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Impact of pre-treatment on the stability and leachability of three different wastes

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Abstract

The effect from mechanical-biological pre-treatment (MBT) of wastes in Sweden and Germany has been studied. The organic matter and biological activities were studied and compared. Other parameters such as heavy metals and nutrients were examined and related to the organic matter. The effect of low water content on degradation was investigated and the relevant legislation in the two countries was studied and compared.

Three different waste materials were used; two from Germany (MBA 1 and MBA 2) and one from Trelleborg, Sweden. The German materials were municipal wastes while the Swedish one was a mixture of building waste with compost and sewage sludge. MBT means that the material is first sorted and crushed and then treated biologically, mainly through composting, to prepare the waste for landfilling, or use within the landfill.

The solid waste and the eluate (leachate) were studied. The eluate was filtrated through four different membranes (cut-offs 0.45 µm, 100 kDa, 30 kDa and 5 kDa) to learn more about the size of the organic matter and its relation to other pollutants. Four bioreactors with different conditions were used to simulate landfilling of the output material.

The organic content decreased during treatment. In MBA 1 DOC decreased more (95%) than TOC (38%); i.e., the organic matter became harder to leach. The biological stability increased; the respiration activity and the gas formation potential decreased with up to more than 90%. This was also shown by parameters such BOD_5/COD ratio, humic acids formation, C/N ratio, FT-IR spectrums and thermal methods. Pollutants such as most heavy metals and nitrogen became less leachable after treatment, thus contributing to a decreased emission potential.

The metals studied were cadmium, chromium, cupper, lead, nickel and zinc. They seemed to be bound to the organic matter to some extent, perhaps with the exception of cadmium. In most cases less than one percent of the metals were eluted. In the cases where the initial leachability of metals was high, it decreased considerably (up to 99%) during treatment.

Considering only the parameters analysed in this study, MBA 1 and the material from Trelleborg could be landfilled in Germany after treatment, and Trelleborg even before. Even though landfilling is allowed, this does not mean that the emission potential is zero. MBA 2 had too high DOC content and could not be landfilled. The German output materials could not be landfilled in Sweden and Trelleborg can only be landfilled if it can be classified as non-hazardous waste.

The Swedish legislation is, unlike the German, not adapted for MBT-treated waste to be landfilled. The Swedish limits are generally stricter than the German ones and the most limiting criterion is TOC. TOC is however not the most relevant parameter since it is not directly associated with the emission potential. It could be replaced by activity measurements like RA_4 or GP_{21} together with DOC. The Swedish limit values are strict but exemptions in the legislation enable waste with high emission potential to be landfilled anyway. The legislation could be better adapted to the actual situation.

The landfill simulation showed that aerobic degradation is more efficient than anaerobic in reducing the respiration activity. It also showed that low water content will slow down the degradation considerably. A slower degradation will cause the degradable material to have a longer lifetime in the landfill.

There is more to learn about the dissolved organic matter and also about its association with heavy metals. If the goal is to study changes during treatment, it is better to follow one batch of material through the whole process than to sample batches at different stages the same day.

Keywords: municipal solid waste, waste management pre-treatment, leachate fractionation, heavy metals, humic acid, waste management stabilisation

Einfluß der Vorbehandlung auf die Stablitität und Eluierbarkeit von drei unterschiedlichen Abfällen

Zusammenfassung

In dieser Arbeit sind die Effekte von mechanisch-biologischer Vorbehandlung auf die Stabilität und die Eluierbarkeit von Abfällen aus Schweden und Deutschland untersucht worden. In Schweden ist die Deponierung von Materialien mit einem Kohlenstoffgehalt von über 10% verboten, es sei denn es handelt sich um anaerob und aerob stabilisierten Belebtschlamm. In Deutschland hingegen ist die Deponierbarkeit von organischen Abfällen abhängig vom Stabilisierungsgrad und des Gehalts von Kohlenstoff im Eluat.

In Abhängigkeit von unterschiedlichen Stabilisierungsgraden sind die Abfälle eluiert und filtriert worden und anschließend auf gelösten organischen Kohlenstoff und auf die Schwermetalle Kadmium, Kupfer, Blei und Zink untersucht worden. Ziel dieser Arbeit war, mögliche Zusammenhänge zwischen der Stabilisierung und der Eluierbarkeit aufzudecken, und zu testen, inwieweit der Totalgehalt Kohlenstoff im Feststoff beziehungsweise im Eluat etwas über verbliebenes Emissionspotential aussagt.

Drei unterschiedliche Abfälle gingen in die Untersuchungen ein: Zwei Siedlungsabfälle aus Deutschland und ein Gemisch aus Reststoff von der Brennstoffaufbereitung, Kompost und Schlamm aus Schweden. Die Abfälle sind alle sortiert und entweder aerob durch Kompostierung oder anaerob durch Rotte vorbehandelt worden. Ziel der Vorbehandlungen ist eine emissionsarme Deponierung im Fall der deutschen Abfälle und eine Verwendung als Baumaterial auf der Deponie oder emissionsarme Deponierung im Fall des schwedischen Abfalls.

Die Eluate wurde mit Membranen der Maschenweiten 0,45 µm, 100 kDa, 30 kDa und 5 kDa filtriert, um die Größenverteilung des gelösten organischen Kohlenstoff zu bestimmen und zu erkennen, ob Schwermetalle bevorzugt in einer gewissen Fraktion zu finden sind, und ob sich diese Verteilung im Laufe der Stabilisierung ändert.

Der Stabilsierungsgrad wurde mit Hilfe von aeroben (AT4) und anaeroben (GP21) Labortests bestimmt. Zusätzlich wurde das verbleibende Emissionspotential noch in Versuchsreaktoren im Labormaßstab untersucht.

Die eingesetzten Analysmethoden wie TOC; BOD5/COD, Huminsäuren, Kohlenstoff-Stickstoffverhältnis, FT-IR Spektroskopie und thermische Analysen deuteten alle auf eine erhöhte biologische Stabilität, d. h. auf eine verminderte Abbaubarkeit durch mikrobiologische Aktivität der vorbehandelten Abfälle, hin. Atmungsaktivität (AT4), Gasbildungspotential (GB21) wurden durch die unterschiedlichen Vorbehandlungen um bis zu 90% verringert.

Außerdem zeigte sich, dass sich die Eluierbarkeit vor allem der Schwermetalle verringerte, die vor der Behandlung eine vergleichsweise hohe Mobilität zeigten. Ein beträchtlicher Anteil der untersuchten Schwermetalle passierte die Membran mit der geringsten Maschenweite. Der Anteil an Huminsäuren am gelösten Kohlenstoff nimmt im Laufe der Abfallvorbehandlung zu. Ein Großteil des DOC verbleibt jedoch unspezifiziert, und daher können mit dieser Datenlage keine allgemeingültigen Schlüsse über das verbleibende Emissionspotential des eluierten Kohlenstoffes gezogen werden.

In Schweden herrscht ein Verbot für die Deponierung von organischen Abfällen, und im Falle von MBA-Abfällen besteht lediglich eine Ausnahme: Ein TOC-Gehalt unter 10%. Mit Bezug auf die untersuchten Parameter, kann der Schluss gezogen werden, dass die Abfälle MBA 1 und Trelleborg in Deutschland deponiert werden dürften, nachdem sie die jeweilige Vorbehandlung durchlaufen haben. Das Material Trelleborg könnte sogar ohne eine Vorbehandlung abgelagert werden. Die DOC-Werte von MBA 2 vereiteln eine direkte Deponierung in Deutschland, allerdings lediglich nach den bei der Durchführung dieser Arbeit geltenden Kriterien. MBA 1 und 2 dürfen in Schweden nicht abgelagert werden, da der TOC-Gehalt zu hoch ist. Trelleborg kann nach Behandlung in Schweden abgelagert werden.

Da der TOC-Gehalt im Vergleich zum DOC, dem AT4 und dem GB21 weniger Aussagekraft über das Emissionspotential von den hier untersuchten organischen Abfällen hat, empfiehlt sich eine Anpassung der schwedischen Gesetzgebung im Stile der Kriterien für MBA-Abfälle in Deutschland.

Als letzter Teil der Arbeit wurde das verbleibende Emissionspotential nach Vorbehandlung und der Einfluss des Wassergehaltes darauf mit dem MBA 1 Abfall mit Hilfe von Deponisimulationsreaktoren simuliert. Vier Reaktoren wurden parallel getestet: Ein belüfteter, ein anaerober, einer mit Sickerwasserrezirkulation und einer mit niedrigerem Wassergehalt. Aerobe Verhältnisse beschleunigten den Abbau des organischen Materials im Vergleich zu anaeroben. Der Wassergehalt scheint für den anaeroben Abbau von stabilisierten Abfällen eine entscheidende Rolle zu spielen, da der Abbau im trockeneren Reaktion wesentlich langsamer verlief.

Stichworte: Siedlungsabfall, Abfallwirtschaft, MBA, Vorbehandlung, Sickerwasserfraktionierung, Schwermetalle, Huminsäuren, Stabilisierung

Förbehandlingens effekter på stabilitet och lakbarhet hos tre avfallsmaterial

Sammanfattning

Effekterna från mekanisk-biologisk förbehandling (MBT) av avfall i Sverige och Tyskland har studerats. Organiskt material och biologisk aktivitet har undersökts och jämförts. Andra parametrar som tungmetaller och närsalter studerades och relaterades till det organiska materialet. Effekten av låg vattenhalt på nedbrytningen studerades också och relevant lagstiftning från de två länderna jämfördes.

Tre olika avfallsmaterial har använts; två från Tyskland (MBA 1 and MBA 2) och ett från Trelleborg. Från Tyskland användes kommunala avfall medan det svenska var en blandning av byggavfall, kompost och avloppsslam. Mekanisk-biologisk avfallsbehandling innebär att avfallet först sorteras och finfördelas varefter det behandlas biologiskt, framförallt genom kompostering. Efter behandlingen skall avfallet deponeras, eller, som i fallet med Trelleborg, användas inom deponin.

