TAMK University of Applied Sciences

Environmental Engineering

Final thesis

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QUANTIFICATION OF NH₃ RELEASED

FROM COMPOSTING OF GARDEN WASTE

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ABSTRACT

The purpose of this study was to measure the amount of ammonia emitted from composting of garden waste. The measurements have been performed at a compost facility called Affaldscenter Århus (Århus waste centre) located in the city of Århus in eastern Jutland, Denmark. This is an outside windrow composting facility, therefore it was interesting to measure the ammonia (NH_3) emission released directly into the atmosphere. Also it was necessary to monitor the carbon dioxide (CO_2) emissions in order to understand the nitrogen (N) and carbon (C) degradation expressed in the C/N ratio. NH_3 is a toxic gas that can affect the environment; it is a course of acidification of aquatic and terrestrial ecosystems as well as of eutrophication of lakes. The study was performed in 7 windrows which age from 40 to 264 days. There were two kinds of measuring methods: gas/liquid absorption so called active method and gas/solid absorption called diffuse 'passive' method. The emission rates of NH_3 from the composting field were between 9 to 112 ppb in average, with a total average of 33 ppb obtained by the passive sampling. The highest NH_3 concentration was 177 ppb from the youngest windrow. NH_3 emission was much lower outside the composting field, with an average of 5 ppb as the background concentration. The active sample emission rates of NH_3 were not obtainable since NH_3 concentration values were beyond the detection limit of the used spectrophotometer. The emission rates of CO_2 were between 3 to 21 ppb in average. The highest CO_2 concentration was 85 ppb from the youngest windrow. The results give an understanding in which cases the NH_3 concentration in the composting of garden waste has lower value with no emission outside the composting field. Active sampling measurement needed to be improved to achieve more accurate result comparable with the one obtained.

TAMPEREEN AMMATTIKORKEAKOULU

Environmental Engineering

TIIVISTELMÄ

Tämän työn tarkoituksena oli mitata puutarhajätteen kompostoinnissa vapautuvan ammoniakin määrä. Mittaukset tehtiin Affaldscenter Århus – kompostointilaitoksessa Århusin kaupungissa itäisellä Juutinmaalla Tanskassa. Laitoksessa on ulkoilmassa sijaitseva aumakompostikenttä, jolla oli mielenkiintoista mitata ammoniakkipäästöjä, jotka vapautuivat suoraan ilmakehään. Oli samalla välttämätöntä valvoa hiilidioksidipäästöjä (CO$_2$), jotta saataisiin selville typen (N) ja hiilen (C) hajoaminen, joka näkyy C/N-suhteessa. NH$_3$ on myrkyllinen kaasu, joka voi vaikuttaa ympäristöön; se on syy vesien ja maaperän ekosysteemien happamoitumiseen ja järvien rehevöitymiseen. Tutkimus tehtiin seitsemässä aumassa, joiden kompostointiaika vaihteli 40 ja 264 päivän välillä. Mittausmenetelmiä oli kaksi: kaasu-nesteabsorptio eli niin kutsuttu aktiivinen menetelmä sekä kaasu-kiinteä aine – absorptio eli diffuusi "passiivinen" menetelmä. Ammoniakkimäärät, joita kompostointikentältä vapautui, vaihtelivat keskimäärin 9 ja 112 ppb:n välillä; passiivisessa näytteenotossa keskiarvo oli 33 ppb. Korkein NH$_3$-pitoisuus oli 177 ppb, joka saatiin iältään nuorimmasta aumasta. NH$_3$-päästöt olivat huomattavasti vähäisemmät kompostointikentän ulkopuolelle: taustapitoisuuden keskiarvo oli 5 ppb. NH$_3$:n aktiivisia näytepäästöarvoja ei saatu mitatuksi, koska ne olivat liian vähäisiä käytettävissä olevan spektrofotometrin tunnistettaviksi. CO$_2$:n päästömäärät vaihtelivat keskimäärin 3 ja 21 ppb:n välillä. Korkein CO$_2$:n arvo mitattiin nuorimmasta aumasta. Tulokset selittävät, millaisissa tapauksissa NH$_3$-pitoisuudet ovat alhaisempia ja päästöjä ei esiinny lainkaan kompostointikentän ulkopuolella puutarhajätteen kompostoinnissa. Aktiivisia näytteenottomenetelmiä on kehitettävä, jotta saataisiin täsmällisempiä tuloksia vertailtavaksi nyt saatuihin.

FOREWORD

This report is a bachelor thesis with the title: "Quantification of ammonia released from composting of garden waste". It refers to an internship work-study carried out at the Department of Environmental Engineering, formerly the Institute of Environment and Resources at the Technical University of Denmark during the period from September 16th, 2007 to January 18th, 2008.

I wish to thank Professor Thomas Højlund Christensen to give me the opportunity to take part in this project work, by teaching and supervising with important hints that he gave to me during the project. I wish to thank Ph.D. student Alessio Boldrin and Ph.D. student Jacob Kragh Andersen for help during the work in the field and with this report.
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Biase Liguori

a mio padre Antonio

mia madre Rosina

mia sorella Maria Antonietta

LIST OF ABBREVIATION

$[CO_2]$	Carbon dioxide
$[NH_3]$	Ammonia concentration
$[NH_4\text{-}N]$	Ammonium ion concentration
BTX	Benzene, Toluene, Xylene
CO_2	Carbon dioxide
CO_3^-	Carbonate ion
DEE	Department of Environmental Engineering,
DTU	Technical University of Denmark
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate ion
N	Nitrogen
NaOH	Sodium hydroxide
NH_3	Ammonia
$NH_4\text{-}N$	Ammonium ion
NO_2	Nitrogen dioxide
O_3	Ozone
OH^-	Hydroxide
ppb	part per billion
ppbv	part per billion by volume air
ppm	part per million
SO_2	Sulfur dioxide

TABLE OF CONTENTS

1 INTRODUCTION

The European Commission Waste Hierarchy strategy proposed already in 1996 is based on three R's motto: "Reuse, Recycle, Recover" and it is aiming to minimize the waste,

"From much waste, some recycling; to some waste, much recycling"

/24/. Furthermore this means that the amount of waste recycled should be increased, and composting is one option to reach this target.

Composting is a natural aerobic degradation of organic material by microorganisms ending in a nutrient-rich product; therefore it is a natural recirculation – (Recycle) of nutrients /1/. The waste that can be composted has a wide-range of all organic material and a mixture of it such as municipal solid waste, garden waste and food waste. In garden waste composting, mainly branches, wood and grass clippings are present.

There are different composting technology systems, starting from domestic backyard composters and simple windrow systems to more complicated systems.

The compost technologies can be classified mainly as: open, enclosed and reactor technology. That can be static, agitated and dynamic depending on how the waste is processed.

The composting facility in Århus, the place where this study has been performed, is an open windrow composting system. In this type of composting technology it is interesting to measure the different emitted gases since they are released directly into the atmosphere.

The windrows composting system is the oldest and simplest composting technology, consisting in extended piles of garden waste. The garden waste is previously pre-processed by removing foreign item, shredding, reducing size and mixing, and then is disposed in windrows.

Windrows are naturally aerated but to increase the degradation and therefore reduce the process time they need to be turned /2/.

Degradation of organic material can cause emissions of gases like NH_3, N_2O and CH_4 to the atmosphere /3, 1, 4, 5/.

NH_3 has been found to be a dominant nitrogen gas emitted in composting of organic wastes, due to mineralization of nitrogen in rich organic material /6,5/. The amount of ammonia emitted is related to factors like pH, C/N ratio value, temperature, aeration, weather conditions. The presence of ammonia in rainwater and thus in the air has been recorded since 1804 /7/.

NH_3 is toxic gas and can have health and environmental effects. NH_3 can affect the oral cavity by inhalation causing respiratory disorder; can affect the inner part of body by ingestion causing haemorrhage in oesophagus, stomach and duodenum; can affect eyes and skin /25/. It is cause of acidification, acid rain and soil acidification; cause of eutrophication of lake /8/.

Emission reduction measures for NH_3 have been planned through the EC Acidification Strategy in 1997; through the EC Directive on Integrated Pollution Prevention and Control (IPPC) in 1996 /9/; and through the Gothenburg Protocol of December 1999 /10/.

Quantification of gaseous emission from composting of garden waste has been already researched at a windrow composting facility called Affaldscenter Århus (Århus waste centre) located in Jutland, Denmark. This has been reported in a M.Sc. master thesis project written by Jacob Kragh Andersen at the Department of Environmental Engineering, DTU. The aim of this study was to estimate the emission of CO_2, CH_4, CO, and N_2O emitted from the composting facility.

From the outcome of this study, the results related to C and N illustrate that 68% of the initial C and 3% of the initial N has been degraded during composting. An amount of 2.8% of degraded C is lost as CO_2, and an amount of 0.4% is lost as CH_4 and CO;

therefore a large parte of C is missing. An amount of 8.4% of degraded N is lost as NO_2 and the other is missing. Some of the nitrogen emission missed can presumably be released in form of NH_3.

The objective of this study is to investigate the NH_3 emission from the garden waste composting performed at Århus waste centre. Moreover also the CO_2 emission will be monitored to define the C/N ratio, necessary to understand the N and C degradation.

2. FIELD LOCATION

This work has been performed at the compost facility at Affaldscenter Århus (Århus solid waste centre) located a few km north of Århus city in Jutland Denmark (figure1).

Figure 1: Denmark /26/.

The Århus solid waste centre consists of an incineration plant, slag treatment facility, facility for bulk waste, crushing of tiles and concrete area and a composting plant (figure 2).
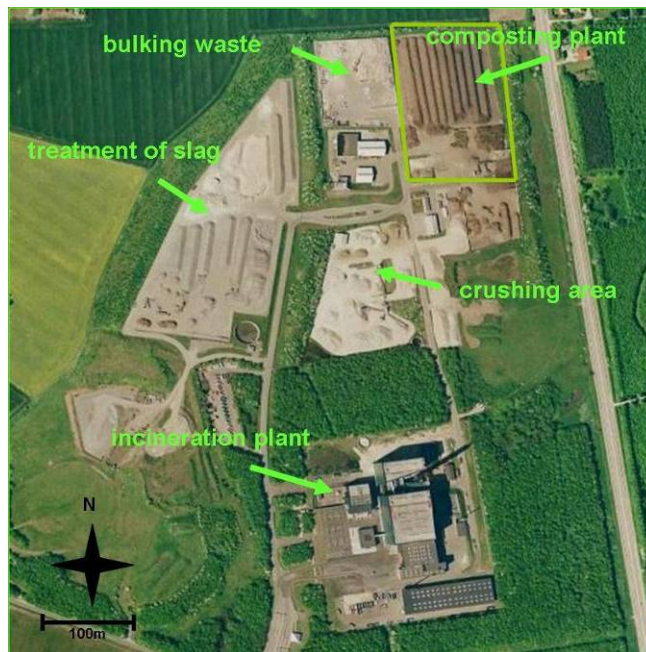
Figure 2: Århus solid waste centre, illustrated picture from Google earth /27/.

The composting plant treats garden waste coming from industries, private sector and maintenance of forests and other green public areas.

