (tap water) in dilutions 1:2 (10 mL sample or control + 10 mL sludge suspension) were pipetted into each 30 mL test tube while gentle mixing was provided to the sludge suspension. One at a time, with one minute interval, 10 mL of sludge suspension were pipetted into the respective 30 mL test tubes which were immediately capped and put onto a shaker with spring-clips at 240 rpm. The controls at t= 0, t= 1 h and t= 2 h were determined by filtration of their respective 30 mL test tubes.
5. **Sample post-characterization**; after incubation time (2 h), the samples were sequentially filtered to stop the reactions and then analyzed with regard to pH, temperature, N-NH_4, N-NO_2 and N-NO_3.

For further explanation of the method, reference is made to Jönsson (2001).

7 Results and discussion

In this section results are presented and discussed. The following paragraphs listed below deal with: the literature work done for further contextualization of the on-site treatment plant in Hedeskoga, the water budget, the nitrogen mass balance, the nitrification and removal efficiencies, the biotest and the potential nitrification inhibition caused by different leachate qualities in the same landfill.

7.1 Case studies

Comparisons between case studies (see section 4.3) and Hedeskoga revealed an important aspect: efficiencies and performances of aerobic-based leachate treatment systems depend mainly on design characteristics typical of that particular landfill. The classic distinction between “young” and “stabilized” leachate, often found in the literature, cannot always be applied *a priori* for every landfill. Rather, site-specific conditions (such as waste cell design) must be considered to evaluate landfill leachate quality and prioritize certain types of on-site treatment technologies with respect to others. For instance, the leachate quality in the area “pre-2001” in Hedeskoga is quite different from the area “post-2001” (see figure 5.2). One important difference is that the area “post-2001” has been designed with more modern criteria of sanitary landfilling, while the waste cells in “pre-2001” was not designed to collect 50 L/m^2 of leachate. Moreover, older areas (e.g. 1972) were not provided with clay-layers lined with synthetic membranes, whereas, some tipped waste cells in “post-2001” and in the “active waste cell” were designed to reduce both precipitation and groundwater infiltration. These decisions, together with an upstream waste management policy meant to reduce the organic material disposed of in the engineered ditches (as seen for Fläskebo in section 2.3.6), have a huge impact in determining the quantity and the quality of leachate collected in both P5B and P0. A similar remark has been done by Frascari *et al.* (2004) where leachate quality was found to be changed after installation of clay-layers from 1992 and onwards. In this 10-years study, treatment of leachate by means of aerated lagoons reduced the impact of leachate on the municipal wastewater plant. For all the case studies analyzed, and particularly for those describe in section 4.3, “lagooning” was an easy-to-maintain and cheap technology capable of maintaining robust and long-term treatment in respect of both organics and ammonia nitrogen.

7.2 Water budget

Water budget calculations reflect the treatment strategy adopted in Hedeskoga: in figure 7.1 values for stored leachate (ΔV) are positive when leachate is stored during autumn and winter, and negative when there is a “loss” during summer months. Negative values are explained by the fact that only the five basins, without the spray irrigation area, were included in the simple model representing the on-site leachate treatment plant; therefore, calculations strictly regard the ensemble of aeration-equalization-storage ponds. The "loss" must rather be seen as an intentional depletion of leachate water which is ultimately used to irrigate the surrounding salix plantations. The purpose with irrigation is to ensure the intake of both dissolved ammonium and nitrate by the plant roots, at the same time, reducing the volume of leachate treated off-site. In this way, the risk that ammonia would inhibit biological nitrogen removal processes at the local wastewater treatment plant is also minimized.

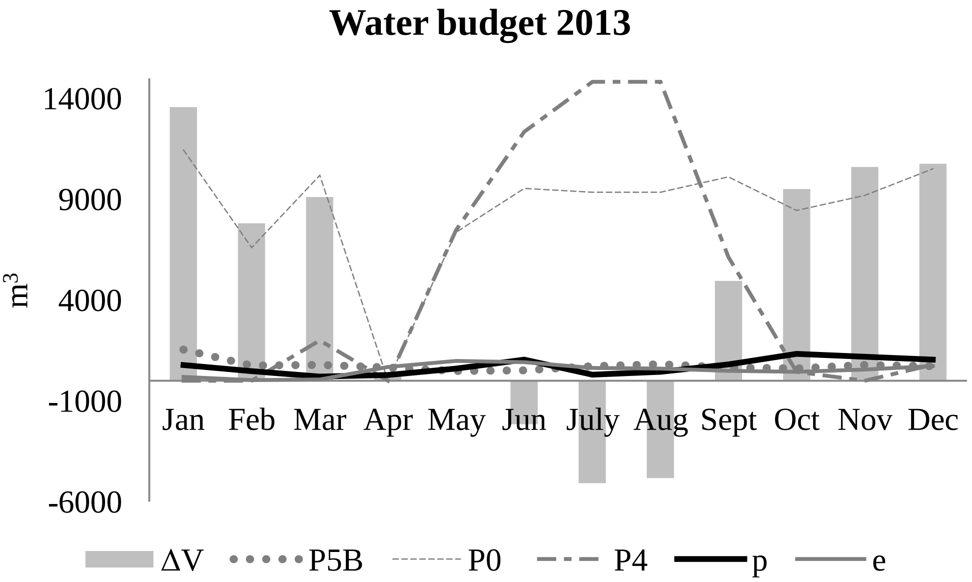


Figure 7.1. *Water budget Hedeskoga for 2013. ΔV= leachate stored by the system; P5B, P0 and p= input; P4 and e= output.*

By a performance standpoint, rounding off the basins altogether to a closed system in steady state conditions can be a good expedient for practical evaluations: assuming unchanging concentration values of soluble species (such as ammonium nitrogen) during a time interval between two measurement points is advantageous for short-term decision making (monthly basis), since leachate is not always generated in a predictable way and treatment strategies must be constantly adapted. In Robinson (1987) and Robinson and Grantham (1988) it has been shown how every landfill, although based on similar treatment implements, is a unique case and on-site treatment strategies must be set in view of: leachate characteristics, law implementations regarding landfilling practices in the country of interest, environmental standards on landfill emissions, best available technology, capital and operational costs.

The quantity of leachate pumped in to the ponds in Hedeskoga is not only a function of how much leachate is generated, but also a consequence on how much storage capacity is available. The total estimated maximum design capacity of Hedeskoga is 42 000 m^3 (see table 5.3). In figure 7.1, January represented the highest peak of stored leachate (roughly 14 000 m^3). It could be argued that leachate volumes are usually bigger after heavy rainfall as reported in Haarstad and Maehlum (1999); from September to December a net increase of precipitation (*p* curve in figure 7.1) is observed in comparison with evapotranspiration (*e* curve in figure 7.1) over a total ponds´ surface area of 13 060 m^2. However, in proportion to the total volume stored by the system, this contribution was not that relevant. Therefore, leachate volumes stored in Hedeskoga cannot overcome the total maximum design capacity of the basins. Contemporarily, hydraulic retention times (HRT) are sufficiently long to ensure enough biological breakdown in the aerated lagoons. Similar HRT values, reported in table 5.3 for Hedeskoga, were also found in Middlebrooks and Pano (1983), Eischen and Keenan (1985), and Robinson and Barr (1999) for aerated lagoons (10 – 17 days) and in Camargo and Mara (2007) for equalization ponds with larger volumes (29 – 31 days). However, it must be addressed that in Hedeskoga the flow rates have been grounded on monthly records, whereas, in the studies listed above, direct daily measurements were used for hydraulic retention time calculations. It is interesting to point out how practical experience often constitutes one of the main driving forces in this field: the monitoring of former leachate volume records together with expert judgment founded on previous years of operations, are two essential tools to ensure sufficiently good system performance in Hedeskoga.

7.3 Nitrogen mass balance

A proportional representation of both contribution (input) and losses (output) of different nitrogen species in Hedeskoga is given on a monthly basis and on a daily basis, respectively in figures 7.2 and 7.3. Compare also with numerical results summarized in tables 5.8 (monthly nitrogen balance) and 5.9 (daily nitrogen balance). The leachate quality data collected at the different pumping stations (P0, P5B and P4) are indicative of the processes happening within each basin. Although assumptions such as complete mixing and steady state conditions are applied, it is difficult to calculate accurate removal performances if flowmeters are not installed in correspondence of both influent and effluent of each basin. However, where detailed scientific investigation is not always possible, and sometimes not really necessary, due to expensive equipment or time consuming measurements, a simple nitrogen mass balance can give important information about nitrogen removal processes.