Fast avfallsmaterial och lakvatten studerades. Lakvattnet filtrerades genom membran med porstorlekarna 0,45 µm, 100 kDa, 30 kDa och 5 kDa för att undersöka storleksfördelningen hos det organiska materialet samt till vilka fraktioner olika föroreningar var bundna. Bioreaktorer i labskala användes för att simulera deponering under olika förhållanden.

Innehållet av organiskt material minskade under behandlingen. Minskningen av organiskt kol var större i lakvattnet från MBA 1 (95%) än i det fasta materialet (38%) vilket visar att urlakning av materialet försvårades av behandlingen. Den biologiska stabiliteten ökade under behandlingen vilket visades av BOD_5/COD-kvot, humussyrabildning, förhållandet kol/kväve, FT-IR-spektroskopi och termiska metoder. Respirationsaktivitet och gasbildningspotential visar på att aktiviteten minskar med runt 90%. Dessutom minskade lakbarheten hos olika föroreningar. Alla dessa förändringar bidrog till att minska emissionspotentialen.

Förekomst och migration av tungmetallerna kadmium, krom, koppar, bly, nickel och zink studerades. De verkade, i alla fall delvis, vara bundna till det organiska materialet, möjligtvis med undantag för kadmium. En stor del av metallerna var dock bundna i former mindre än det minsta membranet så det gick inte att avgöra om de var bundna till organiskt material. I de flesta fall lakades enbart en mycket liten del (en procent eller mindre) av tungmetallerna ut. I de fall där den ursprungliga lakbarheten var stor minskade den under behandlingen med upp till 99%.

Emissionspotentialen hos alla avfallsmaterial minskade under behandlingen. Om bara de parametrar som studerats här tas i beaktande så kan MBA 1 och Trelleborg deponeras i Tyskland efter behandlingen; Trelleborg uppfyllde kriterierna redan före behandlingen. Att det är tillåtet att deponera materialet innebär dock inte att emissionspotentialen är noll. MBA 2 klarade inte av kravet på DOC och kunde inte deponeras. Inget av de tyska materialen kan deponeras i Sverige och Trelleborg kan bara deponeras om det kan klassificeras som icke-farligt avfall. Den svenska lagstiftningen är, till skillnad från den tyska, inte anpassad för att MBT-avfall skall kunna deponeras.

De svenska gränsvärdena är generellt strängare; särskilt TOC-gränsen. TOC är dock inte den mest relevanta parametern; aktivitetsmätningar kombinerat med DOC är bättre för att fastslå emissionspotentialen. Även om gränsvärdena är stränga i Sverige så gör undantag i lagstiftningen att avfall med hög utsläppspotential kan deponeras. Det hade troligen varit bättre att anpassa lagstiftningen så att antalet undantag som måste göras hade kunnat minimeras.

Deponeringssimuleringen visade att aerob nedbrytning är effektivare för att minska den biologiska aktiviteten i avfallet. Det visade sig också att ett lågt vatteninnehåll gjorde att nedbrytningen gick mycket långsammare. Detta leder i sin tur att biologiskt nedbrytbart material kommer att finnas kvar mycket längre i deponin.

I framtida undersökningar vore det intressant att studera det lösta organiska materialet närmare inklusive dess relation till tungmetaller. Om syftet med undersökningen är att studera förändringar under behandlingen så är det bättre att följa en omgång material genom behandlingen snarare än att ta prover på olika behandlingssteg under samma dag.

Sökord: hushållsavfall, avfallsteknik - förbehandling, lakvatten - fraktionering, tungmetaller, humussyror, avfallshantering - stabilisering.

Preface

This is a master's thesis done at the division of Water Resources Engineering at the Faculty of Engineering at Lund University. It was carried out in cooperation with the Institute for Waste Resource Management at Hamburg University of Technology. The thesis is the final part of the education program in Environmental Engineering. All practical work was done in Hamburg at the Institute for Waste Resource Management.

My thanks go to my supervisors Martijn van Praagh and Jörn Heerenklage for all their time and support. Thanks also to Professor Kenneth M. Persson for giving me the possibility of going to Hamburg. The co-workers at the Institute for Waste Resource Management also deserve many thanks for their help with analyses, demonstrations and answers to my questions. Last, but not least, I thank all my new friends who made my stay in Hamburg great.

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/Hanna Modin

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1 Introduction

This thesis deals with mechanically-biologically pre-treated waste in Sweden and Germany. The effects of pre-treatment are examined with a special focus on the organic matter in the waste. The emission potential of the waste, once it has been landfilled, is also discussed. In the following sections the background of this work and the more specific goals and objectives will be presented.

1.1 Background

Landfills affect the environment. The most important pollution pathways are leaching of contaminated water, so called leachate, and greenhouse gas emissions. In the latest years landfills have become subject to an increasingly strict regulation in the EU. The legislation aims at minimizing the environmental risks.

Before landfilling the waste generally has to be treated to reduce the emission potential. In Germany mechanical-biological pre-treatment (MBT) has become important. After treatment the waste can be landfilled if it complies with limit values adapted specially for this type of waste.

In Sweden half of the household waste is incinerated, 34% is source separated and recycled, 11% is treated biologically and 5% is landfilled. Mechanical-biological pre-treatment is normally not used prior to landfilling in Sweden. (RVF 2006, p. 7)

The design and operation of landfills is also subject to strict regulation. There has to be tight covering all around the landfill to prevent leakage of gas and water, and to prevent water from intruding the landfill and create leachate (1999/31/EG, annex 1). This can cause the landfills to become very dry which might slow down the degradation considerably.

It is not yet possible to fulfil all requirements in the new legislation. Especially the limits on organic content are hard to comply with. In Germany the most problematic limit for pre-treated waste is the one on total organic carbon, TOC, in the leachate. The limit is 300 mg TOC/l. The limit was recently raised from 250 mg/l. The previous limit did not correspond to the levels of other parameters (ASA 2006b).

In Sweden the limit values for DOC are even stricter than in Germany. At a liquid/solid ratio of 10 they range from 50 mg/l for inert waste to 100 mg/l for hazardous waste (NFS 2004:4). The Swedish TOC limits for the solid waste are also strict. Non-hazardous waste can be landfilled only if the TOC is less that 10% (NFS 2004:4, 12§, 5). The relevance of the TOC to the emission potential of the waste has been questioned.

Heavy metals are one important group of pollutants to control. They are often toxic to humans and the environment and since they are elements they can never be degraded. Heavy metals in the leachate are restricted in Sweden (NFS 2004:10, 22, 30 and 34§§) as well as Germany (AbfAblV, annex 1 and 2).

1.2 Objectives and Scope

The results of mechanical-biological pre-treatment will be studied in detail to better understand the effects it has on the emission potential of the waste. The three most important areas are organic content, biological stability and leachability of the waste. The environmental relevance of the parameters TOC and DOC will be discussed. Other ways to look at the organic material, for example by studying the humic substances will be used for comparison.

Another goal is to characterise the waste material and the leachate to get a clearer view of the organic material in the waste. This will allow a better understanding of the potential threats posed by this material.

The heavy metals and their interactions with the organic material will be studied. One important question is whether the association to the organic matter changes during treatment.

To look into the effects of dry landfills the consequences of low water content will be examined to see if the biological activity decreases as would be expected.

Differences between the legislation in Sweden and Germany and their consequences will also be discussed.

The investigation is limited to the effect of mechanical biological pre-treatment of waste. A lot of other pre-treatment methods can be used that are not investigated here. The investigation will only allow making conclusions about the MBT methods studied. The results will also only be valid for the wastes investigated. The German wastes used in this study are municipal wastes treated together with some industrial waste. The Swedish waste comes from a project in smaller scale treating certain building waste. Wastes with other properties might behave differently.

When the emission potential is assessed the waste is supposed to be landfilled or used within the landfill. Other types of use or disposal are not discussed. The discussion is also limited to Germany and Sweden.

2 Landfilling

Landfilling is historically a very important way to dispose of waste. Today it has become much less important in Europe but it will always be needed to some extent.

After the waste has been landfilled it will start to degrade. As long as the waste is in contact with the atmosphere it will be aerobic. This period of time is referred to as the landfills' aerobic phase. As the waste is covered with other waste or with covering material the oxygen supply disappears and the oxygen will rapidly be depleted, making the conditions in the landfill anaerobic. Under anaerobic conditions different groups of microorganisms will degrade the waste, producing landfill gas. First, acid components will form, lowering the pH, during the acidic phase of the landfill. Thereafter methane production will start and the landfill will enter the methanogenic phase. The changes in the landfill gas as the landfill goes through the different phases are shown in Figure 1. (Kjeldsen et al. 2002, p. 300)

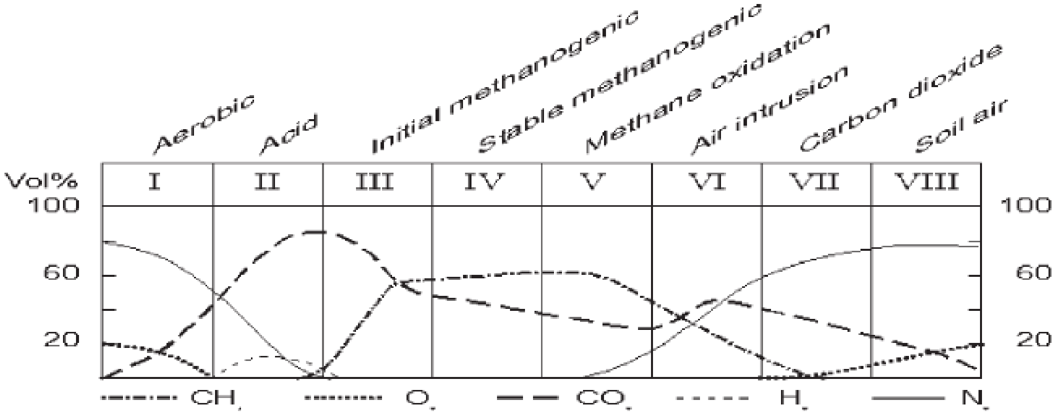

Figure 1 General trends in landfill gas composition during the different phases in the lifetime of the landfill. (Kjeldsen et al. 2002, p. 300)

The degradation is strongly influenced by the water supply. High moisture content will favour anaerobic degradation (Environmental Biotechnology 2004, p. 58). The water content depends on the amount of water contained in the waste when it is landfilled and the infiltration of water after landfilling.