The active method measurements have been performed during days 27th and 28th of November, 2007. The 27th was sunny and temperature average was between 2-3 ℃. The 28th was cloudy and raining and the temperature average was between 4-6 ℃.

The atmospheric conditions are an important issue that can affect the transport of the gases from the windrows compost process. For instance, atmospheric pressure, wind, precipitation and temperature are important factors influencing the vertical transport in the air of gases emitted from compost windrows by affecting the process of convection, thought to be the most important transport mechanism of gases in the air.

3. MATERIAL AND METHODS

3.1 Sampling methods

Airborne gaseous sampling methods can be classified in relation to the type of measurement that is going to be performed. If the interest is in collecting peak concentration of a gas, a so-called grab sampling method should be used where an actual sample of air is collected /11/. If the interest is in collecting air over a measured time-period, a continuous sampling method should be used.

The grab sampling method is of questionable value depending on the range of concentrations to be measured and the actual scenario under study. If very low concentrations of contaminants are expected, a longer exposure time will be required to get a reasonable average value. Changing weather conditions, which could also affect the contaminant flow, should be mentioned in discussion of the results.

Continuous integrated sampling methods could be used instead. In an integrated sampling method, gas samples can be collected from the air in a liquid solution, in reaction with a solution, on a solid sorbent or simply in vial in gaseous form.

In this study collection of NH_3 and CO_2 emitted from composting windrows is performed by:

- An active sampling method, using impinger flasks for absorption of gas in a liquid solution;
- A passive sampling method, using a solid sorbent in plastic vials.

The two different methods are described in more details in the following chapters.

3.1.1 Active sampling

3.1.1.2 Method

There are four basic types of active gas sampling methods using liquid solution as sorbent:

- Simple gas washing bottles;

- Spiral and helical sorbers;

- Sritted bubblers:

- Glass-based columns.

They differ in providing an appropriate contact between gas in the air and liquid sorbent solution. Examples of gas washing bottles are: Petri, Dreschel and midget impingers. A typical schematic design of a midget impinger is shown in figure 3. Midget impingers are the most widely used gas washing bottles /11/ and it is also the equipment that is used in this study.
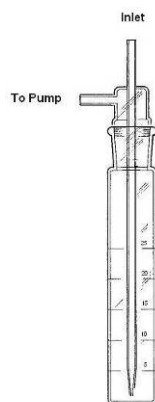

Figure 3: A schematic picture of an impinger flask

In active sampling, a pump is used to force a specified quantity of air through the absorbing solution in the impinger flask. In this method it is important to take in consideration the amount of absorbing solution and the flow rate; too much liquid or excessive flow rate can be reason of a loss of sample. The efficiency of gas sample collected depends on the volume of air sampled as well as the volume of the absorbing

liquid solution and the volatility of the gas being collected /12, 13, 14, 15, 16, 17, 18, 19/. Therefore the efficiency can be increased by reducing the volatility of the gas sample collected or increasing its solubility, by increasing the absorption liquid volume adding bubblers. Absorption of gas sample depends on the size of the air bubbles, the reaction rate and the reagent solution.

3.1.1.2 Field measurement

The composting facility of the field measurement is composed of 7 windrows as showed in schematic picture and photo of figure 4 and 5.
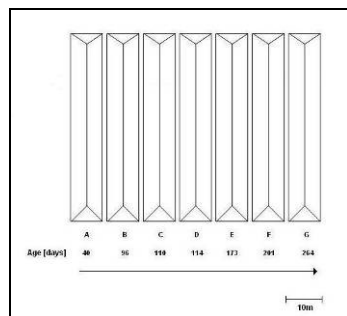

Figure 4: Schematic representation of windrows at Affaldscenter Århus

Figure 5: Aerial view of compost facility /27/.

In the current study NH_3 and CO_2 are the gases of interest and they react with the absorbing solution to form stable substances that will be analyzed to quantify the amount of pollutant. The absorbing solution has been targeted for specific compound. As absorbing liquid solution for NH_3, 10ml of 0.02 N Hydrochloric Acid (HCl) have been used and as absorbing liquid solution for CO_2, 10ml of 1 N Sodium Hydroxide (NaOH) have been used. The two impingers were connected in series, through the first impinger, on the right side in the picture on figure 6, air is coming in and passing through HCl for NH_3 collection and then it is passing into the second impinger through NaOH for CO_2 collection. In this study SKC Standard Midget Impinger (25 ml, glass, with standard nozzle) and three SKC 222-3 Series Low Flow Pumps, with adjustable flow rate range of 50 – 200 ml/min /28/ have been used. This method of measurement has been performed on all the windrows. On the windrow E, F and G (figure 4), the

measurement has been performed with four impingers in series, like it is schematically represented in figure 7.
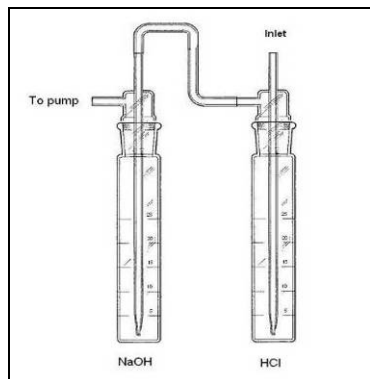

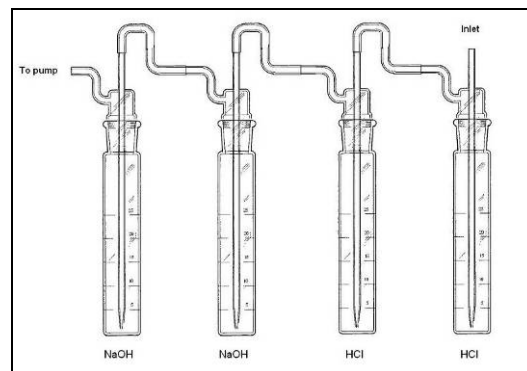Figure 6: A schematic picture of two impingers connected in series

Figure 7: A   schematic picture of four impingers connected in series

This system of four impingers in series has been performed to ensure that one bottle is enough to absorb all the compound of interest contained in the volume of air pumped: the second flask was analysed to make sure nothing was collected there. Figure 8 are pictures from the field showing how the impingers were fixed.

Figure 8: Impingers connected in series in the field (for two measurement points, two impingers per pump).

The measurements have been performed on the 7 windrows at point schematically shown in picture figure 9. For each measuring point, two samples were taken on top of the windrow and one inside the windrow; schematically represented in figure 10. The windrows have been named with the letters A, B, C, D, E, F and G in relation to their age (figure 7).
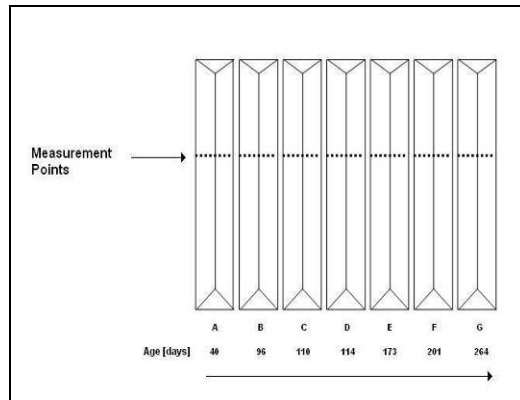
Figure 9: A schematic view of windrows measurement points of active samplers
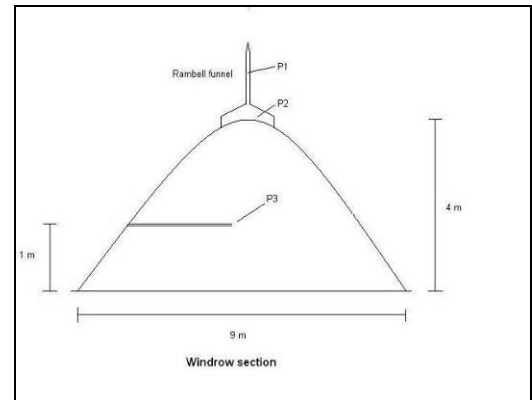

Figure 10: Schematic drawing representing active sampling points on windrow

The measurements performed on top of the windrow have been carried out according to the Rambøll approach. The Rambøll funnel is a mobile device constructed by Rambøll, which is a Danish company. The device consists of an aluminium hood with a surface area of 1 m^2 and attached plastic cloth to ensure that the unit is covering the entire top of the windrow. A 1 m high chimney is attached on top of it (figure 11). It is assumed in the Rambøll approach all the air emission escape through the top of the windrow due to the chimney effect /3/ caused by the rise of warm air produced during the composting process. To avoid turbulence in the stream that could affect the measurements, the chimney height and the funnel-shaped form is significant.

Figure 11: The Rambøll funnel device

Figure 12: Installation of the probe through the windrow

The measurements on top the windrows have been performed in two points; one by connecting the impinger inlet through a plastic pipe to the outlet of chimney Rambøll funnel device (P1 in figure 10) and the second one by connecting the impinger inlet

through a plastic pipe under the hood, at the bottom of the Rambøll device (P2 in figure 10).

A third point of measurement is inside the windrow, the point has been reached through a gas probe introduced to the windrow at a height of approximately 1m and depth of approximately 3m, (figure12, 13, 14) and then connected to the impinger system (P3 in figure 10).

Figure 13: Probe impinger system

Figure 14: Detailed picture of the impinger inlet connection to the probe

The mass concentration of the gas in the air absorbed in the liquid solution can be determined from the following equation (1) /11/:

$$C = \frac{(m - m_{blank})}{SE \times V} \qquad (1)$$

Where: C = mass concentration of the gas in the air (mg/m^3)
             m   = mass of the gas in sample (μg)
             m_{blank} = mass of the gas in blank (μg)
             SE   = sampling efficiency
             V   = volume of air sampled (l)

3.1.2 Passive sampling

3.1.2.1 Method

Diffusive or 'passive' sampling does not involve active movement of air (e.g. with a pump) through a sampler device; samples of gas are taken thanks to physical processes like diffusion through a static air layer or permeation through a membrane /20/. Diffusion and permeation can be described with Fick's first law of diffusion (equation 2). With equation 2 /11/ the mass concentration of gas in air can be determined.

$$C_A = \frac{Q \cdot L}{D \cdot A \cdot t} \qquad (2)$$

$$Q = C_0 \cdot V_w \cdot \frac{M_{NH_3}}{M_N} \qquad (3)$$

Where:
- C_A = concentration in air (mg/m^3)
- Q = mass uptake (mg)
- L = length of diffusion path (m)
- D = coefficient of diffusion (m^2/sec)
- A = cross section area of diffusion path (m^2)
- t = sampling time (sec)
- C_o = external concentration being sampled (mg/m^3)
- V_w = Volume of water (m^3)
- M_{NH_3} = molar mass of ammonia (g/mol)
- M_N = molar mass of nitrogen (g/mol)

There are different types of diffusive samplers /21, 22/. A typical schematic design is shown in figure 15 /11/ and it simply consists of a small (6 ml) plastic vial with a filter in the bottom. There is almost always an equivalent diffusive sampler per each active sampler.
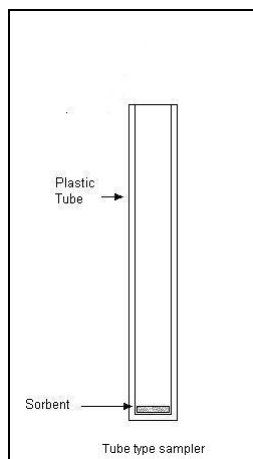
Figure 15: Schematic representation of a passive sampler vial

The theoretical basis for diffusive sampling and comparison with active sampling has been validated from the Luxembourg Symposium /20/; it has been established that there is no significant difference between the accuracy and precision of diffusive sampling and active sampling method.