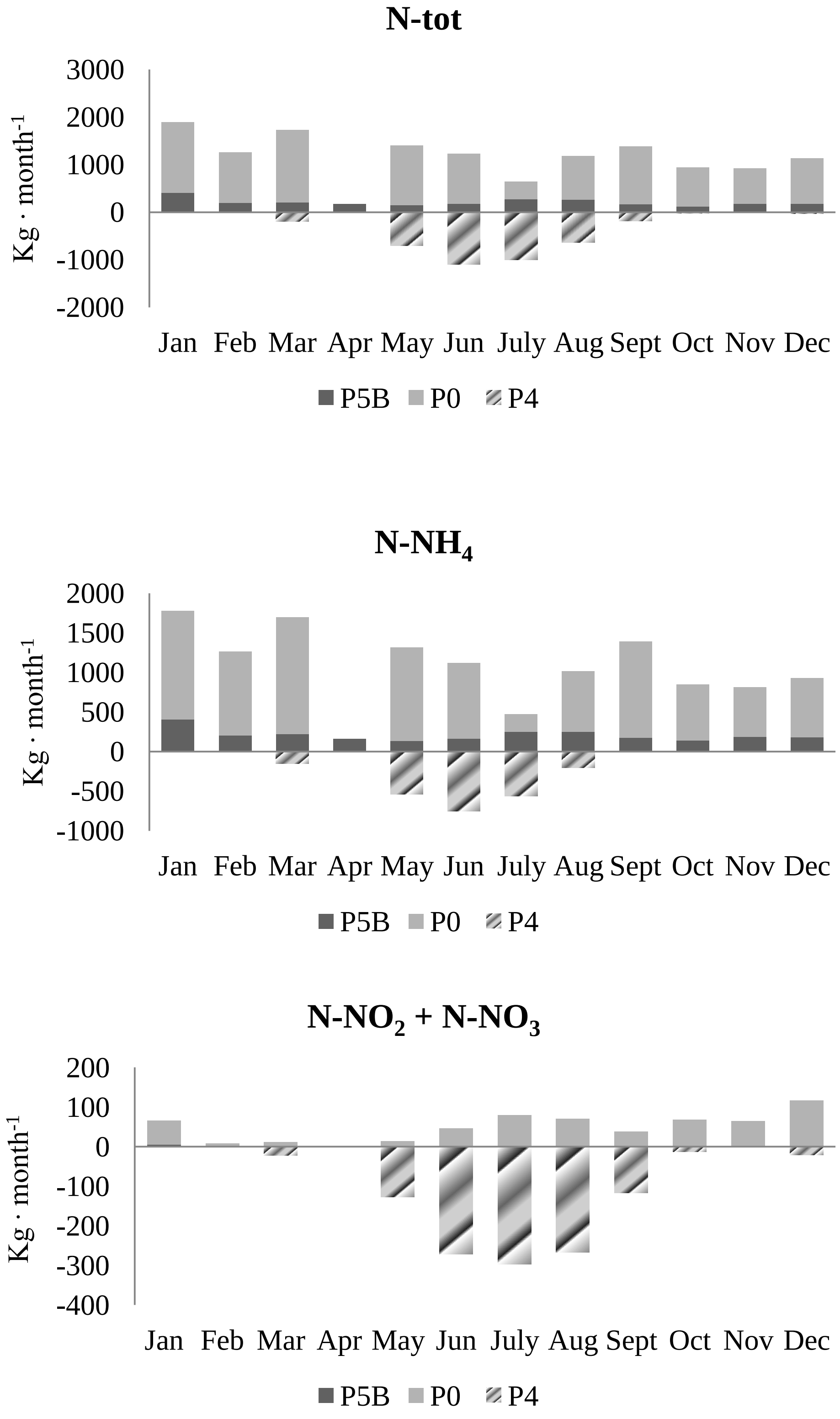


Figure 7.2. *Nitrogen balance Hedeskoga 2013. From the top, the first insert (N-tot) shows the balance for total nitrogen; the second (N-NH_4) shows the balance for ammonium nitrogen; and the third (N-NO_2+N-NO_3) indicates the amount of oxidized nitrogen. P5B and P0= input; P4= output.*

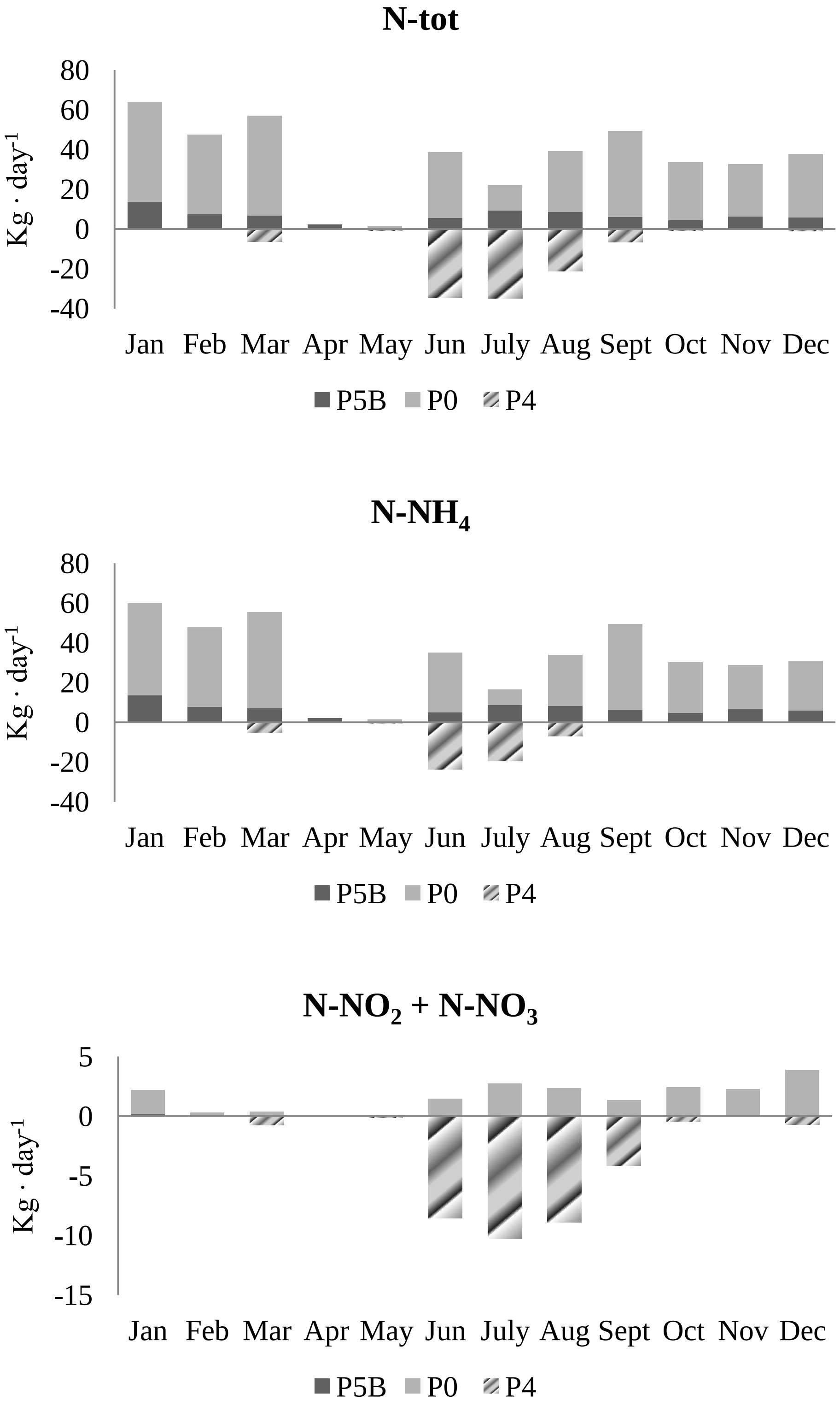


Figure 7.3. *Nitrogen balance Hedeskoga 2013. From the top, the first insert (N-tot) shows the balance for total nitrogen; the second (N-*NH_4*) shows the balance for ammonium nitrogen; and the third (N-*NO_2*+N-*NO_3*) indicates the amount of oxidized nitrogen. P5B and P0= input; P4= output.*

In figure 7.3, for all the three nitrogen species taken into account, P0 represents the highest proportion of daily Kg N- input in comparison with P5B. When using concentration values this situation is inverted: with regard to ammonium nitrogen, for instance, yearly concentration values for P5B ranged from 220 to 340 mg/L whereas for P0 oscillated between 71 and 160 mg/L (see table 5.5). Reasonably, this happens because leachate solutions are more diluted in P0 than in P5B: more leachate is collected from this well throughout the year because of the higher volume of leachate produced in less engineered waste cells (before 2001 and even older). However, it might also be the case that the model constructed here has been based on monthly leachate water records transformed into m^3/d, and nitrogen inputs do not really reflect the actual picture. The apparent and sudden nitrogen increase in P4 during summer months, as for the water budget, must be seen as an intentional depletion of leachate during the irrigation period rather than a “loss”. In correspondence of the end of treatment (Sept-Oct), the amount of $N\text{-}NH_4$ and N-tot is reduced at P4 in comparison with the treatment period (June-July-August). This means that the few nitrogen left is stored and kept in the ponds´ system when irrigation and plant growth are not favorable.

7.4 Nitrification and removal efficiencies

System efficiency has been evaluated with regard to three nitrogen species and nitrification (see table 7.1). The value corresponding to April was not reported due to no appreciable input of oxidized nitrogen.

Table 7.1. *Removal of nitrogen species and nitrification performances in Hedeskoga (%).*

	N-tot	$N\text{-}NH_4$	$N\text{-}NO_2+N\text{-}NO_3$	Nitrification
Jan	100	100	100	0
Apr	100	100	-	0
Jul	56	19	-274	63
Oct	97	100	82	1.5

By comparing table 7.1 with figure 7.2, if P4 is taken as an indication of the environment in the aerated lagoon during the treatment period when full-mixing and maximum flow regime are guaranteed, and, if oxidized nitrogen is taken as an indication of nitrification, it can be inferred that in correspondence of summer months nitrification is at its highest level in the lagoon. According to the model, 63% of nitrification is achieved in July. In fact, the proportion of oxidized nitrogen is higher than in autumn. In parallel, the proportion of ammonium decreases the more the end of the treatment is approached. Considering the oxidized nitrogen as an indication of nitrification, although risky, is not entirely wrong. Both NO_2^- and NO_3^- are products of nitrification and NO_3^- is also used as substrate for consequent denitrification if anaerobic conditions are found in the same pond. During summer months the aerated lagoon in Hedeskoga approaches temperatures of approximately 20°C. In Kim *et al.* (2008) it has been observed that between 10 and 30°C, NO_2^- oxidation is thermodynamically promoted with respect to the specific NH_4^+ oxidation because of the lower activation energy. Above 20°C both nitrification reaction steps are ensured (see section 3.1.3, *temperature*). DO values of 84% and an average pH of 8.1 are also maintained in the lagoon. Therefore, nitrification could constitute one of the major pathway by which ammonium content is reduced. Conversely, during winter, the ponds´ environment is not favorable for active nitrification, and other mechanisms for nitrogen removal should be taken into account in order to ensure sufficient treatment. Bartsch and Randall (1971) concluded that aerated lagoons may not be a feasible year-round treatment method due to excessive power input (to reach complete-mix conditions) and too long retention time. Therefore, provisions for process modification should be made in view of the winter. To sort out this problem, in Hedeskoga the use of the aerated lagoon is limited to summer months and the storage-equalization basins enable longer retention times (~30 days) in winter.

Potential treatment failure in Hedeskoga could derive from sudden ammonia load increase and a simultaneous inefficiency of the aerators (especially the ones blowing air from the bottom which provide resuspension and oxygenation better than the surface aerators) which would increase the ammonia in solution. However, the large surface area of the irrigation land function as a buffer for the Kg of N released. In any case, the ponds offer a sufficiently good initial abatement of both organics and nitrogen (mainly under the form of ammonium), and, considering the ongoing treatment improvement at the time of the writing, there is no reason to send the leachate off-site to the local wastewater treatment plant.

7.5 Biotest and potential nitrification inhibition

Biological activity of the suspended cultures has been measured as ammonium consumption rate for the different leachate treatment ponds. Resulting curves are plotted in figure 7.4. Potential nitrification inhibition is reported in figure 7.5 for both P5B and P0, which represent two different qualities of leachate treated in Hedeskoga.