Landfilling involves a number of environmental and technical challenges. Pollutants can spread from landfills with the leachate or with the landfill gas. The gas mainly consists of carbon dioxide and methane (Environmental Biotechnology, p. 57). They are both greenhouse gases, but methane, which forms under anaerobic conditions, is about 20 times more potent at a 100 years timescale (Guiné red. 2002 see Baumann & Tillman 2004, p. 510). The pollutants in the leachate can be divided into four main groups: dissolved organic matter, inorganic macro components (e.g. calcium, ammonium and sulphate), heavy metals and xenobiotic[1] compounds (Kjeldsen et al. 2002, p. 302). The effects of the pollutants are, for example, toxicity of heavy metals, eutrophication from

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[1] Xenobiotic compounds are compounds that are not naturally occurring in the present environment.

nitrogen ions (Camargo & Alonso 2006, p. 834) and oxygen depletion due to elevated concentrations of organic matter.

To prevent these problems landfills in Europe are subject to an increasingly strict regulation which has drastically changed the conditions for landfill operators.

2.1 Legislation

The EG directive (1999/31/EG) is the basis for legislation on landfilling in both Sweden and Germany. According to the directive the member states should reduce the amount of organic waste being landfilled (art 5). Waste should also be treated before landfilling (1999/31/EG, art 6, a). The treatment should result in a smaller amount of waste or a less dangerous waste or facilitate the handling or recycling (1999/31/EG, art 2, h). In a decision (2003/33/EC) from the European council limit values for the landfilling of waste are stipulated.

In Germany the most important laws on landfilling are "The Third General Provision on the Waste Avoidance and Waste Management Act" (TASi) and "Ordinance on Environmentally Compatible Storage of Waste from Human Settlements and on Biological Waste Treatment Facilities" (AbfAblV). TASi gives technical specifications on landfilling and regulations on testing of waste and operation of landfills. AbfAblV includes allocation criteria for landfills and detailed criteria on the testing of waste before landfilling. Landfills are divided into two categories; class I for waste with very small organic content and that only release small amounts of pollutants during leaching and class II for more polluted wastes (TASi 2.2.1).

Of special interest here are the emission criteria for landfilling. Mechanically-biologically treated (MBT) waste must be landfilled in landfills of class II (AbfAblV, art 4, (1) 1). Allocation criteria exist for several different parameters, including TOC (in original waste as well as in the eluate, i.e. the leachate), heavy metals (in eluate), ammonium-N (in eluate) and biological degradability (AbfAblV, annex 2).The criteria of interest for this work will be discussed further down. Interesting to note is that the criteria for MBT waste allow higher values of TOC (in the eluate as well as in the original substance) than normally for class II landfills (AbfAblV, annex 1 and 2). The criteria for biological degradability are also unique for MBT waste. In Austria similar exceptions are made for MBT waste simply to make this a legal way of waste treatment (Binner 2002, p. 1).

In Sweden landfilling is primarily regulated in SFS 2001:512 (Förordning om deponering av avfall) and NFS 2004:10 (Naturvårdsverkets föreskrifter om deponering, kriterier och förfaranden för mottagning av avfall vid anläggningar för deponering av avfall). In Sweden landfills are put in either of three different categories; landfills for inert, non-hazardous or hazardous waste.

Criteria for landfilling of waste can be found in NFS 2004:10. For inert waste and hazardous waste limits for leaching properties and organic content are given (§§ 22-23 and 34-35). To be landfilled in a cell for non-hazardous waste the material only needs to be classified as non-hazardous according to the waste catalogue in SFS 2001:1063 (appendix 2). Some limits exist if the waste is to be landfilled together with hazardous waste (SFS 2001:512, §§26, 30).

There are also several bans on landfilling specific types of waste, e.g. untreated waste (SFS 2001:512, 11 and 14§§) and organic waste (SFS 2001:512 10§). Important exceptions from the bans will be discussed in the following sections.

In the directive's annex 1 strict regulation on barriers underneath the landfills are prescribed. The member states are also recommended to prescribe covering on the top. Very tight top coverings are required in both Sweden and Germany. In Sweden no more than 50 litres of water per square meter and year should pass the top covering of landfills for non-hazardous waste (SFS 2001:512, 31§). For hazardous waste the number is 5 litres. In Germany the criterion is that the permeability should be no greater than $5 \cdot 10^{-9}$ m/s in laboratory testing (TASi, 10.4.1.4, b). The Swedish limits are stricter; 50 $\mathrm{l/m^2/year}$ equals $1.6 \cdot 10^{-9}$ m/s. The tight coverings are likely to create very low water contents in the landfills.

2.2 Pre-treatment

In the EU waste must be treated before landfilling (1999/31/EG, art 6, a). Treatment includes any physical, thermal, chemical, or biological methods that will render the waste less dangerous, decrease the amount of waste or facilitate handling or recycling, including mere sorting (SFS 2001:512 14§). The goal of pre-treatment is simply to make the waste as safe as possible (Naturvårdsverket 2004, p. 8). The European legislation also stipulates that all waste has to comply with landfilling limit values in order to be landfilled (2003/33/EG, art 3).

In Germany incineration and mechanical-biological pre-treatment are the dominating treatment methods. For MBT wastes limit values which allow higher organic content apply compared to other wastes (AbfAblV annex 2). Since it was allowed in 2001 mechanical-biological pre-treatment has become important and there are today about 50 facilities throughout Germany (ASA s.a.a).

Mechanical-biological pre-treatment has several steps. When the waste is received at the MBT facility it is first sorted, shredded and sieved. The different size fractions are treated differently. The part with high thermal value has to be separated before the biological treatment (AbfAblV art 4, (1) 4) to enable energy recovery by incineration. Fractions that are suited for biological treatment are composted and sometimes also treated anaerobically. (ASA s.a.b)

Many positive effects from MBT-treatment have been observed. Landfill space is saved as the waste's volume decreases during composting and the compactability increases. Leachate quantities are reduced and the quality of the leachate is improved. The production of landfill gas also decreases significantly. One negative effect is that the physical stability of the landfill body can decrease since the particle size is smaller. (Binner 2002, p. 10-15)

One important advantage with MBT treatment is that it increases the biological stability of the waste. A more stable waste will not degrade as quickly and will have a smaller tendency to change than an unstable waste. Since MBT waste is treated through a composting process it should be possible to investigate its biological stability in the same manner as is done with compost. Several different parameters have been put forward as means to determine compost stability. These include plant growth, respiration rates, humification, and C/N ratio but none of them will probably be able to stand alone (Tognetti, Mazzarino & Laos 2007a, p. 1067). In German legislation the respiration rate (interchangeably with anaerobic gas formation potential) is regulated as a measurement of the stability of the MBT-material. Both methods are described briefly below in section 4.1. In Sweden no parameters indicating stability are regulated.

In Sweden MBT-treatment is normally not used. When waste is being treated biologically the purpose is normally to use the end product, not landfill it. Incineration is a very important treatment method in Sweden. Half of the household waste generated in Sweden was incinerated in 2005 (RVF 2006, p. 7). Out of the 1.9 million tonnes of waste that were landfilled in Sweden in 2005 390000 tonnes were ashes from waste incineration. 350000 were leftovers from separation and only 200000 were untreated household waste. (RVF 2006, p. 21)

In Sweden, if the waste is treated, not subject to any bans, and can be classified as non-hazardous it can be put in a landfill for non-hazardous waste (NFS 2004:10, 25§). If there is not enough treatment capacity in the region the regional authorities can exempt waste from the treatment requirement (SFS 2001:512 13§ and NFS 2004:4 15-16§§). This possibility should only be a temporary solution until sufficient treatment capacity can be achieved (NFS 2004:4 16.4§) but is still used in Sweden. In 2005 permits to landfill almost 700000 tonnes without treatment were issued (Eriksson & Östlund 2005, p. 6).

2.3 Organic Material

A very important part when reducing the emission potential of landfills is to reduce the amount of organic material landfilled (Heerenklage & Stegmann 2005, p. 1) since this material will degrade forming greenhouse gases. In Sweden a ban has, as stated above, been implemented on landfilling organic material (SFS 2001:512 10§). Strict allocation criteria have been introduced in both countries. The limitations are to the dissolved organic carbon (DOC), the total organic carbon (TOC) or the loss on ignition (LOI). They are summarized in Table 1.

Table 1 Allocation criteria related to organic parameters for landfilling in Sweden and Germany. All leachate criteria are at a liquid to solid ratio of ten. Percent are given by weight

Country	Context	Limit	Reference
Sweden	Landfills for inert waste	DOC: 50 mg/l TOC: 3%	SFS 2004:10, 22§ SFS 2004:10, 23§
Sweden	Landfilling of non-hazardous and hazardous waste together	DOC: 80 mg/l TOC: 5%	SFS 2004:10, 26§ SFS 2004:10, 29§ SFS 2004:10, 30§
Sweden	Landfills for hazardous waste	DOC: 100 mg/l TOC: 6% or LOI: 10%	SFS 2004:10, 34§ SFS 2004:10, 35§
Germany	Landfills class I	DOC: 20 mg/l TOC: 1% or	AbfAblV, annex 1

		LOI: 3%	
Germany	Landfills class II	DOC: 100 mg/l TOC: 3% or LOI: 5%	AbfAblV, annex 1
Germany	MBT-waste	DOC: 300 mg/l TOC: 18%	AbfAblV, annex 2

There are some important exceptions from the Swedish ban on landfilling organic waste. E.g. non-hazardous waste with TOC less than 10% may be landfilled (NFS 2004:10, 5§). This is a very important criterion for organic material in Sweden.