3.1.2.2 Field measurement

The passive sampling method that has been used was developed at the Technical University of Denmark (DTU). This method has been applied to Nitrogen Dioxide (NO_2), Sulfur Dioxide (SO_2), Ozone (O_3) and Benzene, Toluene, Xylene (BTX) and adjusted to NH_3 sampling /23/.

The diffusive sampler used in this study is a plastic tube type sampler with a length of 5.2cm and a diameter of 1.2cm (figure 16).
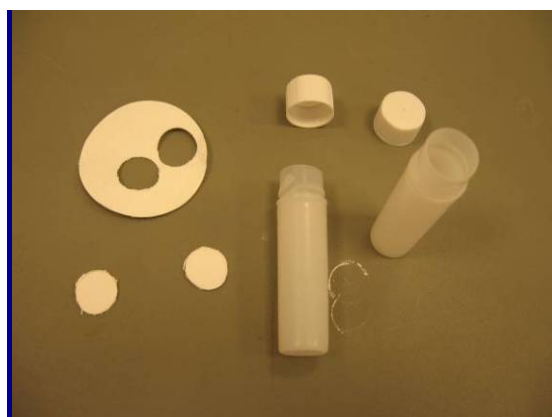

Figure 16: Example of tube-type passive sampler

The solid sorbent in the bottom of the vial has been made with a glass microfibre filter /29/. The filters have been washed three times with 2 % citric acid; then rinsed four times with water. Afterwards the filters were impregnated with 0.1 % citric acid and 1% glycerin solution. Eight blank vials have been left in the laboratory with lids on for later blank determination

The vials in couple, sample and replicate, have been placed with metal clips in plastic wind hoods (see figure 17) and then placed at the measurement points as shown in figure 18. The plastic wind hoods have been placed on top of the windrows and at some distance from the windrows, as shown picture in figure 18 and figure 19.
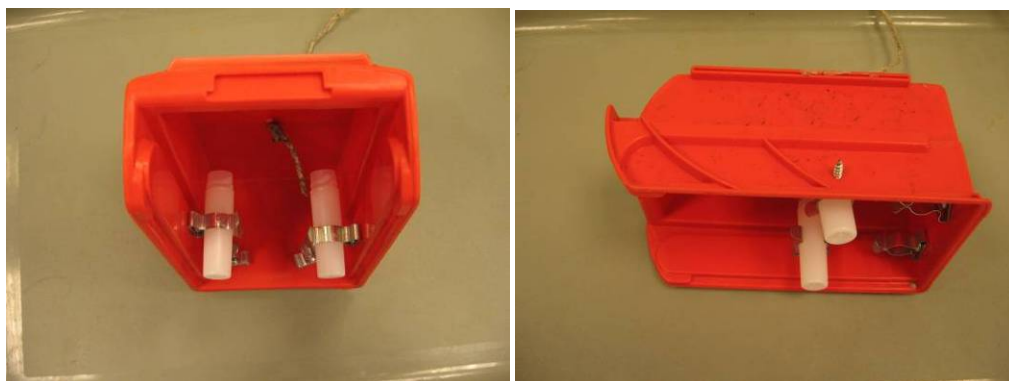
Figure 17: This picture shows the plastic wind hoods containing the passive sampling vials
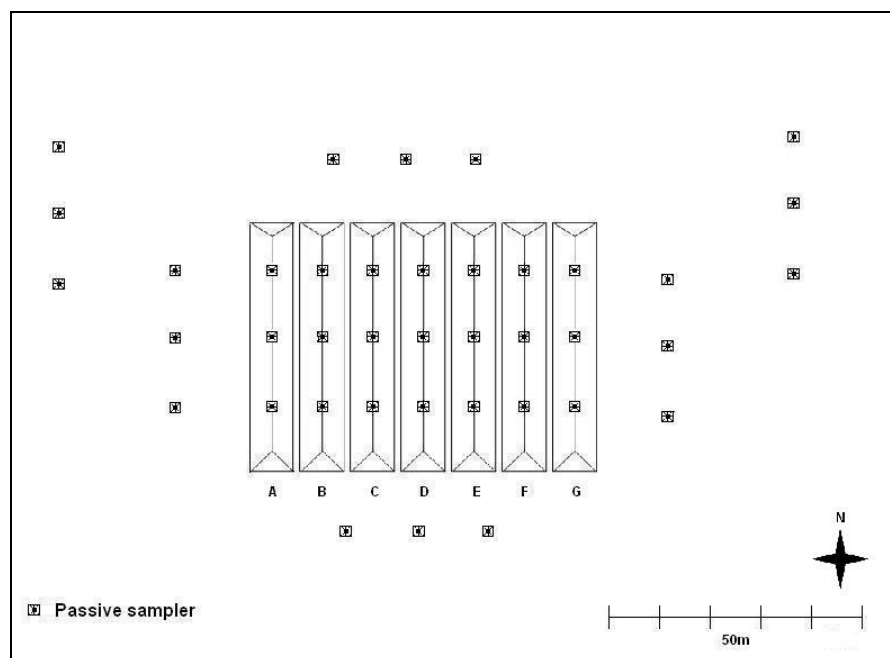
Figure 18: Schematic presentation of the placement of passive samplers in the composting field area.

Figure 19: Placement of the passive samplers on the windrows

3.2 Analysis methods

The number of samples that was analyzed for NH_3 was 106 among which 30 have been collected with the active sampling method and 68 with the passive sampling method. The last 8 were the blanks samples. For the CO_2 determination, 30 samples have been collected with the active sampling method. The determination of NH_3 concentration has been performed by a spectrophotometric method while the determination of CO_2 has been performed by titrimetric method for the determination of total alkalinity.

3.2.1 NH_3 determination

The spectrophotometry analysis has been performed according to the Department of Environmental Engineering (DTU) standard: "Determination of ammonia in water: *ham-DS 224*" (Appendix 1). 2.3 ml of solution (100μl of reagent A and 100μl of reagent B) is analysed on a spectrophotometer.

This method consist of analyzing a solution composed of 2.3ml sample, 100μl of reagent A and 100μl of reagent B with a spectrophotometer. The 2.3ml sample is part of 10ml solution used as absorbing solution in the impingers. The reagent A consists of 1 ml 10% of hypochlorite solution and 66 ml of 0.5M NaOH, diluted to 100ml of deionized water.

The reagent B consists of 13.5g of phenol and 0.15g of dinatrium-pentacyanonitrosylferrat (II), diluted adding deionized water to 500ml.

The lower limit concentration detected for the spectrophotometer with this method is 10ppb (μg/l) A standard solution for calibration curve was made. Standard for 10, 20, 40,100, 200, 500, 800, 1000 and 1200 μg/l was prepared by adding 0.5, 1.0, 2.0, 5.0, 10.0, 25.0, 40.0, 50.0, and 60.0ml of 1ppm ammonium ion NH_4-N to a 100ml flask and dilute to volume with deionized water. In figure 20 an example of calibration curve has been presented. The Y axis shows the absorbance related to the ammonium ion concentration [NH_4-N] sample values.
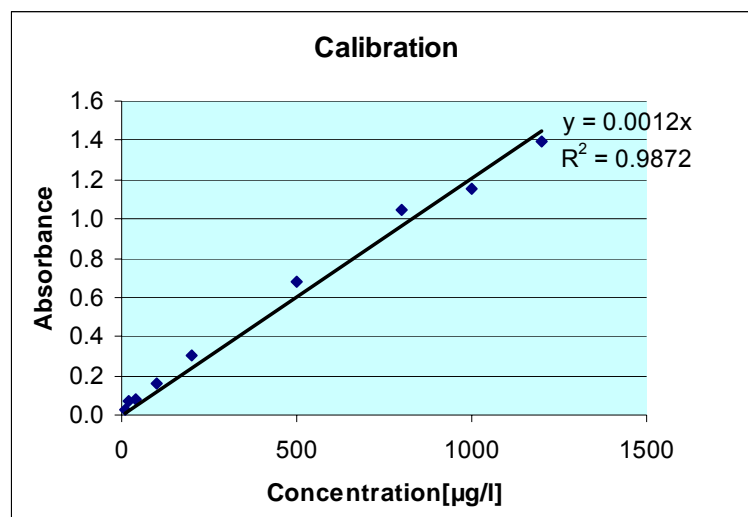

Figure 20: Example of calibration curve chart

When all solution were ready, 2.3ml of sample, 100μl of reagent A and 100μl of reagent B was filled to a cuvette. Hence the cuvettes containing the sample and the standard are left in darkness for two hours and analysed in a spectrophotometer at a selected absorbance at a wavelength of 630nm.Excel is used for processing results and calculating the calibration curve.

3.2.2 CO_2 via titration

The determination of alkalinity via titration method has been performed according to the instruction from Department of Environmental Engineering (DTU) standard: "Instruction for determination of total alkalinity: JCT/NJL/JK" (Appendix 2).

The samples have been titrate with 0.1N hydrochloric acid (HCl) using phenolphthalein indicator to determine the phenolphthalein alkalinity to pH 8.3 and mixed bromcresol green-methyl red indicator to determine the total alkalinity at end point to pH 4.5.

During titration all hydroxide (OH^-) alkalinity is neutralized by pH 10.0 and all Carbonate (CO_3^-) are converted to bicarbonate at pH 8.3. When titrating until the end point at pH 4.5, the total alkalinity (TAL) has been obtained. With formula 4, then the normality meq/l of bicarbonate (HCO_3^-) which is equivalent to the (CO_2) normality meq/l has been calculated.

$$TAL = \frac{(V_T - V_P) \cdot N \cdot 1000}{V_S} \hspace{2cm} (4)$$

Where: TAL =Total alkalinity (*meq/l*)
    V_T =Volume of total alkalinity titration end point; pH= 4.5 (*ml*)
    V_P =Volume of phenolphthalein alkalinity titration point; pH=8.5 (*ml*)
    V_S = Volume of sample analyzed (*ml*)
    N = Normality of acid used in titration (*meq/l*)

4 RESULTS AND DISCUSSION

4.1 Methodology

The results represented in this section have been obtained with spectrophotometric and titrimetric methods. The spectrophotometric method has been utilized to determine NH_3 concentration absorbed in the sorbent of each passive and active sample. Then from the results obtained the concentrations in the air have been calculated. The titrimetric method has been utilized to determine the total alkalinity and then determine the CO_2 absorbed in the sorbent of the active samples. All the results have been collected and presented in the following chapter.

4.2 Ammonia concentration

The result refers to analysis of 106 samples collected with passive and active sampling methods. The calibration curve (figure 21) has been made with standard solution of 10, 20, 40,100 and 200 ml of NH_4-N (Appendix 5) solution with a concentration of 1 µg/l corresponding to 1ppm in a water sample (Appendix 6).