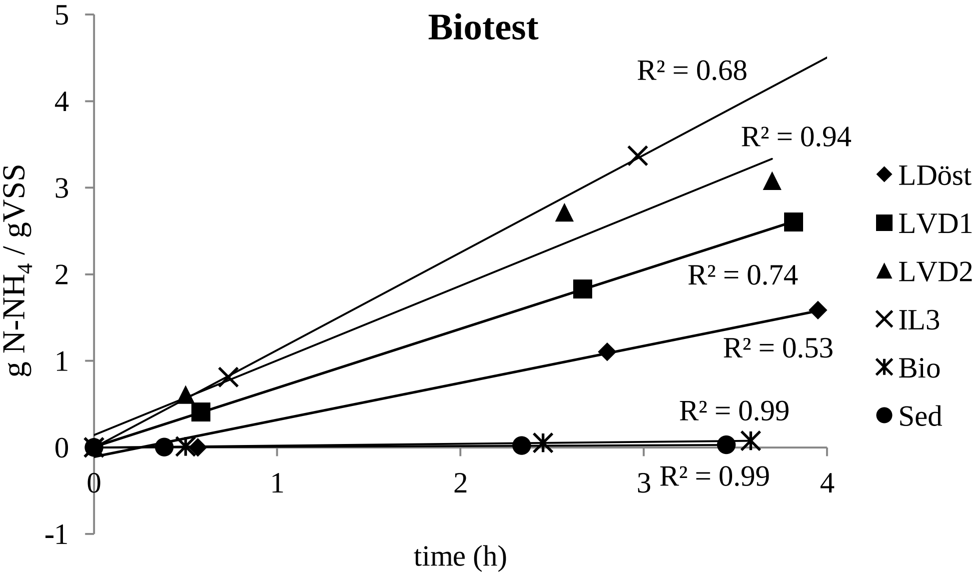


Figure 7.4. *Biotest. Ammonium consumption (y-axis) has been plotted against time (x-axis) to show the rate of biological activity detected for the different samples (see legend to the right).*

Concerning the biotest, it is interesting to see that all the samples taken in the aerated ponds show ammonium consumption rate (*LDÖst*, *LVD1*, *LVD2*, *IL3*). This could be due to active microbial communities present already in the suspended cultures or stimulated by *in vitro* nutrient addition. *Bio* and *Sed* can be excluded because non-representative of the wanted cultures in terms of SS and VSS analysis. It must be addressed that these results are obtained in a laboratory test (adapted from the screening method protocol) where the samples were provided with excess of nutrients and optimal temperature-pH conditions. Due to the experimental nature of the test, quantitative speculation on which samples has the highest or lowest rate must be "handled with care". However, it is interesting to point out how the highest rate is found in correspondence of the sample taken in IL 3, the aerated lagoon initially designed to treat leachate by means of nitrification.

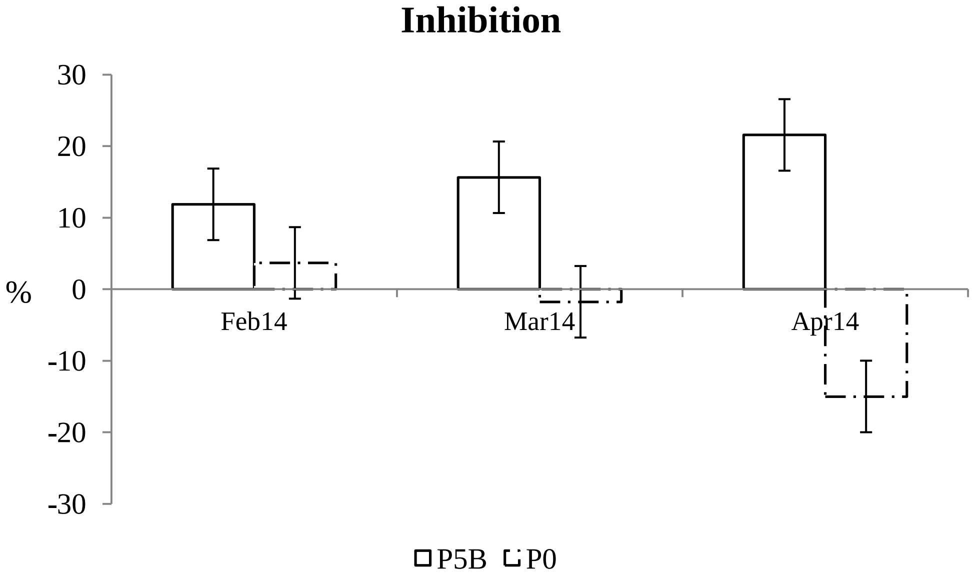


Figure 7.5. *Nitrification inhibition (%). P5B and P0 represent the two types of leachate collected and treated in Hedeskoga; the vertical bars represent the standard error= ± 5. N.B.: nitrification inhibition refers to the active nitrifiers used in the screening method which came from a sewage treatment plant in Klagshamn (Sweden).*

The two qualities of leachate in Hedeskoga, P5B and P0, were tested for potential nitrification inhibition (see figure 7.5). Significant inhibition (>5%) occurs in P5B, with increasingly high percentage going from February to April. An inhibitory value of 13% was obtained for the same type of leachate, with the same sample dilutions (1:2), in Liu (2013). No clear inhibition is observed for P0, although results from previous tests indicate 30% inhibition for the same leachate (Liu, 2013). Negative values might be explained either by the presence of a stimulatory substrate, given that leachate is an heterogeneous mix of substances, or by an experimental error. The purpose with the screening method is to recreate the right environmental conditions for nitrification (activated sludge, nutrients, pH, temperature and oxygen level) so that the major source of uncertainty can come either from the experimenter or from the quality of tested substance. If experiment accuracy is assumed, the causes for limited nitrification in P5B can be narrowed down to the leachate quality collected from the “active waste cell” and “post-2001” areas (compare with figure 5.2).

One possible reason for limited nitrification has been already identified in the high ammonium content present in the leachate coming from both P0 and P5B in Hedeskoga (Liu 2013). In Kim *et al.* (2008) the main cause for inhibition in the nitrifying landfill leachate treatment plant was attributed to high NH_4^+ load and to a substantial failure to lower its concentration in a pre-treatment aeration basin. The higher the NH_4^+ load, the higher the NH_3 (which is the form taken up by nitrifiers and by which they are inhibited), especially when a concomitant role of increasing pH promotes the conversion of NH_4^+ to NH_3. Nonetheless, a strong resistance to substrate inhibition was observed in the same study after acclimation to highly NH_4^+ concentrated waste streams, indicating that adaptation of nitrifying communities to substrate-rich conditions may occur to a certain degree. It might be the case that, although P5B collects more concentrated solutions than P0 in terms of ammonium nitrogen (see table 5.5), nitrification inhibition is not of concern when these two qualities of leachate are mixed together in the equalization basins. Moreover, the complexity of the ponds´ environment could cause a substantial decrease of ammonia level by means of other pathways such as ammonia air stripping or algae assimilation. As a result, the ammonium load received by the aerated lagoon is strongly reduced after the pre-treatment received in the equalization-aeration basins. Therefore, ammonium nitrogen concentration values in Hedeskoga are not to be considered inhibiting for the nitrogen removal processes naturally occurring in the ponds.

If Sysav keeps working with the strategy “storing during winter and treating during summer” (maintaining retention times of 10-17 days for the aerated lagoon *IL3*) and the concentrations are pretty much in the same order of magnitude detected in 2013, there will be no issues regarding high ammonia loads. The reason lies in view of the fact that:

- Aerators are active for most of the year ensuring good mixing
- The capacity of the basins (southern and eastern) are enough to store and to provide enough time for the biological breakdown
- It does not matter if nitrification and denitrification do not occur to a great extent during winter because ammonia can also be released by biomass sedimentation consequent to algae photosynthesis happening during summer months
- Once the landfill staff empty the basins by irrigating the plantations, nitrogen is under organic form (dead bacteria and algae) and further water polishing will be provided by roots adsorption in the spray irrigation land (and also by the reed bed in construction at the time of the writing)
- In other case studies, the on-site treatment plants had often smaller aerated lagoons and high concentrations of initial ammonium nitrogen (e.g. 965 mg/L in the case called "Bell House, UK" reported in section 4.3.2) but the system reached satisfactory ammonia removal anyhow.

8 Conclusions

Lagooning offers a versatile, long-term, and low-cost solution for treating landfill leachate on-site despite yearly climate fluctuations and leachate volume variations. In Hedeskoga landfill, both capacity and hydraulic retention times of the five basins are enough to store and pre-treat leachate during colder months, and to carry out aerobic treatment in the aerated lagoon during summer with a satisfactory ammonia removal.

A simple water budget and a nitrogen mass balance gave important information on the nitrogen pathways: for the on-site leachate treatment system in Hedeskoga, nitrification and denitrification are the main nitrogen removal processes occurring during summer in the ponds´ environment. Retention times longer than 30 days and temperatures lower than 5°C, enhance the possibility for ammonia nitrogen to be removed by sedimentation during winter rather than by active nitrification.

Leachate collected in P5B shows higher potential of nitrification inhibition in comparison with P0. However, this situation is not alarming when these two qualities of leachate are mixed together in the equalization basins.

Because of the standardized nature of the screening test, no direct causal relationship could be established between a toxic effect and a particular contaminant, partly because clear definitions of leachate toxicity are to date still lacking.

9 Future work

For a full biological investigation on the nitrogen removal processes occurring in Hedeskoga throughout the year, microbiological assays based on specific target genes are suggested for the identification of bacterial communities inhabiting the basins. Chlorophyll *a* (chl*a*), correlated with a measure of the volatile suspended solids (VSS), could be used as an indicator for algal biomass growth and comparison could be made between the treatment period (warmer months) and the storage-equalization period (colder months) to see how much nitrogen leaves the ponds through biomass settlement (since the last pond is a sedimentation basin). Consequently, it might be decided when and for how long the working load of the aerators can be reduced since nitrification-denitrification in that case will not be the main pathways for nitrogen to be removed by the system. Monthly measurements of ammonia air stripping grounded on temperature, pH and fraction of ammonium nitrogen transformed into ammonia could be useful to clarify the actual ammonia emissions from the ponds, although the Swedish climate hardly reaches temperature as high as to promote this mechanism to a significant extent. Ponds could be seen more as active ecosystems rather than artificial tanks filled up with leachate.