The German DOC limit may be exceeded up to 600 mg/l in a certain waste material if the three previous measurements of this parameter in the same material were below the 300 mg/l limit. Previously the DOC limits were 250/300 mg/l but that limit caused severe problems for the landfill operators (ASA 2006b).

2.4 Humic Substances

Humic substances (HS) are a large group of complex organic molecules with different structures, sizes and functionalities. They have been defined as "dark coloured amorphous chemical compounds of high molecular weight but without stoichiometric formula" (Ziechmann 1994 see Smidt, Binner & Lechner 2004, p. 143). They consist mainly of a large number of joined structures; aliphatic, aromatic, carbohydrates and peptides, with a big variety of different functional groups attached. They can be roughly divided into three groups; fulvic acids (FA), humic acids (HA) and insoluble humic substances. FA are soluble in acids and HA in basic solutions. The ratio HA/FA in soils vary from 0.4 to 2.7. (EPEA 2004, p. 6, Van den Bergh 2001, p. 1)

Humic substances are formed during degradation of organic matters, but the exact process is unknown (Stevenson 1982, p. 195). Microorganisms, however, play a vital role in the transformation from degradable organic molecules to stable humic acids (Smidt, Binner & Lechner 2004, p. 143).

Organic carbon makes up about 50% of humic substances; HA has a carbon content of about 56% and FA 46% (EPEA 2004, p. 6). Their size ranges typically from 1 kDa[2] to 1000 kDa (Van den Bergh 2001, p. 11) which in the case of HS is around 1 nm to 0.45 µm (Burba et al. 1998, p. 979). Humic substances can also be present as suspended material bigger than 0.45 µm (Burba et al 1998, p. 978).

Humic substances play an important role in composts as well as in nature (Lechner & Smidt, 2003, Van den Bergh 2001, p. 1). They are present in a large number of different locations; in soil, natural waters, sewage, compost, lake sediments, peat bogs and many other places (Stevenson 1982, p. 21). In soils they have a large number of favourable properties (Lechner & Smidt 2003) and this might be the case in landfills as well. They are resistant to degradation and can thus act as a carbon sink; the carbon will be kept in

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[2] Dalton (Da) is another name for the atomic mass unit (u).

the material and not be mineralized into CO_2 as would be the case for example if the waste was incinerated (EPEA 2004, p. 6). They also affect the chemistry of heavy metals (Stevenson 1982, p. 337) and play a key role in the behaviour of pesticides (Stevensson 1982, p. 403). Nitrogen is another important element whose compounds can bind to humic substances (Körner & Stegmann 2002, p. 145).

There are no regulations on humic substances in waste neither in Sweden nor in Germany but they can be used as an indicator of the maturity and the quality of compost (Lechner & Smidt 2003). In the case of pre-treated waste the amount of humic acids should function as a measurement of the maturity of the material as well.

2.5 Heavy Metals

Heavy metals can cause considerable harm if released to the environment since they are toxic to both animals and humans (Naturvårdsverket 2006). Heavy metals are mainly released from landfills via leachate. They can exist in many different forms (free metal ions, hydroxides, carbonates, phosphates and sulphides) and the rates at which they are released depend on the form in which they are present. The dissolved forms are more mobile than precipitated forms. (Flyhammar 1997, p. 14)

The forms in which the metals are present depend largely on the pH and the redox potential (Flyhammar 1997, p. 15). The availability of compounds to bind to e.g. organic matter is also important. The mobility of metals in the environment is strongly influenced by their interactions with humic substances because of the many different functional groups in the HS. This will influence the mobility and bioavailability of heavy metals. The potential toxicity of the heavy metals decreases if they are bound to other substances. (Van den Bergh 2001, p. 21)

Heavy metals in waste are regulated in Sweden as well as Germany. A summary of the legislation can be found in Table 2.

Table 2 Leaching limit values (liquid solid ration1:10) for chosen heavy metals in landfills in Sweden and Germany. The limit fron Cr is for total Cr in Sweden and for Cr (VI) in Germany (Source: AbfAblV, annex 1 and 2, NFS 2004:10, §§22, 30 and 34)

Metal	Sweden, inert waste [mg/l]	Sweden, non-haz. and haz. waste [mg/l]	Sweden, hazardous waste [mg/l]	Germany, class I [mg/l]	Germany, class II [mg/l]
Cadmium	0.004	0.1	0.5	0.05	0.1
Chromium	0.05	1	7	0.05	0.1
Copper	0.2	5	10	1	5
Lead	0.05	1	5	0.2	1
Nickel	0.04	1	4	0.2	1
Zinc	0.4	5	6	2	5

2.6 Nitrogen

Nitrogen is an important nutrient in nature. Organisms need it in particular for protein synthesis. Nitrogen emissions can harm the ecological balance, especially in lakes that are already polluted. The nitrogen content in lakes vary from about 100 to 6000 µg/l. Contents over 1500 indicate that the lake has been polluted by anthropogenic sources. (Brönmark & Hansson 2005, p. 40)

When organic material is degraded the organically bound nitrogen will be mineralised. Proteins are fragmented into smaller organic molecules like amino acids. Then the amino group can be split off and ammonium (NH_4^+) or ammonia (NH_3) is produced. (Körner & Stegmann 2002, p. 144)

Ammonium can be further transformed into nitrate (NO_3^-) through a two step microbial conversion via nitrite (NO_2^-). This transformation, nitrification, requires aerobic conditions. Under anaerobic conditions other microbes can transform nitrate via nitrite to gaseous products like N_2 which will be lost to the atmosphere. Nitrogen can also be lost as ammonia. This gas is in equilibrium with ammonium. At higher temperatures and pH the equilibrium will be shifted towards ammonia. (Körner & Stegmann 2002, p. 144-145)

Microbes use ammonium as their primary nitrogen source but they can also use nitrate or nitrite. This process of integrating compounds into biomass, called immobilisation, is the opposite of mineralisation. Binding into humic substances and transformed lignin molecules can also make NH_4^+ unavailable. All soluble nitrogen containing compounds can also be lost in leachate if such is formed. (Körner & Stegmann 2002, p. 145-146)

In order to be landfilled on a class II landfill in Germany the ammonium-N in the eluate must not exceed 200 mg/l (AbfAblV, annex 1 and 2). The parameter is not regulated in Sweden.

The carbon to nitrogen (C/N) ratio is an important parameter in composting. It will influence the process; too high ratios are unfavourable to the microbes and can lead to a slower degradation and insufficient temperatures. Too low C/N values might lead to a loss of gaseous ammonia. Different substrates have different C/N ratios. Grass clippings are at the lower end of the scale at around 10-20. Wood might amount to several hundred. (Environmental Biotechnology, p. 69)

The paragraph above indicates that a too high C/N ratio (i.e. an insufficient supply of nitrogen) is worse than a too low. Loss of ammonia can cause problems with smell but should not affect the process itself negatively.

The C/N ration can be used to indicate compost stability. As the carbon is mineralized and lost as CO_2 the C/N ration will decrease. A lower C/N ratio will therefore indicate more mature compost. (Norbu, Visvanathan & Basnayake 2005, p. 1000)

3 Waste Materials

Three different waste materials were studied. They originate from three different mechanical biological treatment plants, two in Germany and one in Sweden, and will be described in this chapter.

3.1 MBA 1

This mechanical-biological treatment plant is located in northern Germany and receives both household waste and industrial waste. The waste is first fragmented to pieces smaller than 250 mm. The wet household waste is sieved and the coarser fraction that is energy rich is removed and incinerated together with most of the dry industrial waste. The remaining fine fraction is treated biologically. The biological treatment is achieved by tunnel composting and takes nine weeks. After treatment the material is landfilled.

Four samples were taken the same day. One was from the input material to the biological process. This material had been mechanically treated but had not undergone any biological treatment. Two samples where taken from materials in the composting process, one was treated two weeks and the other six weeks. A sample was also taken from the treated (output) material (after nine weeks if composting). The sampling was done according to AbfAblV (annex 4).

3.2 MBA 2

The second facility is also situated in northern Germany. The treatment plant receives residual waste from households and from companies. If required the wastes are first milled to smaller pieces. Then the material is screened into fractions of different particle sizes that will be treated differently. The smallest particles, below 40 mm are fermented; the 40 – 80 mm fraction is composted and the fraction larger than 80 mm has high energy content and is incinerated to recover the energy that way.

The fermentation process takes about three weeks. The residues from the fermentation are mixed with the medium fraction from the screening and fed to the composting process. During composting the material is turned once a week. The intensive composting goes on for eight weeks, and is followed by four to six weeks of maturing. Both processes are roofed. The mature compost is landfilled.

The materials used in this study are the input and the output from the composting process. The samples were taken the same day in the same manner as the samples from MBA 1.

3.3 Trelleborg

The third waste material examined comes from a facility located in Trelleborg in southernmost Sweden which is owned by SYSAV, the south Swedish regional waste treatment company. This material differs significantly from the two others. The background is a surplus material created at SYSAV’s facility in Malmö, Sweden. Building waste is crushed and sieved before incineration. The fraction with pieces smaller than 0.20 mm is rich in plaster which has a high sulphur content that might disturb the incineration process. Therefore this fraction is removed before incineration. It cannot be landfilled either due to a high organic content. Therefore alternative uses are sought for. The aim with the treatment at the facility in Trelleborg is to make the material suitable for construction purposes. Before composting the plaster rich residue was mixed with digested sewage sludge and composted yard waste. (Karlsson 2006, s. 6)

In this study a mixture of 50% plaster rich residue, 25% digested sewage sludge and 25% composted yard waste was studied. The mixture was composted for six months during which it was watered, aerated and turned. During composting the material was exposed to rain (Karlsson 2006, s. 17). Sampling was done by taking 12 samples from different places in the compost and mixing them. (Karlsson 2006, s. 8)

The input material was not sampled at the start-up of the process but a sample was created later by mixing the original input materials in the same proportions. This was done in lab scale in the scope of another thesis (Karlsson 2006, s. 9). One difference from the input to the process was that the compost used was sieved and smaller than 0.2 mm.