Whit this value of calibration curve it is possible to detect the absorbance in the range from 10 to 200 µg/l. This is also the range that is expected from the collected samples. The result and the calibration curve are presented in figure 21 and table 1.
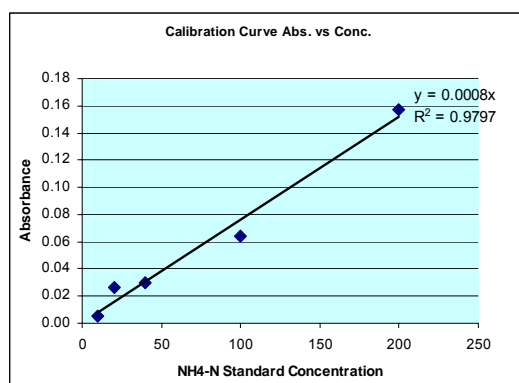
Figure 21: Calibration curve

Table 1: Absorbance of standards with known concentration of NH4-N

[NH4-N] in 2.3ml samples standard solution (µg/l)	Absorbance detected
10	0.005
20	0.026
40	0.030
100	0.064
200	0.157

The NH_3 concentration in all of the active samples is lower then 10ppm, the limit detection value, and therefore the precise ammonia concentration could not be determined.

The NH_3 concentration in the passive samples is collected in table 2. The results value of *i* table 2 can be in contradiction with the calibration curve, since this has been made with upper limit value of 200 µg/l but in column *i* table 2 we got result up to 1100 µg/l. We should consider that the value collected in column *i* table 2 are average value, moreover has been assumed that the calibration curve is linear, thanks to an other sample of calibration curve (figure 20) made in laboratory test, where has been used 1200 µg/l as upper limit value.

The results collected in table 2 refers to the samples collected at 76 sampling points were the passive sampling have been located. The passive samplers have been placed in three points on top of each windrow, three points north, three points east, three points south, three points west of the windrows and in addition to three points faraway west and three points faraway east; as schematically shown in figure 18.
The results in table 2 represent the average of replicates of the three points per windrow.

The results collected in column *i* table 2 have been calculated according to the formula 5.

$$A = 0.0008 \cdot [NH_3] \Leftrightarrow [NH_3] = \frac{A}{0.008} \qquad (5)$$

Where: A = Absorbance value detected from spectrophotometer
        0.008 = Value determined from calibration curve (figure 21)
        [NH₃] = Ammonia concentration

In Appendix 3 all results are presented, with details of value for each windrow measurement point.

Passive sampling has been performed from November 27th starting at 15:30 to December 6th until 14:00, when the samples were collected. The time average of sampling is then 210 hours. The average temperature during sampling time has been 4 ºC according to the Danish Meteorological Institute /30/. Temperature is important to calculate the concentration in the air with the real temperature and pressure condition, according to the ideal gas law. Then taking in consideration this temperature value the concentrations of NH_3 in the air have been calculated, according the equation 2 and 3 described in section 3.1.2.1. The results are shown in column *ii* table 2. The $[NH_3]$ is expressed in part per billion by volume air (ppbv).

Table 2: Ammonia concentration in the air

[NH₃] in 2.3ml sample average value			
Windrow		*i*	*ii*
name	age (days)	(μg/l)	(ppbv)
A	40	1122	112
B	96	525	52
C	110	212	21
D	114	220	22
E	173	51	5
F	201	97	10
G	264	94	9
North		49	5
South		36	4
West		50	5
East		185	18
Faraway		44	4
Faraway		62	6
Blank		66	

From the data in column *ii* table 2 it is possible to observe that the [NH₃] is decreasing with compost age and is getting lower when going away from the composting area due to the dilution of NH₃ in air. It is important to consider the blank concentration value that notifies the background concentration of ammonia in the air, this should be taken in count when observing the NH₃ concentration values; as a matter of fact whether we subtract the concentration value of the blank sample from the others we will obtain that around the composting facility there is no ammonia emission.

The values of the samples collected in the eastern area of facility are higher than the others (north, south, and west). This could be because of the nearest windrow, the windrow A, is younger and in fact here major emissions have been found (Figure 22). It could then be possible that it is affecting the samples closest to this windrow (to the east).

The collection points faraway from the composting field are important checking points. From these concentrations we get two pieces of information, the first one is that the NH_3 concentration is close to the background concentration, the blank sample values; moreover they are checking points of potential ammonia sources outside the composting area. Some potential sources could have given higher concentration effects in these samples.

It can be conclude there are not external sources of ammonia.

A schematic map of the measured concentration of NH_3 from passive sampling at the composting field is presented in figure 22 . In the centre of the map, results from the measurement points on top of each windrow are represented, the windrows are named with capital letter. North, east, south and west represent the three measurement points around the windrows (distance about 10 m). Faraway measurements have been performed on 6 measurement points, three located east and three west of the composting field.

From this schematic map can be observed that there is a tendency reduction of $[NH_3]$ from the measurement point on top to the youngest windrow to the oldest represented with the changing in colour from dark to light blue.
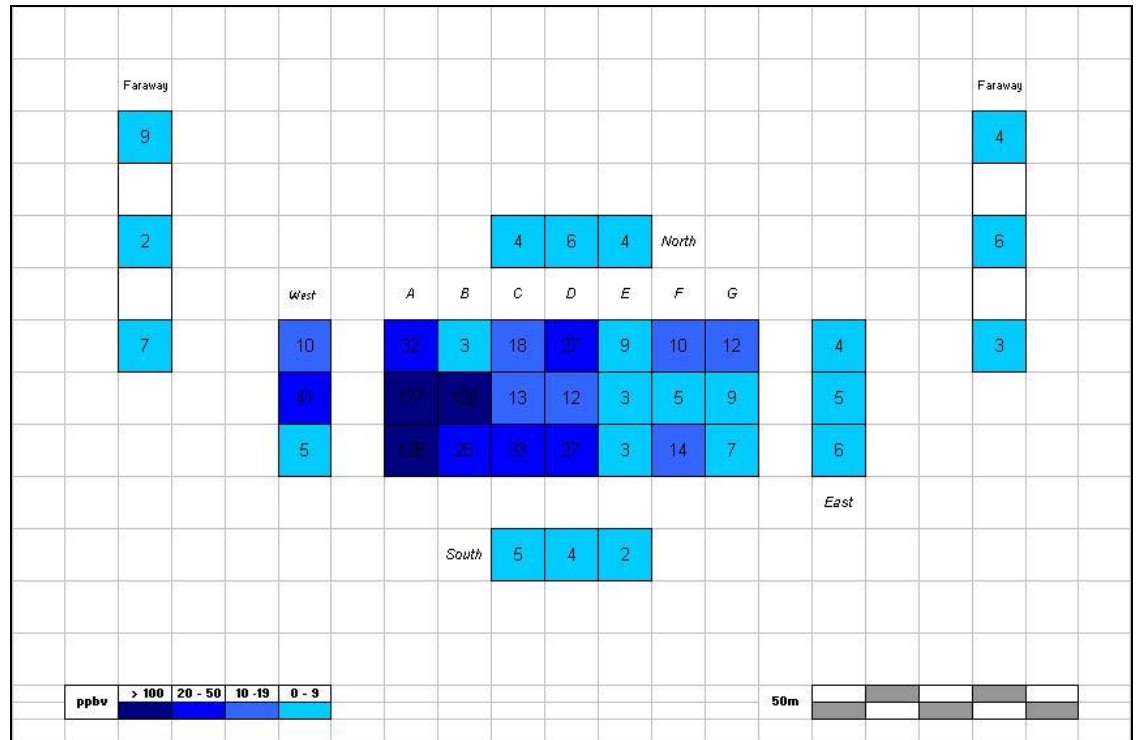
Figure 22: Schematic map of NH_3 concentration (in ppbv) on top and around the composting facility

In figure 23 a trend of ammonia concentration through the three measurement point of each windrow in relation to the windrow age has been presented; moreover the average trend of diffusion of ammonia has been represented. Examining the graph is possible to observe a tendency of decreasing in $[NH_3]$ related to the increasing in the windrow age.
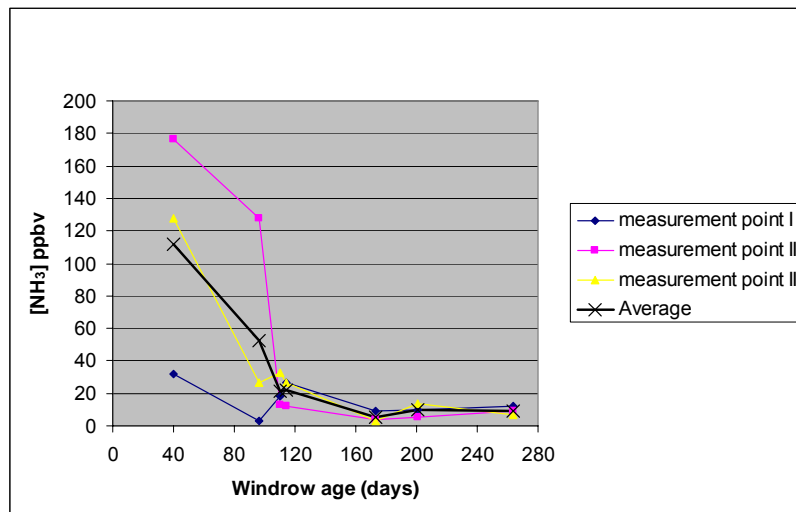
Figure 23: Graphical presentation of [NH3] tendency through the windrows

The passive sample has been performed in three measurement points on top of each windrow, while active sample was taken at one position only. The active measurement point has been performed close to the passive measurement point called II, (Appendix 3) therefore observing the result obtained for the passive sample point II we can make some consideration in relation to the active sample results.

In column *i* of table 3 the [NH_3] (in µg/l) in air obtained by passive sampling at point II are presented. The volume values of column *ii* refers to the volume pumped from the bottom of the Rambøll hood funnel, (point P2 in figure 10)*;* multiplying those values by the values of column *i* the theoretical amount of NH_3 we were suppose to catch with passive sampling is obtained. During passive sampling 10ml of absorbing solution have been used and thus by dividing the value of column *iii* by the 10ml volume the NH_3 concentration that were supposed to be caught during active sampling is obtained. This data is collected in column *iv*.

The highest value in *iv* related to the windrow A is not taking in consideration, since data obtained form active sampling on windrow A is not correct due to mechanical problems with the pumps. Except the value related to windrow A and take in consideration that the value of windrow B is the only value higher than limit value of 10 µg/l, all the others values of column *iv*, 5 of 6 that correspond to *83%*, are consistent with results obtained. Since of value obtained are under the spectrophotometer absorbance lower limit that is 10 µg/l (figure 21, table 1) it has not been possible to determine the [NH_3]. The [NH_3] value is less than 10 µg/l.