The concept of leachate toxicity is not easily definable. At the moment, the best way is to consider this substance as an heterogeneous mixture of chemicals having potential to cause harm to both environment and human health if not treated. However, for pragmatic reasons often regarding the achievement of controlled landfill emissions, standard screening tests aimed to identify any issues related to inhibition of biological treatment are still the best available option in terms of responsiveness and analysis costs.

10 Reference list

Almqvist, A. 2013, Sysav, personal communication.

Avfall Sverige, 2009, "Kvalitet i nya deponiers lakvatten – exemplet Fläskebo", rapport 2009:03, http://www.avfallsverige.se/fileadmin/uploads/Rapporter/Deponering/D2009-03.pdf, accessed June 2014

Bartsch, E.H. and Randall, C.W. 1971, "Aerated Lagoons: A Report on the State of the Art", *Journal (Water Pollution Control Federation)*, vol. 43, pp. 699-708.

Camargo Valero, M.A. and Mara, D.D. 2010a, "Ammonia volatilization in waste stabilization ponds: A cascade of misinterpretations? ", *Water science and technology*, vol. 61, pp. 555-561.

Camargo Valero, M.A. and Mara, D.D. 2007, "Nitrogen removal via ammonia volatilization in maturation ponds", *Water science and technology*, vol. 55, pp. 87-92.

Camargo Valero, M.A., Mara, D.D. and Newton, R.J. 2010b, "Nitrogen removal in maturation waste stabilization ponds via biological uptake and sedimentation of dead biomass", *Water science and technology*, vol. 61, pp. 1027-1034.

Chiu, Y. and Chung, M. 2003, "Determination of optimal COD/nitrate ratio for biological denitrification", *International Biodeterioration and Biodegradation*, vol. 51, pp. 43-49.

Craggs, R. 2005, "Nutrients", in: Shilton, A. (ed.), "Pond treatment technology", IWA publishing, London, pp. 77-99.

Environmental Agency UK, 2006, "Guidance for the treatment of landfill leachate", https://www.gov.uk/government/organisations/environment-agency, accessed February 2014.

European Environmental Agency, 2013, "Environmental terminology and discovery service", http://glossary.eea.europa.eu/terminology/concept_html?term=landfill%20leachate, accessed March 2013.

Eischen, G.W. and Keenan, J.D. 1985, "Monitoring aerated lagoon performance", *Journal (Water Pollution Control Federation)*, vol. 57, pp. 876-881.

Emerson, K., Russo, R.C., Lund, R.E. and Thurston, R.V. 1975, "Aqueous ammonia equilibrium calculations: effect of pH and temperature", *Journal of the Fisheries Board of Canada*, vol. 32, pp. 2379-2383.

Frascari, D., Bronzini, F., Giordano, G., Tedioli, G. and Nocentini, M. 2004, "Long-term characterization, lagoon treatment and migration potential of landfill leachate: a case study in an active Italian landfill", *Chemosphere,* vol. 54, pp. 335-343.

Gayle, B., Boardman, G., Sherrard, J. and Benoit, R. 1989, "Biological denitrification of water", *Journal of Environmental Engineering,* vol. 115, pp. 930-943.

Haarstad, K. and Maehlum, T. 1999, "Important aspects of long-term production and treatment of municipal solid waste leachate", *Waste Management and Research,* vol. 17, pp. 470-477.

Hanaki, K., Wantawin, C. and Ohgaki, S. 1990, "Nitrification at low levels of dissolved oxygen with and without organic loading in a suspended-growth reactor", *Water research,* vol. 24, pp. 297-302.

Hiscock, K., Lloyd, J. and Lerner, D. 1991, "Review of natural and artificial denitrification of groundwater", *Water research,* vol. 25, pp. 1099-1111.

Hogland, W. 2002, "Remediation of an old landsfill site", *Environmental Science and Pollution Research,* vol. 9, pp. 49-54.

Jokela, J.P.Y., Kettunen, R.H., Sormunen, K.M. and Rintala, J.A. 2002, "Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification", *Water research,* vol. 36, pp. 4079-4087.

Juretschko, S., Timmermann, G., Schmid, M., Schleifer, K.H., Pommerening-Roser, A., Koops, H.P. and Wagner, M. 1998, "Combined molecular and conventional analyses of nitrifying bacterium diversity in activated sludge: Nitrosococcus mobilis and Nitrospira-like bacteria as dominant populations", *Applied and Environmental Microbiology,* vol. 64, pp. 3042-3051.

Jönsson, K. (2001), "Inhibition of Nitrification in Municipal Wastewater – Sources, Effects, Evaluation and Remedies", *Doctoral thesis,* ISSN 1650-1650, ISBN 91-7874-127-0.

Kim, D., Lee, D. and Keller, J. 2006, "Effect of temperature and free ammonia on nitrification and nitrite accumulation in landfill leachate and analysis of its nitrifying bacterial community by FISH", *Bioresource technology,* vol. 97, pp. 459-468.

Kim, J., Guo, X. and Park, H. 2008, "Comparison study of the effects of temperature and free ammonia concentration on nitrification and nitrite accumulation", *Process Biochemistry,* vol. 43, pp. 154-160.

Knowles, R. 1982, "Denitrification", *Microbiological reviews,* vol. 46, pp. 43-70.

Knox, K. 1985, "Leachate treatment with nitrification of ammonia", *Water research,* vol. 19, pp. 895-904.

Koenig, A. and Liu, L. 1996, "Autotrophic denitrification of landfill leachate using elemental sulphur", *Water Science and Technology,* vol. 34, pp. 469-476.

Kurniawan, T. 2011, "Biological treatments", in: Kurniawan, T. (ed.), "Treatment of landfill leachate", LAP LAMBERT Academic Publishing, Germany, pp. 110-127.

Kurniawan, T.A., Lo, W., Chan, G. and Sillanpää, M.E. 2010, "Biological processes for treatment of landfill leachate", *Journal of Environmental Monitoring,* vol. 12, pp. 2032-2047.

Landfill directive 1999/31/EC (European Commission), 1999, "Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste", http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:31999L0031, accessed February 2014.

Leander, P. 2013, Sysav, personal communication.

Leite, V., Pearson, H., De Sousa, J., Lopes, W. and De Luna, M. 2011, "The removal of ammonia from sanitary landfill leachate using a series of shallow waste stabilization ponds", *Water Science and Technology,* vol. 63, pp. 666-670.

Liu, S. 2013, "Landfill leachate treatment methods and evaluation of Hedeskoga and Måsalycke landfills", *Master thesis,* Lund University (LTH).

Martins, C.L., Fernandes, H. and Costa, R.H. 2013, "Landfill leachate treatment as measured by nitrogen transformations in stabilization ponds", *Bioresource technology,* vol. 147, pp. 562-568.

Mehmood, M., Adetutu, E., Nedwell, D.B. and Ball, A.S. 2009, "In situ microbial treatment of landfill leachate using aerated lagoons", *Bioresource technology,* vol. 100, pp. 2741-2744.

Middlebrooks, E.J. and Pano, A. 1983, "Nitrogen removal in aerated lagoons", *Water research,* vol. 17, pp. 1369-1378.

Narasiah, K.S. and Larue, M. 1982, "Oxygen up-take and heat loss observations in an aerated lagoon", *Biotechnology Letters,* vol. 4, pp. 425-429.

Narasiah, K.S., Marin, M. and Shoiry, J. 1990, "Sludge accumulation in aerated facultative lagoons operating in colder climate", *Water Science and Technology,* vol. 22, pp. 77-82.

Nilsson, P. 2013, VA-Vattevård, personal communication.

Nilsson, T. 2013, Sysav, personal communication.

Park, H. and Noguera, D.R. 2004, "Evaluating the effect of dissolved oxygen on ammonia-oxidizing bacterial communities in activated sludge", *Water research,* vol. 38, pp. 3275-3286.

Parkes, S.D., Jolley, D.F. and Wilson, S.R. 2007a, "Inorganic nitrogen transformations in the treatment of landfill leachate with a high ammonium load: A case study", *Environmental monitoring and assessment,* vol. 124, pp. 51-61.

Prosser, I. 1989, "Autotrophic nitrification in bacteria", *Adv in Microbial physiology,* vol. 30, pp. 125.

Renou, S., Givaudan, J., Poulain, S., Dirassouyan, F. and Moulin, P. 2008, "Landfill leachate treatment: Review and opportunity", *Journal of hazardous materials,* vol. 150, pp. 468-493.

Robinson, H. and Barr, M. 1999, "Aerobic biological treatment of landfill leachates", *Waste management and research,* vol. 17, pp. 478-486.

Robinson, H. 2007, "The composition of leachates from very large landfills: an international review", *Communications in waste and resource management,* vol. 8, pp. 19-32.

Robinson, H. 1987, "Design and operation of leachate control measures at Compton Bassett landfill site, Wiltshire, UK", *Waste Management and Research,* vol. 5, pp. 107-122.

Robinson, H.D. and Grantham, G. 1988, "The treatment of landfill leachates in on-site aerated lagoon plants: experience in Britain and Ireland", *Water research,* vol. 22, pp. 733-747.

Schiopu, A. and Gavrilescu, M. 2010, "Options for the treatment and management of municipal landfill leachate: common and specific issues", *Clean–Soil, Air, Water,* vol. 38, pp. 1101-1110.

SFS 2001: 512 (Naturvårdsverket), 2004, "Deponering av avfall", http://www.swedishepa.se/Legislation/Guidance/Avfall/Landfilling/, accessed April 2014.

SMHI, 2013, "Vattenbalans med avdunstning för deponier", http://www.smhi.se/professionella-tjanster/professionella-tjanster/statistik-och-data, accessed April 2014.

Smith, P.G. and Arab, F.K. 1988, "The role of air bubbles in the desorption of ammonia from landfill leachates in high pH aerated lagoon", *Water, air, and soil pollution,* vol. 38, pp. 333-343.

Sundberg, C., K Stendahl, J.S., Tonderski, K. and Lindgren, P. 2007a, "Overland flow systems for treatment of landfill leachates—potential nitrification and structure of the ammonia-oxidising bacterial community during a growing season", *Soil Biology and Biochemistry,* vol. 39, pp. 127-138.

Sundberg, C., Tonderski, K. and Lindgren, P. 2007b, "Potential nitrification and denitrification and the corresponding composition of the bacterial communities in a compact constructed wetland treating landfill leachates", *Water Science and Technology,* vol. 56, pp. 159-166.