The material from Trelleborg was used in a study where it was leached at a liquid/solid ration of 10. The solid material left after the leaching is studied here to look at the effect of the leaching. After sampling/mixing/leaching the material was stored at +4°C.

The material from Trelleborg (see section 3.3) has previously been studied by Patrik Karlsson (2006) in his thesis. More data on the material and its behaviour can be found in his report.

4 Methods

MBA 1 and MBA 2 were sampled according to the German legislation (AbfAblV, annex 4, 1). The sampling was performed by the staff of the treatment plants. The waste materials were ground into pieces smaller than 10 mm within hours after sampling. Thereafter they were kept frozen and defrosted before use. In some cases left-over material was refrozen and used later. The samples from Trelleborg were collected earlier as a part of another thesis, as stated above (section 3.3). After sampling (mixing for the input material) the waste was kept at +4°C. After taken to Hamburg the material was frozen until used.

A portion of each material was dried, and all disturbing material such as glass and metal was removed to facilitate grinding and analysing. The dried samples were weighed and the material was ground to a particle size of less than 0.25 mm. From now on this material is referred to as “finely ground”. The dried material was stored in air-tight plastic bags when not used. The results obtained from the finely ground material have been compensated for the disturbing materials removed to relate all concentrations to the total dry matter.

To study the potential emissions through leaching a leachate, or eluate, was created with the German elution method (AbfAblV, annex 4, 2.4). The solid waste was mixed with deionised water at a liquid to solid ratio of one to ten. The bottles with the mixture were turned for 24 hours at a constant rate of 5 routes per minute. To remove big particles and facilitate filtration the eluates were first centrifuged for 20 minutes at 4000-6000 rpm. If filtration was not to take place within the next couple of days the centrifuged eluate was frozen; otherwise it was refrigerated.

After centrifugation the eluate was filtrated through four different membranes with a cut-off of 0.45 µm, 100 kDa, 30 kDa and 5 kDa respectively. The grade of the membranes was ULTRAN® Slice, provided by Schleicher & Schuell, and the membrane areas were all 0.1 m^2. The filtration principle was cross-flow and the pressure of the fluid was less than 6 bar. Due to problems with one membrane the 0.45 µm fraction was also filtrated through pressure filtration. Two stainless steel filtration units were used, and air pressure was applied to press the fluid through the membrane. The filters used were type ME25, d<0.45 mm, 50mm, Cellulose-mix-ester from Schleicher & Schuell and SPARTAN 30/0,45 RC, 30mm, Whatmann from Schleicher & Schuell. After filtration liquid samples were prepared for the different analyses. If the analyses could not be performed the same day the samples were frozen. In some cases the samples were also preserved by adding acid; these are specified below.

A 0.45 µm filter is supposed to remove suspended material and cells, leaving only the dissolved fraction. This cut-off is widely used, but arbitrary according to Burba et al. (1998, p. 978). It was however used here. Macromolecules like humic substances can have sizes down to 1 kDa (Burba et al 1998, p. 978-979). The membranes of 100, 30 and 5 kDa were used to fractionate them further to study the distribution of HA, other organic material and the compounds bound to it in greater detail.

The output material from MBA 1 was also used in a landfill simulation with four bioreactors with different conditions. This experiment is explained in more detail in section 4.2.

The parameters analyzed and the methods used are described in section 4.1 below. In appendix 1 a complete table of all methods and equipment used can be found. When the analyses are done according to standards the name of the standard is given in the appendix. In this case only a brief description of the procedure will be given in the text in this chapter and any deviations from the standard will be mentioned. The margin for error for the different analyses is less than 5%. The results are given as the mean between the replicates. All calculations have been done with Microsoft Excel.

4.1 Analyses

All analyses that were done as a part of this thesis are described in this section. The analyses were performed by the author unless stated otherwise.

The dry matter content is an important parameter since it allows relating other parameters to an amount of dry substance thus making them comparable. It can also influence the behaviour of the waste. To measure the original dry matter content of the wastes an amount of material was weighed and left to dry in 105°C for more than 24 hours. The dried material was weighed and the dry portion of the waste was calculated. Three parallel measurements were done and the mean was used for further calculations.

pH is an important parameter in degradation. The pH of the solid waste was measured at the original water content. The solid material was lixiviated in $CaCl_2$ for one hour and then the pH was measured. The ratio between waste and $CaCl_2$ was 1:2.5 instead of 1:10 as stated in Methods Book for the analysis of Compost (FCQAO, 1994). 20 grams of probe was mixed with 50 grams of $CaCl_2$. The exception was Trelleborg-Output where 10 grams of probe were mixed with 25 grams of solution. Two replicates were measured except for the material from Trelleborg where only one was used.

The pH and conductivity of the eluate was measured directly in the centrifuged eluate and after each filtration step. The conductivity can be used as an estimate of the amount of dissolved salts in the eluate, some of which can be pollutants.

The loss on ignition at 550°C was used as a measurement of the total amount of organic matter (TOM) in the material. The measurement was performed on the finely ground material by the central lab at Hamburg University of Technology, TUHH according to the standard stated in appendix 1. Two replicates were used in the analyses.

The Total Organic Carbon, TOC, was measured in the finely ground material by the central lab at TUHH. First the inorganic carbon was removed by treatment with H_3PO_4. Afterwards the remaining total carbon was combusted, oxidised to CO_2 and determined with IR-detection. Two replicates were used in the analyses.

The total organic carbon (TOC) in the eluate was measured by the personnel at the Institute for Waste Resource Management at TUHH using three replicates. Most samples were preserved with HCl (2 mol/l, 25 µl to 20 ml sample) prior to measurement. Thereafter the measurement took place in the analyser. The total carbon was measured through thermal oxidation. The total inorganic carbon was measured through oxidation with phosphoric acid and the total organic carbon was automatically calculated as TOC=TC-TIC. In this report the term dissolved organic carbon (DOC) is used for the parameter TOC in eluate.

The chemical oxygen demand, COD, was measured in the eluate by the personnel at the Institute for Waste Resource Management by oxidation with potassium dichromate and measurement of the remaining oxidizing agent. The COD gives a good picture of the total amount of organic matter, but does not indicate how much is biodegradable. When using potassium dichromate some inorganic molecules will be oxidized as well so the value might be a bit too high (Environmental Biotechnology, 2004).

BOD_5 is a measurement of how much oxygen that will be consumed when the material is degraded biologically under aerobic conditions during five days; it thus gives a hint of how biodegradable the material is. The BOD_5/COD ratio will indicate how much of the organic material is available for biologic degradation and is thus a way to measure the biological stability of the waste. The biological oxygen demand over five days was measured in the eluate by the personnel at the Institute for Waste Resource Management. The BOD_5 and COD analyses were done with three replicates.

The humic acids, HA, content was measured in the finely ground solid material by the central lab at TUHH. A defined amount of sample was extracted by blending with a solution of sodium hydroxide and sodium oxalate and after thorough mixing leaving it for 15 hours. Thereafter the humic acids were measured photometrically at 530 nm. The humic acids standard was dissolved in the same solvent as the sample. Two replicates were used for the sample.

The humic and fulvic acids in the finely ground material were also measured at the Institute of Waste Management at the University of Natural resources and Applied Life Sciences in Vienna (the method is described in appendix 6). The finely ground material was first extracted with 0.1 mole/l sodium pyrophosphate (ph 10.5) in several steps and centrifuged. Thereafter the humic acids were precipitated with HCl. The remaining, fulvic acids were measured spectroscopically at 400 nm. The humic acid concentration was calculated as the difference between the original extract and the fulvic acids.

The eluate was only examined for humic acids at the central lab at TUHH. The humic acids were dissolved with a solution of NaOH and sodium oxalate and measured photometrically. The optic density of two replicates was measured at 530 nm.

The solid samples and the eluate after each filtration step were analysed for the heavy metals cadmium, chromium, copper, lead, nickel and zinc. These metals were chosen because they are assumed to cause the biggest problems in waste management. The analyses were performed at the central lab at TUHH. The finely ground material was homogenised and boiled with aqua regia. The heavy metal contents were then measured with a spectrometer. The filtrated eluate samples were preserved with 65% HNO_3 (50 µl/25 ml sample). They were boiled with HNO_3 and the heavy metals content was measured spectrometrically. For solids as well as eluate the samples were divided into two in the lab and the metal content was measured separately in each. The data given are the mean.

The total nitrogen content (T-N) was measured in the finely ground solid samples. The ammonium content was measured in the wet solid waste since some ammonium could have been lost when the material was dried. All analyses were done with two replicates at the central lab at TUHH. The T-N was determined from the original sample with an N-analyser. The NH_4^+ in the solid material was investigated with water vapour distillation and back titration. The eluate was preserved with concentrated H_2SO_4 before the analyses. The ammonium content was determined spectrophotometrically in the original eluate sample. The C/N ratio was calculated using the total organic carbon and the total nitrogen in the dried solid material.

The respiration activity (RA_4) was measured during four days using the solid samples. The oxygen consumption (and thus indirectly the CO_2 production) was measured. The respiration activity is one parameter that is controlled before waste can be landfilled in Germany. Instead of RA_4 the anaerobic equivalent GP_{21} can be measured but since this method is more time consuming and thus more expensive RA_4 in normally preferred. The respiration activity was measured using a sapromat (details in appendix 1). A scheme of the test setup is shown in Figure 2 and a photograph can be seen in Figure 3.