Table 3: Theoretical active sample [NH_3] value of measurement point II

Windrow		*i*	*ii*	*iii*	*iv*
name	age (days)	[NH_3] in the air (µg/l)	Volume sampled (*l*)	NH_3 in the air (µg)	[NH_3] in 10 ml (µg/l)
A	40	0.131	4.4	0.575	58
B	96	0.095	4.0	0.379	38
C	110	0.009	3.2	0.030	3
D	114	0.009	3.1	0.028	3
E	173	0.003	4.0	0.010	1
F	201	0.004	4.4	0.018	2
G	264	0.007	4.1	0.028	3

4.3 Carbon dioxide concentration

The result here collected refers to analysis of 30 samples collected with active sampling method. The measurements have been performed on November 27th and 28th. The samples have been analyzed by titration with 0.1N HCl, then according to formula 4 the HCO_3^- concentration has been calculated. This value equals the CO_2 concentration, with this information then multiplying the concentration (meq/l) obtained by the molar mass of CO_2 we get the amount of CO2 absorbed in our sample, then referring to the active sampling volume pumped we can calculate the absorbed [CO_2] in the air.

In figure 24 are presented the results of [CO_2] in air obtained (Appendix 4) from the measurement point performed on top of each windrow as illustrated in figure 10 section 3.1.1.2.
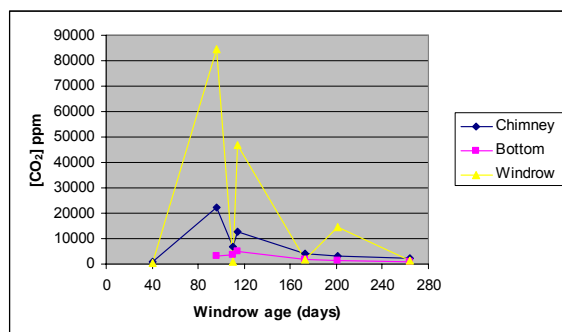
Figure 24: Tendency of [CO_2] through the windrows per each measurement point collected

The value of the first point in the graph regarding the bottom measurement point (P2 in figure 10 section 3.1.1.2) has been left out because this value is not accurate since data obtained from active sampling on windrows A are not correct due to problems with the pumps.

We can observe that the $[CO_2]$ has a decreasing tendency with increasing windrow age and the highest value obtained from data collected were from the windrow measurement points (inside windrows) while the lowest were obtained from the data collected in the bottom part of the Rambøll funnel.

5 CONCLUSION

The concentrations of NH_3 were measured on 7 windrows of a composting plant, with different age and in total 30 samples by active sampling and 68 by passive sampling methods have been collected.

From the analysis of samples collected from the composting facility an average of 33 ppbv (0,033 ppm) of NH_3 and 11 ppbv of CO_2 was measured.

The highest concentration of NH_3 117 ppbv has been recorded on the youngest windrow 40 days old. [NH_3] has been measured as well outside the composting area, and has been obtained an [NH_3] average value of 5 ppbv that means there is no significant NH_3 emission from the composting field since the typical [NH_3] values in rural area are 1-6 ppbv /7/.

Results from passive samples show similar trend of results obtained in others investigation using identical sampling method. The passive sampling method used could be then be recorded as valid.

Comparison between passive samples and active samples results basically confirm the validity of both methods utilized; 83% of results obtained with active sampling method are consistent with result obtained with passive sampling. In fact the average of [NH_3] value obtained from analysis of passive samples by 83% lower than 10ppbv, which is the detection limit value of the spectrophotometer. It has therefore not been possible to detect data from active samples.

Two impingers in the active sampling method have been utilized in series to catch the same gas. According to the result obtained from [CO_2] investigation, tendentially the second impinger is catching half of the concentration caught by the first impinger. Could be interesting investigate to check tendency in getting less [CO_2] in the last impinger whether using three impingers in series. The fact that [NH_3] has not be possible to determine with active sampling and the chance to investigate a three impingers series systems address the necessity of future studies of active sampling method by utilizing the impingers.

NH_3 emission from composting of garden waste is not a big problem, the concentration is getting lower with compost age and since most concentrations are within the ambient concentration

6 REFERENCES

Printed

1. HELLEBRAND, H. J. *Emission of Nitrous Oxide and other Trace Gases during composting of Grass and Green Waste.* Journal of Agricultural Engineering Research,., 1998, no. 69, p. 365-375.

2. KROGMANN, U., KÖRNER, I., DIAZ, L. F. Lecture notes in the course 12130, Solid waste technology and management, Technical University of Denmark (DTU), autumn 2007.

3. HELLMANN, B., L. ZELLES, A. PALOJARVI and BAI, Q... *Emission of Climate-relevant Trace Gases and Succession of Microbial Communities during Open-windrow Composting.* Applied and Environmental Microbiology Journal, 1997, no. 63 p. 1011-1018.

4. BECK-FRIIS, B., M. PELL, U. SONESSON, H. JÖNSSON and H. KIRCHMANN,. *Formation and emission of N_2O and CH_4 from Compost Heaps of Organic Household Waste.* Environmental Monitoring and Assessment Journal, 2000, no. 62 p. 317-331.

5. BECK-FRIIS, B., S. SMÅRS, H. JÖNSSON and H. KIRCHMANN.. *Gaseous Emission of Carbon Dioxide, Ammonia and Nitrous Oxide from Organic Household Waste in Compost Reactor under Different Temperature Regime.* Journal of Agricultural Engineering Research, 2001, no. 78 p. 423-430.

6. MARTINS, O. and T. DEWES. Loss of nitrogenous compounds during composting of animal wastes. Bioresource Technology Journal, 1992, no. 42 p. 103-111.

7.   STRINGER, D., A. *Ammonia Emissions to Air in Western Europe.* ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals, Technical Report. Brussels, Belgium, 1994, no. 62.

8.   IPCS (International Programme on Chemical Safety) *Ammonia - Health and Safety Guide* World Health Organization. GENEVA 1990. Health and Safety Guide No. 37

9.   SUTTON, M. A., MINERS, B., TANGS, Y. S., MILFORD, C., DUYZER, J. H., FOWLER, D.. *Comparison of low cost measurement techniques fro long-term monitoring of atmospheric ammonia,* Environmental Monitoring Journal, 2001 no. 3, p. 446-453

10.   COLLS, J. Air Pollution – 2nd ed. Spon Press London, England, 2002 p. 521 ISBN 0-415-25565-1

11.   HSE Health and Safety Executive MDHS 70 Methods for the determination of Hazardous Substances. *General methods for sampling airborne gases and vapours.* Sudbury Suffolk, United Kingdom: HSE Book, 1993. ISBN 0717606082

12.   ELKINS HB. HOBBY A and FULLER JE *The Determination of Atmospheric contamination; 1: Organic Halogen Compounds,* Industrial Hygiene Association Journal, 1973, no. 19 p. 474.

13.   GAGE JC. *The efficiency of Absorbers in Industrial Hygiene* Analyst Journal, 1960, no.85 p. 196.

14.   PAGNOTTO, L.D. *Collection and analysis of gases and vapors. In: Air Sampling Instruments for Evaluation of Atmospheric Contaminants* (5th edition). American Conference of Governmental Industrial Hygienists, 1978, p. R-2–R-18.

15.   MORITA, H., MITSHUHASHI, T., SAKURAI, H. and SHIMOMURA, S. *Absorption of mercury by solutions containing oxidants*. Analytica Chimica Acta, 1983, no.153 p. 351–355.

16.   FRADKIN, A. *Sampling of microbiological contaminants in indoor air*. In: *Sampling and Calibration for Atmospheric Measurements*, J.K. Taylor (ed.), American Society for Testing and Materials, Philadelphia, 1987, pp. 66–77.

17.   STELMA, G.N. and BRENNER, K.P. *Effect of impaction, bounce and reaerosolization on the collection efficiency of impingers*. Aerosol Science Technology Journal, 1997, no. 26(4) p. 326–342.

18.   LIN, X.J., WILLEKE, K., ULEVICIUS, V. and GRINSHPUN, S.A. *Effect of sampling time on the collection efficiency of all-glass impingers*. American Industrial Hygiene Association (AIHA), 1997, no. 58 (4) p. 480–488.

19.   SPANNE, M., GRZYBOWSKI, P. and BOHGARD, M. Collection efficiency for submicron particles of a commonly used impinger. American Industrial Hygiene Association (AIHA) Journal, 1999, no.60 p. 540–544.

20.   BERLIN A, BROWN RH and SAUNDERS KJ (eds). *Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring,* CEC Pub No 10555EN, 1987

21.   PALMES ED and GUNNISON AF. *Personal Monitoring Device for Gaseous Contaminants*, American Industrial Hygiene Association (AIHA) Journal, 1973, no. 34 p. 241.

22.   SQUIRRELL DCM. *Diffusive Sampling - An Overview Diffusive Sampling: An Alternative Approach to Workplace Air Monitoring* Berlin A, Brown RH and Saunders KJ (eds) CEC Pub No 10555EN 1987

23.   VÖLGER S. *Development of Passive Sampler and Monitoring of Ammonia in Ambient Air* at Department of Environmental and Resources, Technical University of Denmark. Kgs. Lyngby, Denmark, 2004.

Electronic

24.   European Commission Environment DG. [Online] Brussels, Belgium: European Communities, 1995-2007. (Cited: November 14, 2007) Available in the internet: http://ec.europa.eu/environment/waste/pdf/story_book.pdf

25.   PRITCHARD J. D., CHAPD HQ, HPA *Ammonia - Health Effects of Acute / Single Exposure (Human)* [Online] Health Protection Agency Holborn Gate, 330 High Holborn, London WC1V 7PP. Copyright © Health Protection Agency. (Cited January, 17,2008) Available in the internet : http://www.hpa.org.uk/Chemicals/compendium/Ammonia/acute.htm

26.   About, Inc. *Online* www.about.com [Online] Copyright © 2007 (Cited January, 10.2007) Available in the internet: http://geography.about.com/library/cia/blcdenmark.htm

27.   Google earth. *Online* www.Google. Copyright © 2007 (Cited January 10.2008) Available in the internet: http://earth.google.com/

28.   SKC Inc *Online Store Page for items* [Online]. © Copyright 1995-2007. (Cited December 08,2007) Available in the internet: http://www.skcinc.com/product.asp

29.   VWR International, Inc. *Online VWR.COM – VWR Catalogue* [Online]
       Copyright© 2007 VWR International, LLC. All Rights Reserved (Cited
       December 12.2007) Available in the internet:
       http://www.vwrsp.com/catalog/index.cgi?parent_id=5035099

30.   DMI Online www.dmi.dk. Danish Meteorological Institute, November 8th
       2006. (Cited January 10, 2008). Available in the internet:
       http://www.dmi.dk/eng/index/forecasts.htm

7 APPENDICES

APPENDICES

Appendix 1: Determination of NH₃ in water

1. Name of the analysis:

Determination of ammonia in water

2   Date the instruction was formulated: Name:

24-9-2007   ham - DS 224

*   Date for last revision of instruction   Name:*

3. Matrix / sample type

Aqueous solutions, drinking water, recipients, waste water *The salinity of the samples should be less than 0.8%*

4. Concentration range / limit of detection

LOD: approx. 5 microgram/l *Useful to 1.2 mg/l*

5. Principle of analysis:

NH3 reacts with ClO⁻ to make mono chlor amine which reacts with phenol *in a surplus of ClO⁻ to a blue coloured compound, indo phenol blue*

6. Interferences / precision / restrictions / suitability.

7. Sampling / sample preparation:

8. Preservation / durability:

9. Risc and working environment:

10.   Equipment and apparatus used for the analysis:

11. Preparation of reagents and chemicals:

Reagent A: 13.5 g phenol and 0.15g disodium pentacyano nitrosyl ferrat in distilled water and dilute to 500 ml. Can be stored for 2 months

Reagent B: 1.2 ml 10% sodium hypo chlorite and 66 ml o.5 N NaOH is added to a 100 ml measuring flask and diluted to volume. The solution should be stored in a fridge and can be stored for 3 weeks

Reagent C: (If the samples contain Ca and Mg: 175 g tri sodium citrate is dissolved in 600 ml water in a beaker. Add 10 ml of 0.5 M NaOH and boil this solution for 30 minutes to expel NH3. You should remove more than 100 ml of water by boiling
After cooling the solution is diluted to 500 ml . The solution can be store for

12. Preparation of standards

Standard for 10,20,40,100,200,500,800,100 and 1200 µg/l is prepared by adding 0.5, 2.0, 2.0, 5.0, 10.0, 25.0, 40.0, 50.0, and 60.0 to a 100 ml measuring flask and dilute to volume with boiled water.
The standards should not be stored.