Sutka, R., Ostrom, N., Ostrom, P., Gandhi, H. and Breznak, J. 2003, "Nitrogen isotopomer site preference of N_2O produced by Nitrosomonas europaea and Methylococcus capsulatus Bath", *Rapid Communications in Mass Spectrometry,* vol. 17, pp. 738-745.

Sysav, 2003 to 2013, "Miljörapporterna Hedeskoga" (Environmental reports), http://www.sysav.se/Om-oss/Kontakt/, accessed February 2014.

Swedish Water and Wastewater Association (Svenskt Vatten), 2013, "What is REVAQ?", http://www.svensktvatten.se/Vattentjanster/Avlopp-och-Miljo/REVAQ/om-REVAQ/, accessed February 2014.

Takamizawa, K., Mori, S., Fukunaga, I. and Inoue, Z. 1991, "Plankton and macrobenthos in the combined facultative pond and aerated lagoon system at a sea-based solid waste disposal site", *Environmental technology,* vol. 12, pp. 97-105.

Thorneby, L., Hogland, W., Stenis, J., Mathiasson, L. and Somogyi, P. 2003, "Design of a reverse osmosis plant for leachate treatment aiming for safe disposal", *Waste management and research: the journal of the International Solid Wastes and Public Cleansing Association, ISWA,* vol. 21, pp. 424-435.

US Environmental Protection Agency, 2013, "Waste and Cleanup Risk Assessment", http://www.epa.gov/oswer/riskassessment/index.htm, accessed March 2014.

Valero, M., Read, L., Mara, D., Newton, R., Curtis, T. and Davenport, R. 2010, "Nitrification-denitrification in waste stabilization ponds: a mechanism for permanent nitrogen removal in maturation ponds", *Water Science and Technology,* vol. 61, pp. 1137-1146.

Welander, U., Henrysson, T. and Welander, T. 1997, "Nitrification of landfill leachate using suspended-carrier biofilm technology", *Water research,* vol. 31, pp. 2351-2355.

Wiszniowski, J., Robert, D., Surmacz-Gorska, J., Miksch, K. and Weber, J. 2006, "Landfill leachate treatment methods: A review", *Environmental Chemistry Letters,* vol. 4, pp. 51-61.

Xie, S., Zhang, X. and Wang, Z. 2003, "Temperature effect on aerobic denitrification and nitrification", *Journal of Environmental Sciences,* vol. 15, pp. 669-673.

Ystad Kommun, 2013, "Allmänna Bestämmelser för brukande av Allmänna Vatten- och Avloppsanläggningar (ABVA)", http://www.ystad.se/boende--miljo/vatten-och-avlopp/lagar-och-regler/abva/, accessed June 2014.

Zimmo, O., Van der Steen, N. and Gijzen, H.J. 2003, "Comparison of ammonia volatilization rates in algae and duckweed-based waste stabilization ponds treating domestic wastewater", *Water research*, vol. 37, pp. 4587-4594.

Zimmo, O.R., Van Der Steen, N.P. and Gijzen, H.J. 2004, "Quantification of nitrification and denitrification rates in algae and duckweed based wastewater treatment systems", *Environmental technology*, vol. 25, pp. 273-282.

11 Table of abbreviations

Alkalinity ($CaCO_3$ or HCO_3^-): is the capacity of an aqueous solution to neutralize acidity. In wastewater science this parameter can be estimated by measuring the concentration of carbonates in a system and usually it is expressed in mg/L.

Ammoniacal nitrogen or ammonia nitrogen ($N\text{-}NH_3$): in wastewater and leachate treatment it is the measure of an inorganic (see headword "inorganic nitrogen"), undissociated form of ammonia that can be found in water. Undissociated ammonia is the form taken up by microorganisms (bacteria and algae). The letter "N" before "NH_3" signifies that the parameter is calculated in terms of mass of N.

Ammonium nitrogen ($N\text{-}NH_4$): in wastewater and leachate treatment, it is the measure of an inorganic (see headword "inorganic nitrogen"), dissolved form of nitrogen that can be found in water.

BOD/COD ratio: in waste science, it is a unitless parameter that identifies the degree of release of recalcitrant substance by a landfill which can be indicative (in some cases) of the biological decomposition state of the landfill.

Biochemical Oxygen Demand (BOD): a measure of how much dissolved oxygen is being consumed as microbes break down organic matter. In water science, it is expressed in terms of concentration, usually mg/L.

Biological nitrogen removal (BNR): it is a term that identifies the ensemble of engineering strategies designed to treat wastewater in respect of nitrogen by means of artificial or semi-natural technologies.

Chemical oxygen demand (COD): it is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant, usually potassium permanganate. It gives information about organic compounds contained in leachate.

Chlorides (Chlor): Chloride is a salt compound resulting from the combination of the gas chlorine and a metal. It is usually expressed as mg/L.

Chlorophyll *a* (chl*a*): chlorophyll *a* is the green pigment in plants that is used for photosynthesis. Chlorophyll *a* is used in water science as an indicator of the total quantity of algae and it is commonly expressed in terms of µg/L.

Compacted Constructed wetlands (CCWs): also called reed beds or simply constructed wetlands, they basically are aquatic ecosystems designed to treat wastewater by means of various aquatic macrophytes species, most commonly *Phragmites australis*. Usually they constitute the last polishing step in on-site biological landfill leachate treatment.

Conductivity (Cond): it is a property of matter to conduct electricity. In water science, it gives information about the ionic content of an aqueous solution by measuring its electrolytical content; for leachate it is usually expressed in the order of milliSiemens per meter (mS/m).

Dissolved oxygen concentration (DO): in wastewater and leachate treatment context it represents the oxygen content in aqueous solution, usually measured by means of oxygen-meters and expressed most commonly in terms of % or mg/L.

Fatty acids (FAs): molecules characterized by carbon chains of various length originating from the anaerobic degradation of organic matter. Present in wastewater and leachate water, they are indicative of biological processes in the activated sludge. They can be determined through different analytical techniques, among others, distillation and chromatography. Usually, they are expressed in mg/L.

Hydraulic retention time (HRT or sometimes HRT_{th}): it is the average time during which a soluble compound is retained in a constructed bioreactor. In steady-flow conditions is calculated as the volume of the bioreactor divided by the influent flow rate.

Inorganic nitrogen: it is one of the three main fractions in which total nitrogen (see headword “total nitrogen”), present in both terrestrial and marine ecosystems, is divided: organic, mineral and inorganic nitrogen; in turn, inorganic nitrogen is subdivided in free ammonia (i.e. unionized NH_3, undissociated ammonia, ammonia or simply NH_3), ammonium (i.e. ionized ammonia, dissociated ammonia, ammonium ion, $NH_4^+{}_{(aq)}$ or simply NH_4^+), dinitrogen gas (N_2), nitrous oxide (N_2O), nitric oxide (NO), nitrite (NO_2^-), nitrate (NO_3^-). In wastewater and leachate water treatment it is also expressed as the sum of $N\text{-}NH_4^+$, $NO_2\text{-}N$ and $NO_3\text{-}N$.

MV-irrigation system: from the Swedish “Mark-Vatten” = “soil-water”, an area within the landfill site where both salix and grassland plantations are sprayed with treated leachate; it is used as ultimate step in the treatment process in Hedeskoga during the growing season. It goes also under the name of “energy crops system”.

Nitrate nitrogen ($NO_3\text{-}N$): parameter used in wastewater and leachate water science to estimate the concentration of NO_3^- ions. It is usually expressed as mg/L. The letter “N” before “NO_3” signifies that the parameter is calculated in terms of mass of N.

Nitrite nitrogen ($NO_2\text{-}N$): parameter used in wastewater and leachate water science to estimate the concentration of NO_2^- ions. It is usually expressed as mg/L. The letter “N” before “NO_2” signifies that the parameter is calculated in terms of mass of N.

Organic nitrogen: it is the byproduct of living organisms. It includes such natural materials as proteins and peptides, nucleic acids and urea, and numerous synthetic organic materials.

Phosphorus (P-tot or $P\text{-}PO_4$): Chemical element that can be found in wastewater partly as organically bound form (e.g. in algae), and partly as inorganic form of polyphosphates and orthophosphates (e.g. in detergents). Its concentration is measured either as mg/L of total phosphorus (P-tot) or as mg/L of phosphorus as phosphates (P-PO_4).

Suspended solids (SS): it is a measure of the concentration of solid particles in wastewater and is expressed as mg/L.

Total ammonia (tot-NH_3): the sum between unionized and ionized ammonia concentrations (see headword "inorganic nitrogen").

Total Kjeldahl nitrogen (TKN): in wastewater management, it is a parameter that identifies the sum of organic nitrogen and ammonium nitrogen (see headword "ammonium nitrogen"). The analytical method used is named after Johan Kjeldhl, a Danish chemist lived in the 19th century. It is commonly expressed in mg/L.

Total nitrogen (N-tot): it is the sum of organic nitrogen and nitrogen in the form of ammonium, nitrite and nitrate (see headword "inorganic nitrogen") expressed in mg/L.

Total organic carbon (TOC): in water science, it is a parameter indicating the organic matter content of a solution, which is determined by measuring the amount of carbon dioxide generated by burning a sample. It is usually expressed in mg/L.

Sulphates (SO_4^{2-}): one of the most common fraction of sulphur (S) encountered in aquatic environments in a dissolved form. Together with fatty acids and amines are responsible for the strong odor in leachates. It is usually expressed in mg/L.

Volatile suspended solids (VSS): in wastewater science, it is the measure of organic content of the activated sludge, and in most cases can be equated to the bacterial content. They constitute a fraction of the suspended solids. They can be quantified after burning the samples in a furnace at 550 °C.