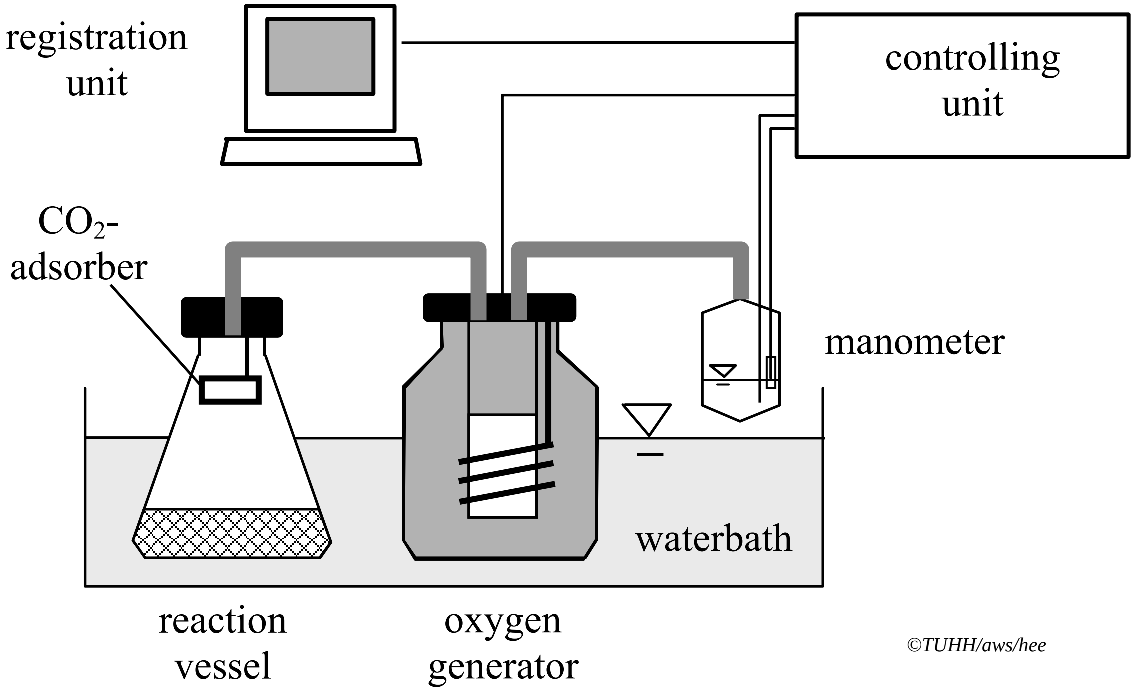

Figure 2 Scheme and photo of the test setup for the sapromat. (Institute for Waste Resource Management, TUHH)

In the sapromat three replicates were used from each material. Instead of adjusting the water content with underpressure as stated in the method (AbfAblV, annex 2 nr. 5) it was manually adjusted to approximately 50% of the water holding capacity of the waste. This method was preferred since it is simpler and faster and has a smaller risk of giving too high water content[3]. The amount of sample used in the sapromat varied; the different

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[3] Instructions from Jörn Heerenklage, Institute for Waste Resource Management, TUHH, october 2006.

amounts can be found in Table 3. The reason to use a smaller amount of sample than the 40 grams stated in the method was either that a very high respiration activity was expected or that there simply was not enough material to use the full 40 grams.

Figure 3 Photo of reaction vessels, oxygen generators and manometers of a Sapromat at the Institute of Waste Resource Management at TUHH

As can be seen in Table 3 each material was analyzed to assess the effect of the pre-treatment. The leached samples from Trelleborg were also analyzed to see the effect of leaching on the RA_4. In some cases different dry matter contents were used to examine the effect of water content on the activity. This is the meaning of "dry", "wet" etc in Table 3. The goal of the experiment that started on November 16th was to assess the effect of non-optimal dry matter content. The material had already more or less optimally dry matter content and was therefore dried about two hours at 35°C. The dried material was then used for all samples after adjustment of the dry matter content.

Table 3 Measurements made in the saprormat, their start dates, dry matter content and the amount of sample used. The motive to use this particular amount of sample is also given. The dry matter contents are after manual optimisation

Material	Start date	Dry matter content [%]	Approx. amount of sample used, explanation
MBA 1 (0 weeks)	20.09.2006	51	40 g, standard amount
MBA 1 (2 weeks)	20.09.2006	51	40 g, standard amount
MBA 1 (6 weeks)	20.09.2006	61	30 g, high activity expected
MBA 1 (9 weeks)	20.09.2006	61	25 g, high activity expected
MBA 2 (input)	20.09.2006	62	25 g, high activity expected
MBA 2 (output)	20.09.2006	70	40 g, standard amount

Trelleborg (input)	31.10.2006	58	25 g, not enough material
Trelleborg (input dry)	31.10.2006	61	25 g, not enough material
Trelleborg (output)	31.10.2006	57	25 g, not enough material
Trelleborg (output dry)	31.10.2006	60	25 g, not enough material
Trelleborg (input leached)	07.11.2006	53	25 g, not enough material
Trelleborg (output leached)	07.11.2006	55	25 g, not enough material
Trelleborg (output dry)	16.11.2006	62	20 g, not enough material
Trelleborg (output optimized)	16.11.2006	56	20 g, not enough material
Trelleborg (output wet)	16.11.2006	49	20 g, not enough material

GP_{21} stands for the potential for gas formation potential measured during 21 days. The measurement was performed on the solid waste samples listed in Table 4. The test setup used is presented in Figure 4 and a photo can be seen in Figure 5. The equipment is somewhat different but equivalent to the one described in the legislation (AbfAblV, annex 2 nr. 6). The produced gas will cause the fluid level in the gas collection equipment to change. The level was read once or twice every day except for weekends towards the end of the experiment period. No stirrer was used. Instead the reaction vessels were manually swirled approximately every second day. Three replicates were used from each material.

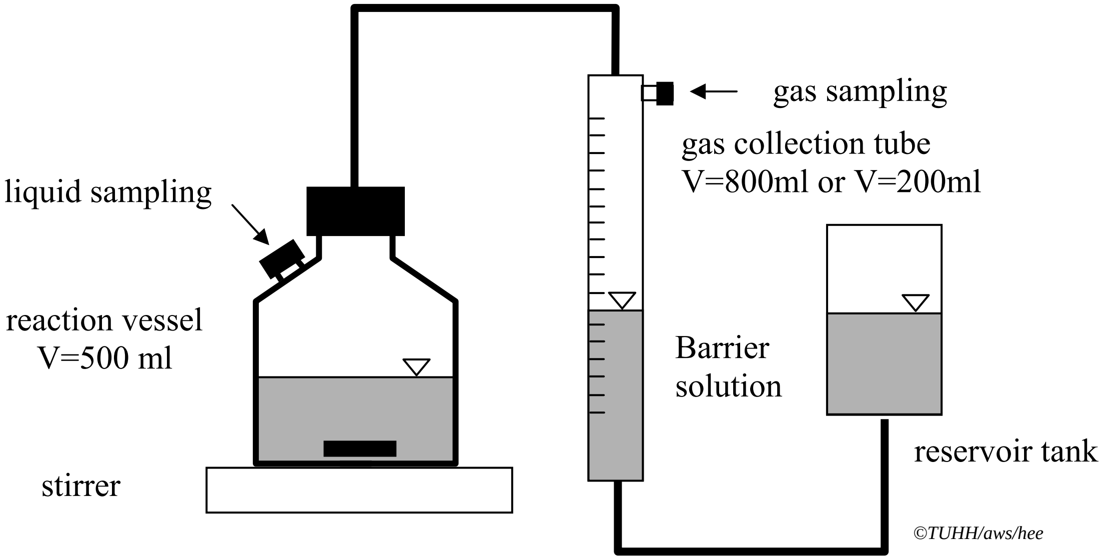

Figure 4 Diagram of the anaerobic testsystem with eudiometer (Source: Institute for Waste Resource Management, TUHH)

Figure 5 Photo of the anaerobic test system used to assess the gas formation potential

The standard amount of sample was not always used. The deviations from this are presented in Table 4 along with the explanations why.

Table 4 Measurements made in the anaerobic test system, their start dates and the amount of sample used. The motive to use this particular amount of sample is also given

Material	Start date	Approx. amount of sample used
MBA 1 (9 weeks)	20.09.2006	25 g, high activity expected
MBA 1 (6 weeks)	20.09.2006	25 g, high activity expected
MBA 1 (2 weeks)	20.09.2006	40 g, high activity expected
MBA 1 (0 weeks)	20.09.2006	50 g, standard amount
MBA 2 (input)	20.09.2006	25 g, high activity expected
MBA 2 (output)	20.09.2006	50 g, standard amount
Trelleborg (input)	07.11.2006	40 g, not enough material
Trelleborg (output)	07.11.2006	40 g, not enough material
Trelleborg (input leached)	07.11.2006	40 g, not enough material

FT-IR spectroscopy will help to characterise the waste material. It gives information about functional groups and thereby the chemical structure and behaviour of molecules. This information will help to assess the maturity of the pre-treated material. At the Institute of Waste Management at the University of Natural Resources and Applied Life Sciences in Vienna the finely ground material was examined with FT-IR spectroscopy. The material was pressed to a pellet with KBr (1:100) and subsequently measured. (Smidt & Lechner 2003)

The finely ground material from MBA 1 was analysed with thermal methods at the Institute of Waste Management at the University of Natural resources and Applied Life Sciences in Vienna. These methods can be used for many different purposes (Smidt, E. s.a., p. 1), but here they are mainly used to assess the stability of the material. The sample was burned under controlled circumstances and several measurements were made simultaneously to assess loss of mass, heat flow and ion flow. This data can be used to look at the different processes and compare different materials. In this case the gas flux was 150 ml/min (80% He, 20% O_2), the heating rate 10 K/min and the temperature program was linear between 30 °C and 950 °C. The heating took 90 minutes.

4.2 Landfill Simulation

Two of the waste materials used in this study (MBA 1 and MBA 2) were to be landfilled after treatment. The material from Trelleborg will probably also be used in a landfill. To study what will happen to the material once it is landfilled four bioreactors were used. One of the output materials, the one from MBA 1, was filled in four reactors with different conditions. The goal of this experiment was to simulate landfilling of the pre-treated waste. More specific details about the reactors are presented in Table 5.