13. Quality control. Suggestions for quality control.

A solution 100 /l for conlity control can be obtained from the autoanalyser determination of NH4

14. Procedure

If no Ca and Mg is present

2.3 ml of sample or standard is added to a cuvette.
100 µl of reagent A is added
100 µl of reagent B is added
The mixture is left in the dark for 2 hours and analysed in a
spectrophotometer at 630 nm
The colour is stable for 24 hours
The spectrophotometer is zeroed using a sample containing 2.3 ml of
distilled water, 100 µl of Reagent A and 100 µl of reagent B
The readings is tranfered to an excel sheet for calibration and where the
content of the samples also are calculated

If Ca and Mg is present then start with adding 100 µl of reagent C then 100
µl of reagent A and then 100 µl of reagent B (The citrate will complexs with
Ca and Mg and keep these cations in solution

15. Waste disposal:

16. Calculation

N/A

17. References:

Appendix 2: Instruction for determination of total alkalinity (TAL)

1. Name of the analysis:

Instruction for determination of total alkalinity (TAL)

2   Date the instruction was carried out: Name:

Juni 1992   JCT/NJL/JK

         Date for last revision of Instruction   Name:

04.01.20056   MRS/NIC

3. Matrix / sample type

All kind of water samples.

4. Concentration range / limit of detection

Alkalinity values between 0,1 and 10 mmol/l: Manuel titration.   Alkalinity levels under 0,1 mmol/l: Gran-titration.

5. Principle of analysis:

Alkalinity: The ability of water to react with hydrogen ions. The alkalinity is determined by a titration with diluted sulphuric acid. During the titration the present weak bases are transformed to the corresponding weak acids.   Under normal conditions, the major part of the bases will be the ions from the carbonate system: pH 6 –10: HCO_3^- pH > 10: CO_3^{--} Total alkalinity: The amount of acid, which will be needed to change the pH-value from the present pH to pH 4,5. It is measured in milli equivalents/ litre H_3O^+ (meq/l) and at the endpoint pH 4,5 all the ions from the carbonate system are at CO2-form.   Determination of total-alkalinity (TAL):   In this schedule, there are 2 different methods to determinate TAL. The determination can be a simple manual titration with an indicator or a potentiometric end-point titration: 1. Manuel titration with an indicator: The sample is titrated with sulphuric acid with an added indicator with a colour change at pH 4,5. This method will often do, but if there are many samples or the sample is turbid or coloured, it is not suitable.   2. TAL after the Gran-method:

When the TAL level is very low < 0,1 mmol/l , a titration after the Gran-method is the most precisely method. After titration to pH 4,5 the H^+-concentration will increase after a linear function, with the added ml acid. From this linear function the equality point can be determined more precisely.

6. Interference / precision / restrictions / suitability.

Other bases which can react with H^+-ions will contribute to the TAL result, fx ortho-phosphate, ammonia, borate, acetate, sulphide, humus.

The magnetic stirring must be calm, so that the formed CO2 stays in the solution.

7. Sampling / sample preparation:

The sample bottle/flask must be filled up completely and closed very tight.

9. Preservation / durability:

The sample must be analysed within 24 hours after the sample has been taken. If there is a high amount of ion or biological activity in the sample it must be analysed within 2 hours.

9. Risk and working environment:

Sulphuric acid: Corrosive.

10. Equipment and apparatus used for the analysis:

1. Manuel titration with an indicator:
Pipette, 50 ml
Burette with 0,0500 N sulphuric acid
Magnetic stirrer
Conical flasks, 250ml

2. TAL after the Gran-method:
pH-meter
Magnetic stirrer
Micro burette with 0,0500 N sulphuric acid

11. Preparation of reagents and chemicals:

In the 2 methods a 0,0500 N sulphuric acid is used.
This is made from a pre-produced ampoule (Titrisol) and diluted with CO2-free distilled water.

CO2-free distilled water: Distilled water is blowed with nitrogen for 5 minutes or the water is boiled for 10-15 min. and cooled to room-temperature afterwards.

1. Manuel titration with an indicator:

0,0500 N sulphuric acid
Indicator: 0,020 g methyl red and 0,100 g brom cresol green dissolved in 100 ml ethanol.

2. TAL after the Gran-method:
Micro burette with 0,0500 N sulphuric acid

13. Quality control. Suggestions for quality control.

For controlling the analysis a simple sample of tap water from the laboratory can be used.
Turn on the water for 2 minutes and take out a sample when the water is running calmly.
Titrate the sample and calculate the result and write the result in the logbook.

14. Procedure

1. Manuel titration with an indicator:
A sample volume, fx 50 ml (a ml) is transferred with a pipette to a conical flask. 6 drops
of indicator is added and the sample is titrated with 0,0500 N sulphuric acid to the colour
change from green/blue to colourless/pink. Read the volume of the sulphuric acid for the
titration at the burette. (b ml)

2. TAL after the Gran-method:
Transfer the 0,0500 N sulphuric acid to the micro burette. Fill the burette and ensure that
there are no air bubbles present. Zero the burette.
Transfer 20 ml sample or a diluted sample to a 50 ml beaker. Place a magnet in the
sample and place the beaker on the stirrer and low the pH-electrode and the burette tube
into the sample.
Titrate quickly down to pH 4,5.
Read the used acid volume and the pH-value.
Add 0,5 ml acid and read the pH-value. Repeat the adding of 0,5 ml at least 5 times or
until the pH-value 3,5 is reached.

15. Waste disposal:

Chemical waste from this analysis can be poured out in the sink.

16. Calculation

1. Manuel titration with indicator:

TAL = b x N   x   1000
_____
         a   meq/l

where b is the sulphuric acid used for the titration, ml .

N is the normality of the sulphuric acid, 0,050 N.
a is the sample volume, ml.

2. Manuel potentiometricaly Gran-titration:

$F = (V + V_0) \cdot 10^{-pH}$
where V_0 = the original sample volume, ml.
V = the volume of the acid used for the titration, ml.

Or : $Log\ F = Log\ (V + V_0) - pH$

In a diagram is F x 1000 drawn as a function of ml used acid. At the linear part of the function the value F=0 is readed. The corresponding value of the acid volume is the equality-point.

TAL can be calculated afterwards:

$$TAL\ meq/L = \frac{1000\ x\ B\ x\ C}{A}$$

where A is the sample volume, ml.
B is the sulphuric acid used to reach the equality point, ml .
C is the normality of the sulphuric acid, 0,050 N.

Appendix 3: NH₃ calculation table

NH4-N (µg/l or ppb) 2.3ml standard solution	Abs. Calibration curve
10	0.005
20	0.026
40	0.030
100	0.064
200	0.157

Calibration Curve Abs. vs Conc.

$y = 0.0008x$
$R^2 = 0.9797$

(Chart: Absorbance vs NH4-N Standard Concentration)
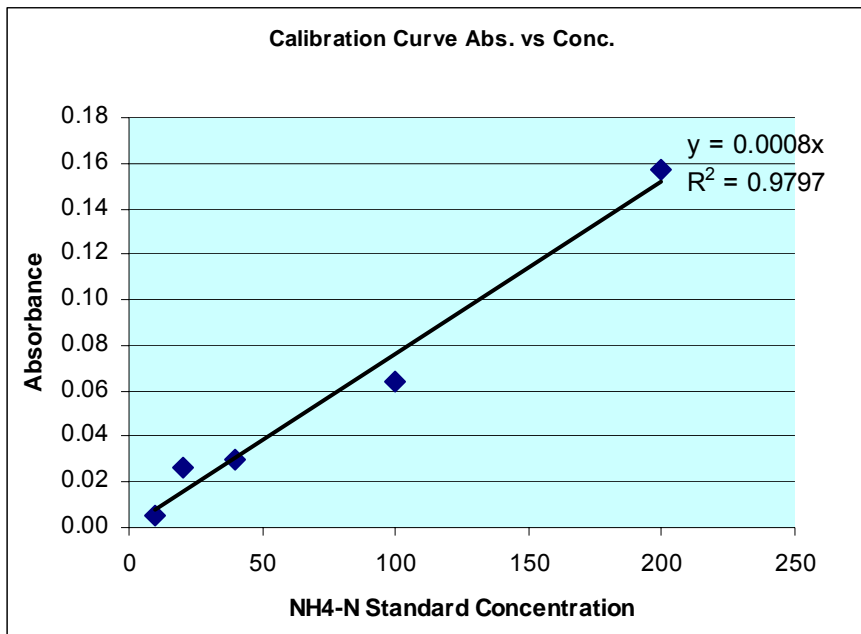
Absorbance standard values	
min	**max**
0.005	**0.157**

y = 0.0008x

$$A = 0.0008 \cdot [NH_3] \Leftrightarrow [NH_3] = \frac{A}{0.008}$$

Where: *A*   = Absorbance value detected from spectrophotometer

         0.008 = Value determined from calibration curve (figure 21)

         [NH₃] = Ammonia concentration

NH$_3$							
PASSIVE SAMPLE		**I** - **II** - **III** : Points of position of passive sampler					
		Absorbance from 2.3ml sample					
Windrows		I		II		III	
name	age (days)	Repicates		Repicates		Repicates	
A	40	0.345	0.166	1.415	missing	0.869	1.175
B	96	0.020	0.023	1.417	0.636	0.204	0.218
C	110	0.162	0.128	0.160	0.044	0.297	0.227
D	114	0.213	0.218	0.099	missing	0.225	0.203
E	173	0.030	0.113	0.030	0.025	0.030	0.016
F	201	0.057	0.105	0.076	0.012	0.145	0.072
G	264	0.087	0.109	0.078	0.069	0.088	0.019
North		0.056	0.013	0.063	0.035	0.016	0.051
South		0.073	0.012	0.019	0.044	0.011	0.016
West		0.035	0.060	0.052	0.031	0.041	0.020
East		0.089	0.068	0.086	0.572	0.015	0.058
Faraway		0.034	0.035	0.045	0.049	0.022	0.024
Faraway		0.076	0.072	0.016	0.015	0.064	0.054
Blank							
0.027	0.046	0.051	0.051	0.057	0.061	0.065	0.066