12 Appendices

Biotest

Field equipment:

- 5 L plastic containers
- 0.5 L plastic bottles
- laboratory spatula
- wading rod with a claw-like tip at one end
- waders

Laboratory equipment:

- 30 mL glass reaction tubes with screw stoppers
- rakes
- shaker with spring-clips
- timers
- micropipettor and pipettes
- pH-meter
- oxygen-meter (with thermometer included)
- magnetic stirring plates
- analytical scale
- filtering flasks, filter funnel buchner, clamps and membrane filters (particle retention= 1.6 µm) for membrane filtration
- graduate cylinders (100 ± 0.5 mL)
- beakers and flasks (various sizes)
- round filters, funnels and glass tubes
- oven at 105°C
- muffle furnace at 550°C
- desiccators
- spectrophotometer *Dr. Lange*™
- standardized *Lange*™ test cuvettes for $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$ and COD analysis

Reagents

- ammonium sulphate, $(NH_4)_2SO_4$
- sodium hydrogen carbonate, $NaHCO_3$
- potassium dihydrogen phosphate, KH_2PO_4
- distilled water
- deionized water
- tap water

Table 13.1. *Samples pre-characterization. All the measurements were done in triplicates and the numbers do represent average values.*

Sample	pH	DO (mg/L)	T (°C)	SS (mg/L)	VSS (mg/L)
IL3	8	10.5	20.1	70	28
LDÖst	7.9	10.2	19.2	425	141
LVD1	7.9	10.9	20.3	303	61
LVD2	7.7	10.4	20.3	369	55
Bio	7.9	7.0	20.1	13 692	1 250
Sed	7.7	6.8	19.9	39 958	2 467

Table 13.2. *Amounts of chemicals used to prepare the nutrient-enriched sample suspensions.*

Sample	$(NH_4)_2SO_4$ (g)	$NaHCO_3$ (g)	KH_2PO_4 (g)	sample vol. (mL)
IL3	-	0.336	0.022	up to 500
LDÖst	0.118	0.336	0.022	up to 500
LVD1	-	0.336	0.022	up to 500
LVD2	-	0.336	0.022	up to 500
Bio	-	0.336	0.022	up to 500
Sed	-	0.336	0.022	up to 500

Table 13.3. *Working protocol; each sample was run in four replicates at 1 min interval one each other.*

Sample	label	start (min)	end (min)	tot. reaction time (min)
IL3	A0	0	0	0
	B	1	45	44
	C	2	180	178
	D	3	251	248
LDÖst	A0	11	11	0
	B	12	46	34
	C	13	181	168
	D	14	251	237
LVD1	A0	20	20	0
	B	21	56	35
	C	22	182	160
	D	23	252	229
LVD2	A0	27	27	0
	B	28	58	30
	C	29	183	154
	D	30	252	222

Bio	A0	35	35	0
	B	36	66	30
	C	37	184	147
	D	38	253	215
Sed	A0	43	43	0
	B	44	67	23
	C	45	185	140
	D	46	253	207

Screening method

The main principle behind this method resides in the quantification of bacterial nitrification rates which are given by either oxidized nitrogen (NO_x-N) increase or ammonium nitrogen ($N\text{-}NH_4$) decrease per sludge concentration (VSS) and time (h):

mg N-NO_x/g VSS · h

mg N-NH_4/g VSS · h

Both of the expressions above can be used when testing acute inhibiting effects on nitrifying activated sludge in industrial and domestic wastewater. This method can also be adapted to test other substances that are considered to affect nitrifiers activity, such as leachate water.

The main abiotic factors affecting the experiment´s performance are:

- Molecular oxygen; a concentration of 3-4 mg/L is enough to ensure an efficient nitrification. If oxygen level is too low, heterotrophic bacteria can shift the reaction equilibrium towards the formation of dinitrogen gas (i.e. denitrification).
- Ammonium; too high ammonium concentration can strongly hamper nitrification rates. Normally, tests are conducted with an ammonium concentration as high as 50 mg/L or lower.
- Alkalinity; nitrification is an acidic process, therefore sufficient alkalinity must be provided from the very beginning of the experiment to buffer dramatic pH drops.
- pH; nitrification proceeds at an optimal pH of 7.5 ± 0.5.
- Temperature; the experiment has to be conducted at room temperature, between 20 and 25^{o}C, although variation of more than ± 0.5 are not permitted during the experiment.

Hedeskoga

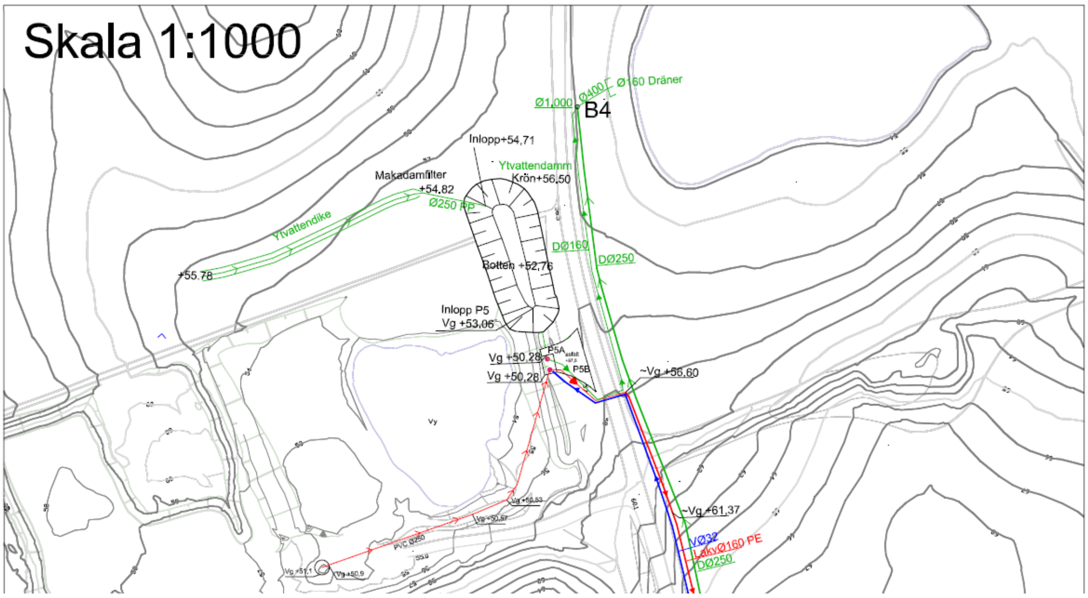


__Figure 13.1.__ Topographic map of the northernmost area of the landfill showing the construction of a drainage pipeline that connects the active waste cell to the pumping station P5B; the highest and the lowest points in the northern area are respectively 60 and 53 m above the sea level. Picture from Nilsson, P. 2013, VA-Vattevård. Elaborated with permission of the author.

Investigation of an on-site landfill leachate treatment plant

Alessandro Sarno

Department of Chemical Engineering, Lund University, Sweden

May 2014

Abstract

A water budget and a nitrogen mass balance underlined that nitrification and denitrification are the main nitrogen removal processes occurring during summer months in Hedeskoga, a Swedish landfill provided with a series of aeration ponds and a spray irrigation area meant to treat leachate on-site. Retention times longer than 30 days and temperatures lower than 5°C enhance the possibility for ammonia nitrogen to be removed by sedimentation during winter rather than by active nitrification. Further biological assays should be made in the future to elucidate just as important nitrogen removal pathways within the ponds, such as ammonia volatilization and algae nitrogen assimilation.

Keywords: on-site treatment, landfill leachate, aerated lagoon, nitrification, nitrogen removal, waste stabilization pond, nitrogen mass balance, ammonia

Introduction

In Sweden, discharge concentration limits for municipal wastewater treatment plants have been tighten in order to meet higher effluent and sludge quality standards [1]. According to the national regulatory framework, wastewater facilities may decide at the local level whether accept or not influents reputed to interfere with activated sludge based treatment methods [2]. Landfill leachate, a liquid emission generated as a consequence of water infiltration and biological breakdown in the waste body, contains potentially harmful and inhibitory compounds and environmental pollutants such as man-made organics, heavy metals, and ammonia [3]. Therefore, there is a growing interest in investigating actual capacities of landfills to treat leachate on-site rather than off-site, especially with regard to ammonia which is a potential inhibitor of nitrification [4]. Since the 1980s, lagooning represents among biological treatment methods a versatile, long-term, and low-cost solution for removing organics and ammonia despite yearly climate fluctuations and leachate volume variations [5]. The pathways by which ammonia is removed in aerated lagoons, and generally in waste stabilization ponds, are: nitrification, denitrification, algae nitrogen assimilation with consequent sedimentation of dead biomass, and ammonia air stripping [6], [7]. The purpose of this investigation is to verify that nitrification is the main ammonia removal pathway which occurred in the aeration ponds destined to self-management of leachate in Hedeskoga landfill throughout 2013.

Material and Methods

Hedeskoga is a small village situated 3 km north of Ystad, Sweden. The landfill occupies an area of 21 ha and can be divided into three parts: an asphalted area composed of old waste cells (the first dates back to 1972), an area which to date is partly covered by grassland and by asphalt, and an operational partly-tipped area with one active waste cell. Leachate drains into two main pipelines, P0 and P5B, which are connected to their respective wells. From the wells, leachate is pumped in to the on-site treatment plant constituted of one eastern basin, two southern basins, an aerated lagoon and a sedimentation basin. P4 is the ultimate well which pumps leachate towards a spray irrigation land composed of salix plantations. The leachate quality at both influent (P5B and P0) and effluent (P4) is shown in table 1. For those months where leachate quality data was lacking, interpolation (linear regression) was used between known concentration values.

Table 1. Leachate quality at the influent (P5B and P0) and at the effluent (P4) in Hedeskoga. All the parameters are expressed in mg/L except pH and conductivity (Cond= mS/m). The values in *italics* for the four nitrogen species were obtained by interpolating known values. The negative symbols must be read as “less than”.