Table 5 Parameters of four different bioreactors used to simulate landfilling of pre-treated waste

No.	Volume [litres]	Input wet material [g]	Dry matter content [%]	Input dry mass [g]	Leachate recirculation	Aeration
1	5	3412	61	2077	No	Yes
2	5	5423	48	2580	Yes	No
3	5	5245	49	2589	No	No
4	5	2627	66	1739	No	No

The reactors were kept at a temperature of 35°C to speed up the processes. Reactor one was aerated from the start to keep the conditions aerobic. From the second day of the experiment the air was passed through a humifier to prevent drying out of the reactor. The water content was approximately 50% of the water holding capacity of the material which should be about optimal for aerobic conditions. Therefore this reactor should represent a maximum degradation under aerobic conditions, and thus a maximum CO_2 production.

Reactor 2, 3 and 4 were operated anaerobically. To achieve anaerobic conditions the free spaces in the reactors were initially filled with a mixture of 20% CO_2 and 80% N_2. The material in reactor 2 and 3 were moistened to approximately 100% of its water holding capacity which should represent optimal conditions for anaerobic degradation, and thus a maximum gas production. From the 9th day the leachate from reactor two was recirculated into the waste material. The recirculation was turned on twice a day and went on for 30 minutes. At two occasions the leachate was exchanged for fresh water. This was done to simulate rain which would cause some of the carbon in the waste to leave the landfill in the leachate. The material in reactor 4 was dried for approximately two hours in 35°C before reactor set up. The goal was to make the material drier than under optimised conditions to simulate the situation that might appear when landfills are supplied with very tight covers.

In the beginning of the experiment gas samples were taken every day except weekends and analysed for H_2, CO_2, N_2O, C_2H_6, O_2, N_2, CH_4 and CO in a gas chromatograph. After about three weeks the samples were taken less frequently. The gas from the anaerobic reactors was collected in gas bags. Occasionally they were emptied and the volumes removed were measured. The aerated reactor was connected to a gas outlet. The flow at the inlet of the aeration was read and if needed adjusted as the gas sample was taken.

The leachate in reactor 2 was exchanged after nine days (500 ml) and after 16 days (190 ml). 16 days after the start-up of the reactors solid samples were taken. This was done by opening the reactors at the top and removing approximately 400 g of material. A sample was taken from the top of each reactor. Some extent of mixing was achieved before taking the sample. The dry matter content of the samples was measured and they were kept frozen until defrosted and eluted. The elution was performed the same way as for the other samples (see above). The eluates were filtrated through a pore size of 0.45 µm by pressure filtration. They were analysed for the same parameters as the other eluates, i.e. pH, EC, DOC, COD, BOD_5, humic acids, heavy metals and NH_4^+. The analyses were performed in the same way as for the other eluates.

After 117 days the last measurements were made and the experiment was stopped. The final product was examined and the dry matter content, respiration activity and DOC were measured.

5 Results and Discussion

In this chapter the results are presented, compared and discussed. Towards the end of the chapter the statistical significance of the findings is discussed briefly.

5.1 Dry Matter Content

The initial dry matter contents of the wastes are presented in Table 6. The increase in dry matter content for the German materials can be explained with a net evaporation since these materials were not exposed to rain during treatment. The water holding capacity of the waste will also change during treatment. A decreasing water content during composting is normal according to Norbu, Visvanathan & Basnayake (2005, s. 999). They also found that optimal water content for composting is 40 to 50%, i.e. a dry matter content of 50 to 60%. If that is true the dry matter contents here are slightly too high in most cases. The leached materials are wet because of the leaching.

Table 6 Original dry matter content of pre-treated waste

Material (stage in treatment)	Dry matter content [%]
MBA 1 (0 weeks)	54
MBA 1 (2 weeks)	54
MBA 1 (6 weeks)	67
MBA 1 (9 weeks)	66
MBA 2 (input)	67
MBA 2 (output)	81
Trelleborg (input)	61
Trelleborg (input leached)	53
Trelleborg (output)	60
Trelleborg (output leached)	55

5.2 pH and Conductivity

The pH values in the solid materials and the eluates are presented in Table 7. The pH in the solid material and the eluate can be very different. One important reason is that the solids had to be treated to enable measurement. The solids that can affect the pH differently from the dissolved material are largely removed in the filtration process which can enhance the difference between solids and eluate. In this case, however, the difference is relatively small as can be seen in Table 7.

The only consistent trend during filtration is that the pH in the eluate is lower before than after the first filtration. The reason for this is probably that some solids that can affect the pH still remain before filtration; the centrifugation was not very effective.

Table 7 pH in pre treated waste samples and their eluates

Material (stage in treatment)	pH in solid material	pH in eluate for different filtration cut-offs				
		Before filtration	0.45 µm	100 kDa	30 kDa	5 kDa
MBA 1 (0 weeks)	5.5	5.8	5.9	5.9	6.0	6.1
MBA 1 (2 weeks)	6.9	6.7	7.3	7.1	6.8	6.8
MBA 1 (6 weeks)	7.9	7.2	8.2	7.9	8.1	7.8
MBA 1 (9 weeks)	7.5	7.3	8.1	7.6	7.7	7.5
MBA 2 (input)	7.3	6.9	7.4	7.8	7.9	8.0
MBA 2 (output)	7.7	7.3	7.7	8.4	8.2	8.3
Trelleborg (input)	Not measured	Not measured	7.6	7.5	7.5	7.8
Trelleborg (output)	7.3	Not measured	7.6	7.5	7.6	7.8

Most materials have a pH around or slightly above neutral (Table 7). The input from MBA 1 has a lower pH but this is not surprising. Part of the MBA 2 sample had been treated anaerobically before sampling and parts from Trelleborg has been digested or composted. The material from MBA 1, on the other hand, was fresh. Therefore it probably started to degrade rapidly even before the biological treatment started. This can cause anaerobic zones in the material where the degradation of organic material forms acids and thus lowers the pH (Norbu, Visvanathan & Basnayake 2005, p. 1001). MBA 1 also has the highest water content among the input materials, something that will increase the risk of formation of anaerobic zones (Environmental Biotechnology 2004, p. 68). According to Norbu, Visvanathan and Basnayake (2005, p. 1001) who also observed low pH values in raw waste this is primarily due to the accumulation of CO_2 in the waste pile. CO_2 will be in equilibrium with carbonic acids and can cause a low pH. But when the waste is mixed with water and eluted which also causes a mixture with air the CO_2 should leave the waste. If an accumulation of CO_2 is the main reason for the low pH in this case the pH in the eluted sample should be closer to neutral. Therefore the most probable explanation in this case is the formation of acids.

Tognetti, Mazzarino and Laos (2007b, p. 389) studied composting of municipal organic waste. They found slightly acidic values at the beginning of composting. Later the pH rose and in the end it decreased slightly. At the end of the 17-weeks-long composting period the pH values were between 8 and 8.5. In comparison to that the values around eight found here seem normal.

Allocation criteria for pH exist in Germany. For both class I and class II the pH has to be within the range of 5.5 and 13.0 in the eluate. All output samples were well within this range.

The electrical conductivity (EC) in the different samples is presented in Figure 6. As can be seen in the figure the filtration does not affect the EC at all. Not even the unfiltrated samples deviate even though these sometimes contained quite high amounts of suspended solids since the centrifugation not always worked very well. These results are not surprising since the EC measures the amount of dissolved salts and these should pass all the filters unaffected.

The EC seems to decrease during treatment, at least for MBA 1. A decrease in EC during composting was also found by Tognetti, Mazzarino and Laos (2007, p. 1069). Their opinion is that EC above 4 mS/cm is problematic for plant growth (p. 1088). They found that the EC was mainly related to nitrogen salts (p. 1088), but all ions will contribute. In the plaster rich material from Trelleborg sulphates could also be important. Plant growth is not relevant in the case of MBT waste but a lower EC is correlated to lower salt concentrations in the leachate and less contaminated leachate means a lower emission potential.

The EC is limited to 50 mS/cm for MBT waste as well as other waste landfilled on class II landfills in Germany (AbfAblV, annex 1 and 2). All samples in this study are far below the limit. In Sweden this parameter is not regulated.

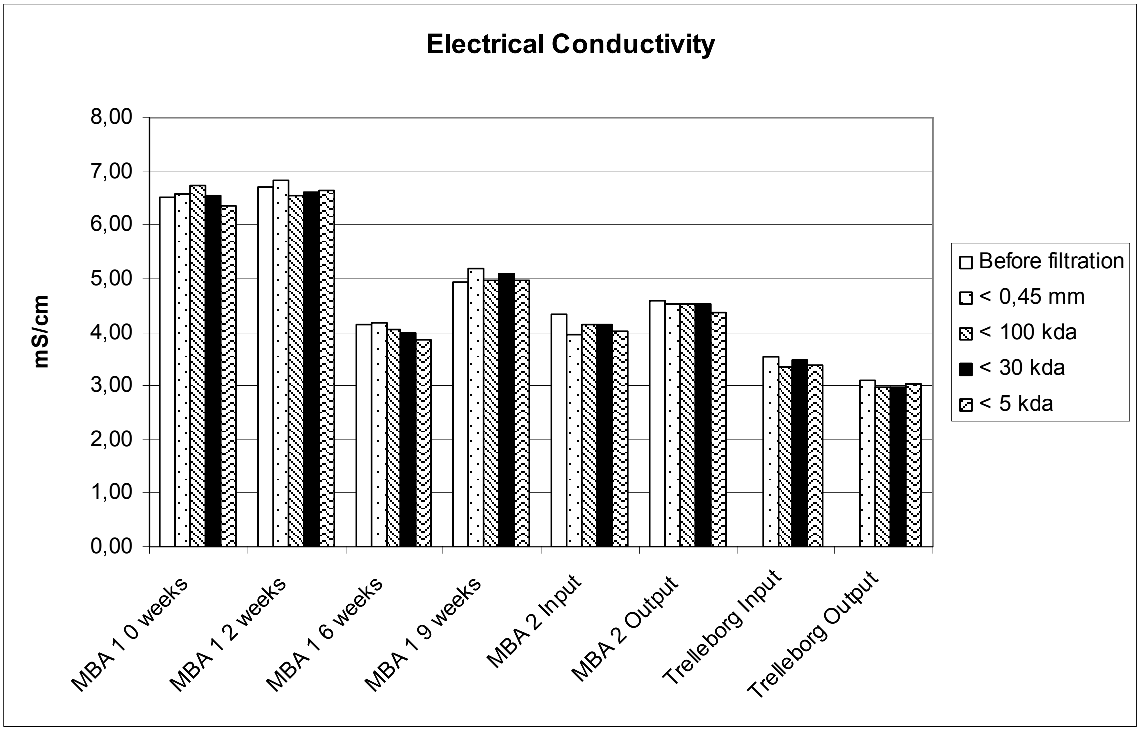

Figure 6 Electrical conductivity in eluted waste samples

5.3 Organic Matter

Two parameters were used to assess the organic content in the solid wastes; total organic matter (TOM) measured as loss on ignition and total organic carbon (TOC). The results are presented in Table 8.