$y=0.0008x$		Ammonia Concentration in 2.3ml sample (µg/l or ppb)					
Windrows		I		II		III	
name	age (days)	Repicates		Repicates		Repicates	
A	40	431.250	207.500	1768.750	missing	1086.250	1468.750
B	96	25.000	28.750	1771.250	795.000	255.000	272.500
C	110	202.500	160.000	200.000	55.000	371.250	283.750
D	114	266.250	272.500	123.750	missing	281.250	253.750
E	173	37.500	141.250	37.500	31.250	37.500	20.000
F	201	71.250	131.250	95.000	15.000	181.250	90.000
G	264	108.750	136.250	97.500	86.250	110.000	23.750
North		70.000	16.250	78.750	43.750	20.000	63.750
South		91.250	15.000	23.750	55.000	13.750	20.000
West		43.750	75.000	65.000	38.750	51.250	25.000
East		111.250	85.000	107.500	715.000	18.750	72.500
Faraway		42.500	43.750	56.250	61.250	27.500	30.000
Faraway		95.000	90.000	20.000	18.750	80.000	67.500
Blank							
33.750	57.500	63.750	63.750	71.250	76.250	81.250	82.500

Ammonia Concentration in 2.3ml sample average per windrow (µg/l or ppb)											
Windrows		I			II			III			windrow
name	age (days)	Repicates		Average	Repicates		Average	Repicates		Average	average
A	40	431.250	207.500	319.375	1768.750	missing	1768.750	1086.250	1468.750	1277.500	1121.875
B	96	25.000	28.750	26.875	1771.250	795.000	1283.125	255.000	272.500	263.750	524.583
C	110	202.500	160.000	181.250	200.000	55.000	127.500	371.250	283.750	327.500	212.083
D	114	266.250	272.500	269.375	123.750	missing	123.750	281.250	253.750	267.500	220.208
E	173	37.500	141.250	89.375	37.500	31.250	34.375	37.500	20.000	28.750	50.833
F	201	71.250	131.250	101.250	95.000	15.000	55.000	181.250	90.000	135.625	97.292
G	264	108.750	136.250	122.500	97.500	86.250	91.875	110.000	23.750	66.875	93.750
North		70.000	16.250	43.125	78.750	43.750	61.250	20.000	63.750	41.875	48.750
South		91.250	15.000	53.125	23.750	55.000	39.375	13.750	20.000	16.875	36.458
West		43.750	75.000	59.375	65.000	38.750	51.875	51.250	25.000	38.125	49.792
East		111.250	85.000	98.125	107.500	715.000	411.250	18.750	72.500	45.625	185.000
Faraway		42.500	43.750	43.125	56.250	61.250	58.750	27.500	30.000	28.750	43.542
Faraway		95.000	90.000	92.500	20.000	18.750	19.375	80.000	67.500	73.750	61.875
Blank		33.750	57.500	63.750	63.750	71.250	76.250	81.250	82.500		66.250

- X -

NH₃ concentration total average per windrows and area near composting plant

name	age (days)	in water (mg/m³)	in the air mg/m³	in the air µg/m³	in the air ppbv (277K)	in the air ppbv (STP)
A	40	1121.875	0.084	83.833	**112.011**	110.393
B	96	524.583	0.039	39.200	**52.376**	51.619
C	110	212.083	0.016	15.848	**21.175**	20.869
D	114	220.208	0.016	16.455	**21.986**	21.669
E	173	50.833	0.004	3.799	**5.075**	5.002
F	201	97.292	0.007	7.270	**9.714**	9.574
G	264	93.750	0.007	7.006	**9.360**	9.225
North		48.750	0.004	3.643	**4.867**	4.797
South		36.458	0.003	2.724	**3.640**	3.588
West		49.792	0.004	3.721	**4.971**	4.900
East		185.000	0.014	13.824	**18.471**	18.204
Faraway		43.542	0.003	3.254	**4.347**	4.285
Faraway		61.875	0.005	4.624	**6.178**	6.089
Blank average		66.250	0.005	4.951	**6.615**	6.519
Blank	33.750	57.500	63.750	63.750		
(mg/m³)	71.250	76.250	81.250	82.500		

NH₃ concentration average I point measurement per windrows and area near composting plant

name	age (days)	in water (mg/m³)	in the air mg/m³	in the air µg/m³	in the air ppbv (277K)	in the air ppbv (STP)
A	40	319.375	0.024	23.866	**31.887**	31.427
B	96	26.875	0.002	2.008	**2.683**	2.645
C	110	181.250	0.014	13.544	**18.096**	17.835
D	114	269.375	0.020	20.129	**26.895**	26.507
E	173	89.375	0.007	6.679	**8.923**	8.795
F	201	101.250	0.008	7.566	**10.109**	9.963
G	264	122.500	0.009	9.154	**12.231**	12.054
North		43.125	0.003	3.223	**4.306**	4.244
South		53.125	0.004	3.970	**5.304**	5.228
West		59.375	0.004	4.437	**5.928**	5.843
East		98.125	0.007	7.332	**9.797**	9.656
Faraway		43.125	0.003	3.223	**4.306**	4.244
Faraway		92.500	0.007	6.912	**9.235**	9.102
Blank average		66.250	0.005	4.951	**6.615**	6.519

NH$_3$ concentration average II point measurement per windrows and area near composting plant

name	age (days)	in water (mg/m^3)	in the air mg/m^3	in the air µg/m^3	in the air ppbv (277K)	in the air ppbv (STP)
A	40	1768.750	0.132	132.171	**176.596**	174.046
B	96	1283.125	0.096	95.883	**128.110**	126.260
C	110	127.500	0.010	9.528	**12.730**	12.546
D	114	123.750	0.009	9.247	**12.356**	12.177
E	173	34.375	0.003	2.569	**3.432**	3.383
F	201	55.000	0.004	4.110	**5.491**	5.412
G	264	91.875	0.007	6.865	**9.173**	9.041
North		61.250	0.005	4.577	**6.115**	6.027
South		39.375	0.003	2.942	**3.931**	3.875
West		51.875	0.004	3.876	**5.179**	5.105
East		411.250	0.031	30.731	**41.060**	40.467
Faraway		58.750	0.004	4.390	**5.866**	5.781
Faraway		19.375	0.001	1.448	**1.934**	1.907
Blank average		66.250	0.005	4.951	**6.615**	6.519

NH$_3$ concentration average III point measurement per windrows and area near composting plant

name	age (days)	in water (mg/m^3)	in the air mg/m^3	in the air µg/m^3	in the air ppbv (277K)	in the air ppbv (STP)
A	40	1277.500	0.095	95.462	**127.549**	125.707
B	96	263.750	0.020	19.709	**26.333**	25.953
C	110	327.500	0.024	24.473	**32.698**	32.226
D	114	267.500	0.020	19.989	**26.708**	26.322
E	173	28.750	0.002	2.148	**2.870**	2.829
F	201	135.625	0.010	10.135	**13.541**	13.346
G	264	66.875	0.005	4.997	**6.677**	6.581
North		41.875	0.003	3.129	**4.181**	4.121
South		16.875	0.001	1.261	**1.685**	1.661
West		38.125	0.003	2.849	**3.806**	3.752
East		45.625	0.003	3.409	**4.555**	4.490
Faraway		28.750	0.002	2.148	**2.870**	2.829
Faraway		73.750	0.006	5.511	**7.363**	7.257
Blank average		66.250	0.005	4.951	**6.615**	6.519

[NH3] ppbv average I - II - III point measurement per windrows and area near composting plant					
Windrow		**I**	**II**	**III**	**Average**
name	age (days)	in the air ppbv (277K)	in the air ppbv (277K)	in the air ppbv (277K)	in the air **ppbv** (277K)
A	40	32	177	128	112
B	96	3	128	26	52
C	110	18	13	33	21
D	114	27	12	27	22
E	173	9	3	3	5
F	201	10	5	14	10
G	264	12	9	7	9
North		4	6	4	5
South		5	4	2	4
West		6	5	4	5
East		10	41	5	18
Faraway		4	6	3	4
Faraway		9	2	7	6
Blank average		7	7	7	7
Average per point (ppbv)		16	50	34	
Average in the composting plant area		33			

$$C_A = \frac{Q \cdot L}{D \cdot A \cdot t} \qquad (2)$$

$$Q = C_0 \cdot V_w \cdot \frac{M_{NH_3}}{M_N} \qquad (3)$$

Where:
C_A = concentration in air (mg/m^3)
Q = mass uptake (mg)
L = length of diffusion path (m)
D = coefficient of diffusion (m^2/sec)
A = cross section area of diffusion path (m^2)
t = sampling time (sec)
C_o = external concentration being sampled (mg/m^3)
V_w = Volume of water (m^3)
M_{NH_3} = molar mass of ammonia (g/mol)
M_N = molar mass of nitrogen (g/mol)

Example:

$$L = 5,2 \cdot 10^{-2} \ m$$
$$D = 2,275 \cdot 10^{-6} \ m^2/sec$$
$$A = 1,13 \cdot 10^{-4} \ m^2$$
$$t = 7,56 \cdot 10^{5} \ sec$$
$$C_o = 1121,875 \ mg/m^3$$
$$V_w = 2,3 \cdot 10^{-6} \ m^3$$

$$C_A = \frac{5,2 \cdot 10^{-2} m}{2,2,75 \cdot 10^{-6} \frac{m^2}{s} \cdot 1,13 \cdot 10^{-4} m^2 \cdot 7,56 \cdot 10^{5} s} \cdot 1121,875 \frac{mg}{m^3} \cdot 2,3 \cdot 10^{-6} m^3 \cdot \frac{17 \frac{g}{mol}}{14 \frac{g}{mol}}$$

$$C_A = 0,084 \ mg/m^3 = 83,833 \ \mu g/m^3$$

According with Ideal gas law PV=nRT

In respect of T= 4ºC = 277K

$$C_A = \frac{83,833 \frac{\mu g}{m^3} \cdot R \cdot T}{17 \frac{g}{mol} \cdot P} = \frac{83,833 \frac{\mu g}{m^3} \cdot 0,821 \cdot 10^{-5} \frac{m^3 \cdot atm}{K \cdot mol} \cdot 277K}{17 \frac{g}{mol} \cdot 1 atm} = 112 \ ppbv$$