P5B	pH	Cond	BOD$_7$	COD	TOC	Chlo	SS	HCO$_3$	N-tot	N-NH$_4$	N-NO$_2$	N-NO$_3$
Jan	7.5	924	58	680	160	940	60	2 800	260	260	0.9	2.2
Feb	-	-	-	-	-	-	-	-	*260*	*267*	0.6	*1.4*
Mar	-	-	-	-	-	-	-	-	*260*	*274*	0.3	*0.6*
Apr	7.5	878	67	730	220	930	58	2 500	260	240	0.0	-0.2
May	-	-	-	-	-	-	-	-	*296*	273	0.0	-0.2
June	-	-	-	-	-	-	-	-	*332*	306	0.0	-0.2
July	7.3	970	86	810	200	1 000	28	3 500	370	340	0.0	-0.2
Aug	-	-	-	-	-	-	-	-	*313*	*300*	0.0	*-0.1*
Sept	-	-	-	-	-	-	-	-	*256*	*260*	0.0	*0.0*
Oct	7.2	832	73	680	180	870	35	2 600	200	220	0.0	0.1
Nov	-	-	-	-	-	-	-	-	*224*	*235*	0.0	*0.2*
Dec	-	-	-	-	-	-	-	-	*248*	*250*	0.1	*0.3*

P0	pH	Cond	BOD$_7$	COD	TOC	Chlo	SS	HCO$_3$	N-tot	N-NH$_4$	N-NO$_2$	N-NO$_3$
Jan	8.5	337	14	200	58	370	94	1 300	130	120	0.1	5.2
Feb	8.1	390	16	230	71	410	73	1 900	160	160	0.0	1.0
Mar	-	-	-	-	-	-	-	-	*150*	*145*	*0.1*	*1.0*
Apr	7.2	357	13	220	72	370	39	1 500	140	130	0.2	1.0
May	7.6	353	10	260	40	430	98	1 800	170	160	0.1	1.8
June	7.2	352	12	210	61	400	61	1 400	110	100	0.3	4.6
July	7.7	187	13	360	86	300	280	640	40	24	0.4	8.1
Aug	7.0	354	15	210	34	460	55	1 200	98	82	0.3	7.2
Sept	7.3	384	14	250	69	470	79	1 400	120	120	0.2	3.5
Oct	7.6	349	11	220	63	430	90	1 300	97	84	0.1	7.9
Nov	7.9	304	5	160	55	360	42	1 000	81	68	0.1	6.9
Dec	7.8	298	7	180	66	370	50	1 000	91	71	0.2	11.0

P4	pH	Cond	BOD$_7$	COD	TOC	Chlo	SS	HCO$_3$	N-tot	N-NH$_4$	N-NO$_2$	N-NO$_3$
Jan	8.1	278	8	170	52	360	32	830	100	80	0.1	11.0
Feb	8.2	256	11	170	50	330	26	770	96	75	0.1	11.0
Mar	-	-	-	-	-	-	-	-	*97*	*78*	*0.2*	*11.0*
Apr	8.2	250	7	220	61	350	61	710	98	80	0.3	11.0
May	8.1	228	7	180	47	370	27	690	95	72	1.0	16.0

June	8.2	278	6	190	56	400	30	670	89	61	2.5	19.0
July	7.4	287	9	240	74	460	34	630	68	38	1.5	18.0
Aug	8.0	278	15	230	55	440	43	590	43	14	1.8	16.0
Sept	8.1	315	11	270	66	490	53	520	30	0	0.1	19.0
Oct	8.0	296	15	220	62	450	110	530	55	1	0.2	28.0
Nov	8.3	269	3	180	53	420	10	480	38	2	0.4	27.0
Dec	8.1	252	5	160	59	380	54	500	40	1	0.1	27.0

Biotest

Leachate water and sediment samples collected out of the basins in Hedeskoga were analyzed in order to identify any bacterial activity attributable to nitrification. Three leachate water samples were taken from the aerated lagoon (*IL3*, *Bio* and *Sed)*, one from the eastern basin (*LDÖst*) and two from the southern basins (*LVD1* and *LVD2*) with plastic containers. The aerated lagoon and the eastern basin have a bottom air injector, whereas the southern basins are provided with surface aerators. The samples were characterized in respect of pH, oxygen level (DO), temperature, suspended solids and volatile suspended solids (table 2). A suspension of ammonium sulfate, sodium hydrogen carbonate, and potassium dihydrogen phosphate was prepared to maintain controlled conditions for the *in vitro* nitrification. Nitrification was expressed as ammonium consumption rates in g N/g VSS · h where N is ammonium nitrogen (N-NH_4). Ammonium nitrogen concentrations were quantified by spectrophotometric analysis.

Table 2. Samples characterization. The parameters are expressed in mg/L except pH and temperature.

Sample	pH	DO	T (°C)	SS	VSS
IL3	8	10.5	20.1	70	28
LDÖst	7.9	10.2	19.2	425	141
LVD1	7.9	10.9	20.3	303	61
LVD2	7.7	10.4	20.3	369	55
Bio	7.9	7.0	20.1	13 692	1 250
Sed	7.7	6.8	19.9	39 958	2 467

Ponds´ performance

A hydrological and a nitrogen mass balance were calculated for the on-site treatment plant according to the model represented in figure 1, which took into account the monthly volume records of leachate entering (P5B and P0) and leaving (P4) the ponds, the amount of daily precipitation (p) and evapotranspiration (e) relative to the area occupied by the ponds (S_{tot}= 13 060 m^2). The amount of leachate stored by the system on a monthly basis (ΔV) was obtained as the difference between input and output flows.

To calculate the input and output of nitrogen in Hedeskoga, three chemical species have been taken into consideration: total nitrogen (N-tot), ammonium nitrogen (N-NH_4) and oxidized nitrogen (N-NO_2 + N-NO_3).

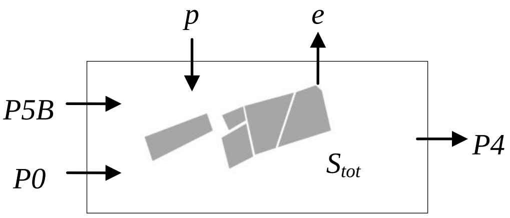


Figure 1. Schematic model of the ponds´ system. P5B, P0 and precipitation (p) are the input and P4 and evapotranspiration (e) are the output of the system; S_{tot} is the sum of all the ponds´ areas.

The amount of nitrogen (N) was calculated adopting monthly leachate volume measurements both at the input and at the output of the system as shown in equation (1):

$$N = V_m \cdot C \qquad (1)$$

where,

N = amount of nitrogen (Kg/month)

V_m = monthly leachate volumes (m^3/month)

C = concentration values for the different chemical species (mg/L)

Nitrification efficiency has been estimated as the ratio between the amount of Kg nitrogen leaving P4 under the form of oxidized nitrogen and the amount of Kg nitrogen entering both P5B and P0 under the form of ammonium nitrogen. The ponds system performance in respect of the three nitrogen species removal is expressed as:

$$removal = \frac{KgN\ in - KgNout}{KgN\ in} \cdot 100 \qquad (2)$$

where,

Kg N in = input of nitrogen measured as the sum of N- (in different form) P5B and P0 (Kg)

Kg N out = output of nitrogen measured as N- (in different form) in P4 (Kg)

Results and Discussion

It is interesting to see that the samples *LDÖst, LVD1, LVD2, IL3* taken in the aerated ponds show ammonium consumption rate (figure 2). *Bio* and *Sed* were excluded because non-representative of the wanted cultures in terms of SS and VSS analysis. It must be addressed that all the samples were provided with nutrients in excess, a non inhibitory concentration of ammonium, and optimal temperature-pH conditions. Therefore, quantitative speculation on which samples had the highest or lowest rate must be “handled with care”. However, the highest ammonium consumption rate was found in correspondence of *IL3,* the aerated lagoon initially designed to treat leachate by means of nitrification. This could be due to stable nitrifiers colonies living in the pond environment, whose activity is increasingly stimulated by resuspension and oxygenation which, in turn, are provoked by the bottom air diffuser put up in the lagoon.

The aerated lagoons are designed to reach full-mixing conditions and dissolved oxygen values above 2 mg/L which are recommended for nitrification [6], [8]. In [9] acclimation phenomena in nitrifying communities have been observed even when dissolved oxygen concentration values were as low as 0.5 mg/L. Therefore, it is likely that in Hedeskoga nitrification is achieved in the aerated lagoon and in all the other ponds showing increasing ammonium consumption rates. Successive *in vitro* nutrient addition might have increased what already was going on in the ponds.

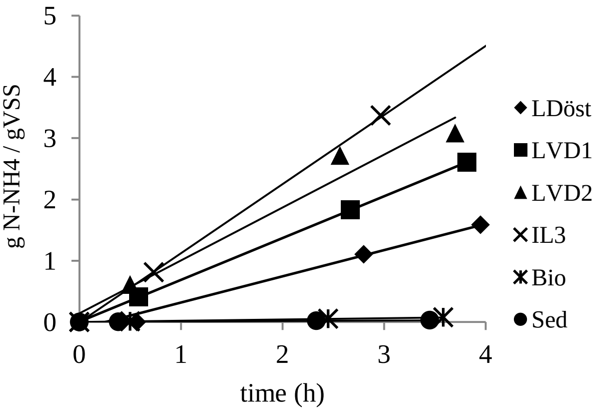


Figure 2. Biotest. Ammonium consumption (y-axis) has been plotted against time (x-axis) to show the rate of biological activity detected for the different samples.

Water budget calculations reflected the treatment strategy adopted in Hedeskoga: in figure 3 values for stored leachate (ΔV) are positive when leachate is stored during autumn and winter, and negative when there is a “loss” during summer months. The “loss” must rather be seen as an intentional depletion of leachate water, which is ultimately used to irrigate the surrounding salix plantations. The purpose with irrigation is to ensure the intake of both dissolved ammonium and nitrate by the plant roots, at the same time, reducing the volume of leachate treated off-site. In this way, the risk that ammonia would inhibit biological nitrogen removal processes at the local wastewater treatment plant is also minimized.

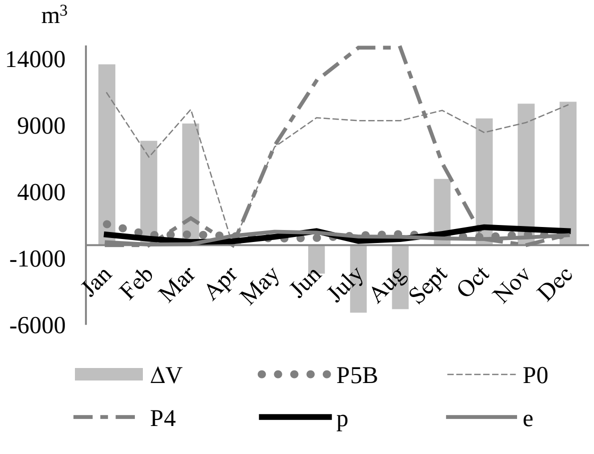


Figure 3. Hydrological balance Hedeskoga 2013. ΔV= stored leachate; P5B, P0 and p= input; P4 and e= output.