Appendix 4: CO₂ calculation table

Windrows name	Age (days)	Sample volume analized	Windrow measurement points	Replicates	pH starting point	V1 (ml)	V2 (ml)	V TAL (ml)	Measurement points	TAL (meq/l)	[CO2] (mg/l)	CO2 in the sample (mgl)	Pumped volume (L)	[CO2] pumped (mg/l =g/m³)	[CO2] pumped (mg/m3)	[CO2] in air at 4°C (ppm)
			I	*a*	12.0	9.6	9.8	0.2	chimney	20	880	9	4.4	2	2000	1033
A	40	1ml	II	*a*	11.8	9.6	10.0	0.4	windrow	40	1760	18	4.4	4	4000	2067
			III	*a*	11.8	9.8	9.9	0.1	windrow	10	440	4	5.3	1	830	429
			I	*a*	11.4	5.6	9.1	3.5	chimney	350	15400	154	3.6	43	42778	22105
B	96	1 ml	II	*a*	11.9	8.9	9.4	0.5	bottom	50	2200	22	4.0	6	5500	2842
			III	*a*	11.5	6.6	10.7	4.1	windrow	410	18040	180	1.1	164	164000	84745
			I	*a*	12.6	44.6	48.8	4.2	chimney	84	3696	37	2.8	13	13200	6821
C	110	5 ml	II	*a*	12.5	45.5	47.9	2.4	bottom	48	2112	21	3.2	7	6600	3410
			III	*a*	12.5	47.7	48.9	1.2	windrow	24	1056	11	7.4	1	1427	737
			I	*a*	12.4	38.3	45.4	7.1	chimney	142	6248	62	2.5	25	24992	12914
D	114	5 ml	II	*a*	12.6	45.3	48.7	3.4	bottom	68	2992	30	3.1	10	9652	4987
			III	*a*	12.5	42.7	46.8	4.1	windrow	82	3608	36	0.4	90	90200	46610
			I	*a*	11.9	9.5	10.0	0.5	chimney	50	2200	22	4.1	5	5366	2773
			I	*b*	12.0	9.4	9.6	0.2		20	880	9	4.1	2	2146	1109
E	173	1 ml	II	*a*	12.0	10.4	10.6	0.2	bottom	20	880	9	4.0	2	2200	1137
			II	*b*	12.0	10.2	10.3	0.1		10	440	4	4.0	1	1100	568
			III	*a*	12.0	9.6	9.8	0.2	windrow	20	880	9	4.1	2	2146	1109
			III	*b*	12.0	9.7	9.8	0.1		10	440	4	4.1	1	1073	555
			I	*a*	12.6	48.0	49.9	1.9	chimney	38	1672	17	3.9	4	4287	2215
		5 ml	I	*b*	12.6	48.9	49.6	0.7		14	616	6	3.9	2	1579	816
F	201		II	*a*	12.5	48.0	49.0	1.0	bottom	20	880	9	4.1	2	2146	1109
			II	*b*	12.6	50.1	50.5	0.4		8	352	4	4.1	1	859	444
		1 ml	III	*a*	11.9	8.1	9.5	1.4	windrow	140	6160	62	3.0	21	20533	10610
			III	*b*	11.9	9.4	9.9	0.5		50	2200	22	3.0	7	7333	3789

G	264	1 ml	I	*a*	12.0	9.4	9.6	0.2	chimney	20	880	9	3.7	2	2378	1229
				b	11.8	9.4	9.6	0.2		20	880	9	3.7	2	2378	1229
			II	*a*	12.0	9.5	9.6	0.1	bottom	10	440	4	4.1	1	1073	555
				b	12.0	9.8	9.9	0.1		10	440	4	4.1	1	1073	555
			III	*a*	12.0	10.0	10.1	0.1	windrow	10	440	4	3.1	1	1419	733
				b	12.0	9.4	9.5	0.1		10	440	4	3.1	1	1419	733

[CO2] average value					
		Chimney (ppm)	Bottom (ppm)	Windrow	
Name	Age (days)			(ppm)	(ppbv)
A	40	1033		429	
B	96	22105	3100	84745	85
C	110	6821	3410	737	1
D	114	12914	4987	46610	47
E	173	3882	1705	1664	2
F	201	3032	1553	14400	14
G	264	2458	1109	1467	1
Average per point (ppm):		**7464**	**2644**	**21436**	
Average per point (ppbv):		7	3	21	
Average (ppm):		**10515**			
Average (ppbv):		11			

XVII
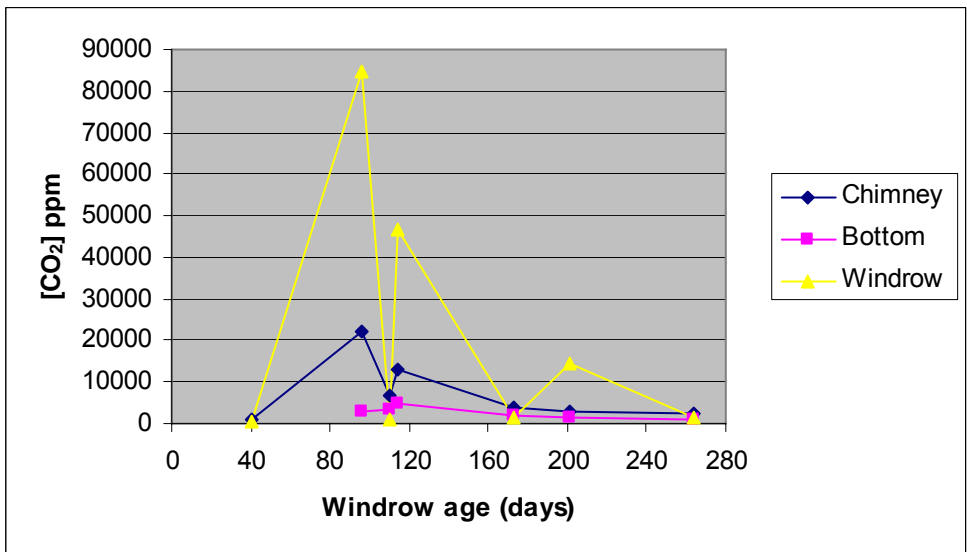
Appendix 5: NH$_3$/NH$_4$-N equilibrium

The NH$_3$ molecule has a large dipole moment, and this is consistent with its geometry, a trigonal pyramid.

The H–N–H bond angle of 107 degrees is close to the tetrahedral angle of 109.5 degrees.
The polarity of NH$_3$ molecules and their ability to form hydrogen bonds explains to some extent the high solubility of ammonia in water.
However, a chemical reaction also occurs when ammonia dissolves in water. In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from H$_2$O to yield ammonium and hydroxide ions.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
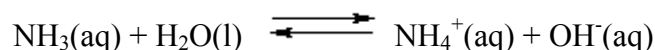
The production of hydroxide ions when ammonia dissolves in water gives aqueous solutions of ammonia their characteristic alkaline (basic) properties. The double arrow in the equation indicates that an equilibrium is established between dissolved ammonia gas and ammonium ions. Not all of the dissolved ammonia reacts with water to form ammonium ions. A substantial fraction remains in the molecular form in solution. In other words, ammonia is a weak base.

In contrast, the ammonium ion acts as a weak acid in aqueous solution because it dissociates to form hydrogen ion and ammonia.

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$
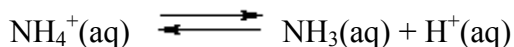
The ammonium ion is found in many common compounds, such as ammonium chloride, NH$_4$Cl. Typically, ammonium salts have properties similar to the corresponding compounds of the Group IA alkali metals.

Appendix 6: Concentration ppm, ppbv, in water and in air

Unlike units for soil and water concentrations, μg/m3 **are not** equivalent to parts per billion in air; μg/m3 is **a weight-to-volume** ratio, while parts per billion in air is a **volume-to-volume** ratio.

Soil	Water	Air
μg/kg = ppb	μg/L ≈ ppb	μg/m3 ≠ ppb
w/w = w/w	w/v ≈ w/v	w/v ≠ v/v

Solids

Concentrations of substances in a solid are generally given as *mass of substance per unit mass of solid*:

1 μg/kg = 1 ppb (part per billion – by weight)

1 mg/kg = 1 ppm (part per million by weight)

Liquids

Concentrations of substances in a liquid (that will usually mean water) are generally given as *mass of substance per unit volume of solution*.

Conventional units are mg/l, μg/l, ng/l (mg = milligram, l = liter, μg = microgram, ng = nanogram).

Things get confusing when we have to deal with ppm or ppb units. Part of the confusion originates from the definition of ppm or ppb. One should really define ppm (or ppb, ppt, etc.) in terms of whether the units are on a weight (w/w) or volume (v/v) basis, or a combination of the two (w/v or v/w) basis.

Note, the equality:

1 mg/l = 1 ppm (w/v or weight/volume)

1 μg/l = 1 ppb (w/v)

does not depend on the specific gravity of the solution.

If we are dealing with ppm (or ppb, etc.) on a weight (w/w) basis, things get a little more complicated. For dilute solutions, where 1 liter of solution weights approximately 1000 g (i.e., the specific gravity of the solution is 1.0) the following set of equivalencies are true.

Then:

1 mg/l = 1 g/m^3 ≈ 1 ppm (w/w)

1 μg/l = 1 mg/ m^3 ≈ 1 ppb (w/w)

In some situations, the solution is concentrated or we must deal with a non-aqueous liquid (such as gasoline), the specific gravity may not be equal to 1.0 and mg/l = ppm (w/w) × Specific gravity of the solution; μg/l = ppb (w/w) × Specific gravity of the solution

For example, a sediment – water mixture contains 1 μg/l of PCBs (polychlorinated biphenyls). The specific gravity of the sediment – water mixture is 1.06.

Than the concentration of PCBs in ppm (w/w) is:

$$\frac{1\,\mu g/l}{1.06} = 0.9\,\text{ppb (w/w)}$$

Gases

For most air pollution work, it is customary to express pollutant concentrations in volumetric terms. For example, the concentration of a gaseous pollutant in ppm units is the volume of the pollutant per million volumes of the air mixture:

$$\frac{1\,\text{volume of gaseous pollutant}}{10^6\,\text{volumes of air}} = 1\,\text{ppm (v/v)}$$

One can use the notation (v/v) or by volume to denote that the concentrations are given in volumetric units.

At times, gaseous concentrations are expressed using mixed units of mass per units volume (e.g., μg/m^3 or mg/m^3). The relationship between ppm (v/v) and mg/m^3 depends on the density of the pollutant which depends on its pressure, temperature and molecular weight.

The ideal gas law (PV = nRT, where P = pressure (atm), V = volume (1), n = mass of substance (moles),

R = ideal gas constant (0.082 atm l mol^{-1}K^{-1}), T = absolute temperature (ºC + 273) in degrees Kelvin) is used to convert units.

Standard temperature and pressure are defined as 1 atm and 0 °C (273 K). Under these conditions one mole of an ideal gas occupies a volume of 22.4 l.

$$\frac{V}{n} = \frac{RT}{P} = \frac{(0.082\,\frac{atm \cdot l}{mol \cdot K})(273\,K)}{1\,atm} = 22.4\,\frac{l}{mol}$$

Using Boyle's Law (PV = constant or $P_1V_1 = P_2V_2$) for constant temperature conditions and Charles's Law (V/T = constant or $V_1T_1 = V_2T_2$) for constant pressure conditions, we can develop an equation to convert ppm to mg/m^3 or visa versa.

$$\frac{mg}{m^3} = \frac{ppm \times molecular\ weight}{22.4\,\frac{l}{mol}} \times \frac{273}{T(K)} \times \frac{P(atm)}{1\,atm}$$

Thus, as you raise the temperature of a gas mixture, the volume of the mixture increases. Since the pollutant mass is constant, the concentration in units of mg/m^3 must decrease. As you raise the pressure of a gas mixture, the volume of the mixture decreases. Since the pollutant mass is constant, the concentration in units of mg/m^3 must increase. (Remember the mass of the pollutant is independent of pressure).