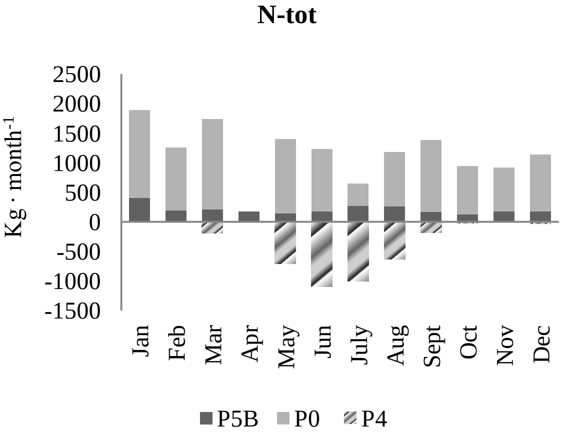
The quantity of leachate pumped in to the ponds in Hedeskoga is not only a function of how much leachate is generated, but also a consequence on how much storage capacity is available. The total estimated maximum design capacity of Hedeskoga is 42 000 m^3. In figure 3, January reported the highest peak of stored leachate (roughly 14 000 m^3). It could be argued that leachate volumes are usually bigger after heavy rainfall as reported in [10]; from September to December a net increase of precipitation (*p*) was observed in comparison with evapotranspiration (*e*) over the total ponds´ surface area. However, in proportion to the total volume stored by the system, this contribution was not that relevant. Therefore, leachate volumes stored in Hedeskoga cannot overcome the total maximum design capacity of the basins. Contemporarily, hydraulic retention times (HRT) were sufficiently long to ensure enough biological breakdown in the aerated lagoons. Similar HRT values were also found in [6], [11], [12] for aerated lagoons (10 – 17 days) and in [13] for equalization ponds with larger volumes (29 – 31 days). However, it must be addressed that in Hedeskoga the flow rates have been grounded on monthly records, whereas, in the studies listed above, direct daily measurements were used for hydraulic retention time calculations.

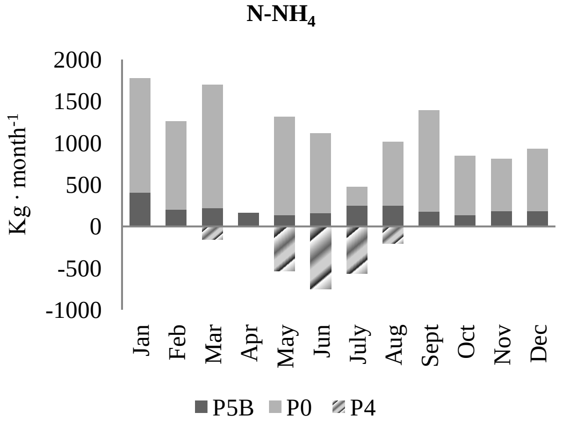
By comparing table 3 with figure 4, if P4 is taken as an indication of the environment in the aerated lagoon during the treatment period when full-mixing and maximum flow regime are guaranteed, and, if oxidized nitrogen is taken as an indication of nitrification, it can be inferred that in correspondence of summer months nitrification is at its highest level in the lagoon. According to the model, 63% of nitrogen removal is accountable for nitrification in July. Similar results were reported in [14] and in [15] where the occurrence of nitrification was studied, respectively, in aerated lagoons and waste stabilization ponds.

Table 3. Removal of three nitrogen species and nitrification efficiency.

	N-tot	N-NH_4	N-NO_x	Nitrification
Jan	100	100	100	0
Apr	100	100	-	0
Jul	56	19	-274	63
Oct	97	100	82	1.5

In July, the fraction of oxidized nitrogen detected in P4 was higher than in December (figure 3). In parallel, the proportion of ammonium decreased the more the end of the treatment in autumn approached. Reasonably, this means that nitrification is favored during warmer months (T= 15 – 20°C) whereas nitrate reduction is promoted during colder months, until at 5°C (and below) both nitrification and denitrification are strongly limited [16], [17]. In fact, only 1.5% nitrification is detected in October when the system “run out” of ammonium. A similar remark was done in [18] concerning an aerated lagoon meant to treat leachate in which increasing nitrates level, decreasing ammonium concentrations and decreasing nitrate-reducing bacteria populations were observed during summer months in comparison with decreasing nitrates level, increasing ammonium concentrations and increasing nitrate-reducing bacteria populations during the low temperature season.





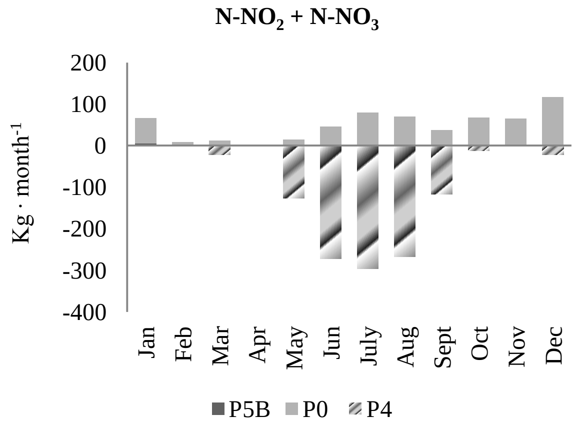


Figure 4. Nitrogen mass balance. From the top, the first insert (N-tot) shows the balance for total nitrogen; the second (N-NH$_4$) shows the balance for ammonium nitrogen; and the third (N-NO$_2$+N-NO$_3$) indicates the amount of oxidized nitrogen. P5B and P0= input; P4= output.

Considering the oxidized nitrogen fraction at the output (P4) as an indicator of nitrification-denitrification, although risky, is not entirely wrong. Both NO_2^- and NO_3^- are products of nitrification, and NO_3^- is also used as substrate for consequent denitrification if anaerobic conditions are found in the same pond. During summer months the aerated lagoon in Hedeskoga approached temperatures of approximately 20°C, water surface DO values of 84% and an average pH of 8.1. In [19] it has been observed that between 10 and 30°C, NO_2^- oxidation is thermodynamically promoted with respect to the specific NH_4^+ oxidation because of the lower activation energy; above 20°C both nitrification reaction steps are ensured. In addition, at 20°C, denitrifiers thrive where low-turbulence and scarcely aerated microniches are formed, e.g. in the bottom sediment or on the pond edge as seen in [20]. Therefore, coupled nitrification-denitrification constitute one of the major pathway by which ammonia is reduced in Hedeskoga. Conversely, during winter, the ponds´ environment is not favorable for active nitrification, and other mechanisms for nitrogen removal, such as sedimentation of dead biomass, should be taken into account.

In [21] the authors concluded that aerated lagoons may not be a feasible year-round treatment method due to excessive power input (to reach complete-mix conditions) and too long retention time. To sort out this problem, in Hedeskoga the use of the aerated lagoon is limited to the summer months and the storage-equalization basins enable longer retention times (~30 days) during winter, although some surface aeration is also provided throughout the year.

Conclusion

The aerated lagoon in Hedeskoga provided sufficiently good ammonia removal for year 2013, mainly by combined nitrification-denitrification.

Nitrification is promoted during summer months at temperature values between 15 – 20°C, whereas nitrate reduction is promoted during colder months, until at 5°C (and below) both nitrification and denitrification are strongly limited.

During the storage phase (winter), retention times longer than 30 days and temperature below 5°C enhance the possibility for ammonia nitrogen to abandon the system by nitrogen removal pathways other than nitrification.

Further investigation may clarify the extent at which ammonia can be removed by algae assimilation, sedimentation, or air stripping.

References

[1] Swedish Water and Wastewater Association (2013). What is REVAQ?, http://www.svensktvatten.se/Vattentjanster/Avlopp-och-Miljo/REVAQ/om-REVAQ/, accessed February 2014

[2] Ystad Kommun (2013). Allmänna Bestämmelser för brukande av Allmänna Vatten- och Avloppsanläggningar, http://www.ystad.se/boende--miljo/vatten-och-avlopp/lagar-och-regler/abva/, accessed June 2014

[3] Renou S, Givaudan J, Poulain S, Dirassouyan F, Moulin P (2008). Landfill leachate treatment: Review and opportunity, Journal of hazardous materials 150: 468-493

[4] Kim D, Lee D, Keller J (2006). Effect of temperature and free ammonia on nitrification and nitrite accumulation in landfill leachate and analysis of its nitrifying bacterial

community by FISH, Bioresource technology 97: 459-468

[5] Robinson H D, Grantham G (1988). The treatment of landfill leachates in on-site aerated lagoon plants: experience in Britain and Ireland, Water research 22: 733-747

[6] Middlebrooks E J, Pano A (1983). Nitrogen removal in aerated lagoons, Water research 17: 1369-1378

[7] Camargo M A, Mara D D, Newton R J, (2010). Nitrogen removal in maturation waste stabilization ponds via biological uptake and sedimentation of dead biomass, Water science and technology 61: 1027-1034

[8] Knox K (1985). Leachate treatment with nitrification of ammonia, Water research 19: 895-904

[9] Park H, Noguera D R (2004). Evaluating the effect of dissolved oxygen on ammonia-oxidizing bacterial communities in activated sludge, Water research 38: 3275-3286

[10] Haarstad K, Maehlum T (1999). Important aspects of long-term production and treatment of municipal solid waste leachate, Waste Management and Research 17: 470-477

[11] Eischen G W, Keenan J D (1985). Monitoring aerated lagoon performance, Journal of Water Pollution Control Federation 57: 876-881

[12] Robinson H, Barr M (1999). Aerobic biological treatment of landfill leachates, Waste management and research 17: 478-486

[13] Camargo M A, Mara D D (2007). Nitrogen removal via ammonia volatilization in maturation ponds, Water science and technology 55: 87-92

[14] Mehmood M, Adetutu E, Nedwell D B, Ball A S (2009). In situ microbial treatment of landfill leachate using aerated lagoons, Bioresource technology 100: 2741-2744

[15] Valero M, Read L, Mara D, Newton R, Curtis T, Davenport R (2010). Nitrification-denitrification in waste stabilization ponds: a mechanism for permanent nitrogen removal in maturation ponds, Water Science and Technology 61: 1137-1146

[16] Prosser I (1989). Autotrophic nitrification in bacteria, Adv in Microbial physiology 30: 125

[17] Knowles R (1982). Denitrification, Microbiological reviews 46: 43-70

[18] Takamizawa K, Mori S, Fukunaga I, Inoue Z (1991). Plankton and macrobenthos in the combined facultative pond and aerated lagoon system at a sea-based solid waste disposal site, Environmental technology 12: 97-105

[19] Kim J, Guo X, Park H (2008). Comparison study of the effects of temperature and free ammonia concentration on nitrification and nitrite accumulation, Process Biochemistry 43: 154-160

[20] Sundberg C, Tonderski K, Lindgren P (2007). Potential nitrification and denitrification and the corresponding composition of the bacterial communities in a compact constructed wetland treating landfill leachates, Water Science and Technology 56: 159-166

[21] Bartsch E H, Randall C W (1971). Aerated Lagoons: A Report on the State of the Art, Journal of Water Pollution Control Federation 43: 699-708