Compared to other studies of composted waste the TOC values here are rather low. Others have found values of 15-29% (Lechner & Smidt 2003) and 16-38% (Iglesias Jiménez & Pérez García 1992, p. 267-268).

Table 8 Total organic matter (TOM) measured as loss on ignition and TOC for pre-treated waste samples. The change during treatment and the difference between TOM and TOC can also be seen

Material (stage in treatment)	TOM [%]	TOC [%]	Change TOM [%]	Change TOC [%]	TOC/ TOM [%]
MBA 1 (0 weeks)	43	19	0	0	44
MBA 1 (2 weeks)	44	20	+4	6	44
MBA 1 (6 weeks)	28	13	-34	-32	45
MBA 1 (9 weeks)	26	12	-40	-38	45
MBA 2 (input)	45	22	0	0	49
MBA 2 (output)	29	14	-37	-36	50
Trelleborg (input)	30	14	0	0	48
Trelleborg (input leached)	28	9	-9	-36	34
Trelleborg (output)	23	7	-25	-50	32

As can be seen in Table 8 both TOM and TOC decrease during treatment. For MBA 1 there seems to be a small increase in both parameters during the first two weeks but the change is very close to the margin for error. Normally the degradation should be quite fast in the beginning and even no change is a surprising result. This is probably the cause of variations in the input material. For MBA 1 the treatment resulted in a 40% decrease in both parameters and for MBA 2 the decreases were around 35%. The TOM in Trelleborg decreased 25% and the TOC decreased 50%.

The material from Trelleborg has lower input values than the others (30% compared to more than 40% for TOM). This is probably because half of the material that used in the mix in Trelleborg was treated before. The end value for Trelleborg was still lower, but the difference from the other materials had shrunk. Accordingly, the final decrease in TOM was smaller for Trelleborg. This might partly be explained by the low input value; there was simply less organic matter to degrade. The fresh part of the material was building waste which should have a lower degradation rate than some of the contents of the other material (e.g. food waste). The lower rate could, however, be compensated for by the longer composting period (six months instead of eight and nine weeks) but this seems only partly to have happened; the total decrease is smaller for the material from Trelleborg.

The TOC is a part of the total organic matter, and in this case the TOC values are around 45% of the TOM values except for the leached material and the output from Trelleborg where the values are closer to 30%. Lechner and Smidt (2003) measured TOC and TOM in composted organic waste and the TOC in their study made up half of the TOM. Iglesias Jiménez and Pérez García (1992, p. 270) found the carbon content in TOM of composted refuse to be between 51 and 58%. The values here are just below that range, i.e. not in any case exceptional, with the exception of the leached and output materials from Trelleborg. For Trelleborg the carbon content of the TOM decreases as the material is treated or leached so the carbon seems to leave the material at a higher extent than other elements in the organic matter. No explanation for the shrinking TOC/TOM rate could be found.

Loss on ignition is regulated for other waste than MBT waste in Germany and for hazardous waste in Sweden. The German limits do not apply to MBT waste and they are also very low; 3% for class I landfills and 5% for class II (AbfAblV, annex 1 and 2). In Sweden the maximum value for hazardous waste is 10% which should correspond to a TOC level of 6% (NSF 2004:10, 35§). None of these limits is really relevant in the case of MBT waste and they make the values around 25% in the treated waste seem relatively high. In a study of composted city refuse (Iglesias Jiménez & Pérez García 1992, p. 267-268), the loss on ignition at 600°C ranged from 31.6% to 68.3% after the removal of plastics. Lechner and Smidt (2003) found values between 29% and 38% in composted organic waste measured at 545°C. In comparison with these values the materials at hand have very low TOM after treatment.

On TOC there is much more relevant legislation. For MBT waste in Germany there is a limit on 18% by weight (AblAblV, annex 2). In Sweden several criteria might be relevant. A limit of 5% applies to non-hazardous and hazardous waste being landfilled together. There is also the limit of 6% for hazardous waste that can be used instead of the 10% loss on ignition. Finally organic waste that has a TOC lower than 10% can be landfilled thanks to the exception from the ban on landfilling organic waste. As can be seen in Table 8 all the wastes studied here comply with the German criterion which is adapted to MBT waste and much higher than the 3% limit for other waste in Germany. The Swedish legislation is much stricter in this respect. Trelleborg is the only output material that comply with the limit of 10%. As stated above (section 3.3) one of the reasons that the mixed material in Trelleborg was created in the first place was that the building waste had a too high organic content. These results show that the material could in fact be landfilled if it could be classified as a non-hazardous waste.

The DOC contents in the eluates are presented in Figure 7. MBA 1 starts at a much higher value than the other materials. This is not surprising since this material is fresh while parts of the other two input materials have been previously treated. During treatment the DOC content in MBA 1 decreases by 95%. In MBA 2 49% is removed and in Trelleborg 11%. After treatment the differences in DOC are much smaller, MBA 1 even has a lower concentration than MBA 2. Trelleborg had extremely low concentrations to start with; the leachability of the organic carbon was already low.

The limit value for DOC is 300 mg/l for MBT waste in Germany but at the time of sampling the limit was 250 mg/l. In Sweden the limits are 50 mg/l for inert waste, 80 mg/l when hazardous waste and non-hazardous waste are landfilled together and 100 mg/l for hazardous waste (summary in Table 1 above).

The DOC content after filtration with the first (0.45 μm) membrane is used for comparison with the legislation. After treatment MBA 1 has a low enough DOC to be landfilled in Germany. The material from MBA 2 does not; the DOC even exceeds the new limit at 300 mg/l. The material would be able to be landfilled in Germany if the control value at 600 mg/l could be used but this is was not yet the case when this sample was taken. Remarkably the DOC in the material from Trelleborg is lower than all limits even before treatment.

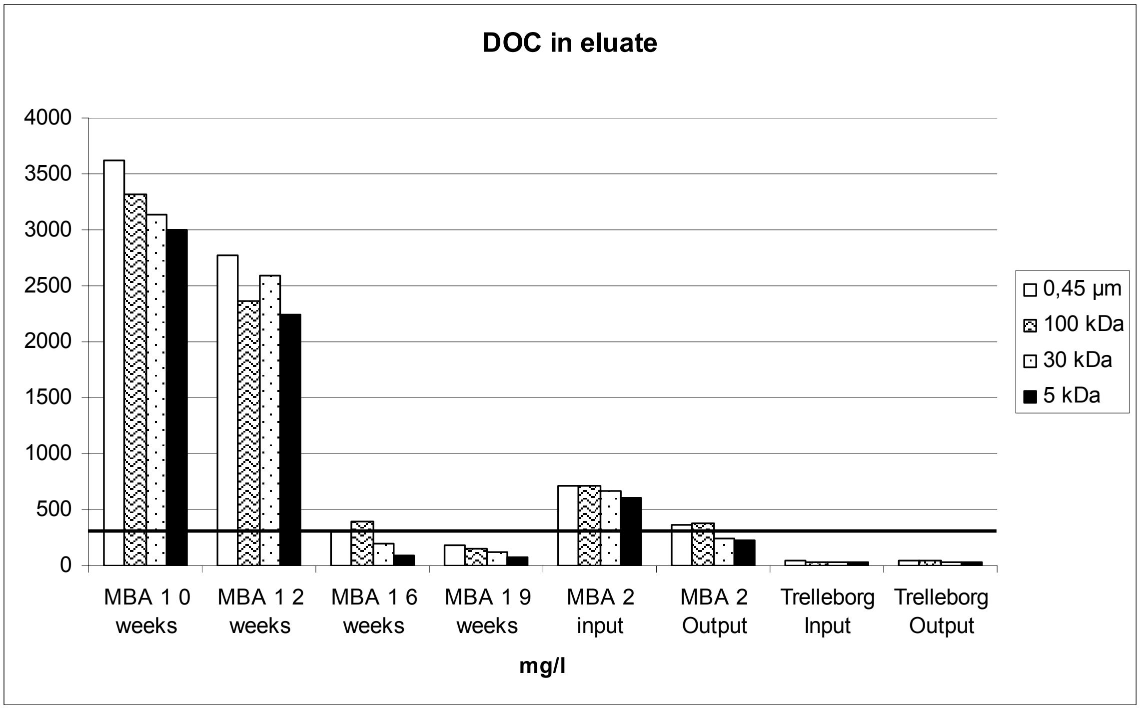

Figure 7 Dissolved organic carbon, DOC, in filtrated waste eluates. The German limit value of 300 mg/l is also shown in the figure.

As can be seen in Figure 7 the DOC is removed by filtration. With a few exceptions each step removes a part of the DOC. An increase in DOC should be impossible since each fraction also contain the smaller fractions. The exceptions should therefore be the cause of some sort of error.

A quite large part of the DOC is found in the smallest fraction. In the input material from MBA 1 83% of the DOC is smaller than 5 kDa. In the output 40% is that small. For MBA 2 these same values are 87% and 61% and for Trelleborg 57 and 73%. For MBA 1 and MBA 2 the DOC seems to become bigger during treatment. One possible reason for a growing DOC is that large molecules like humic substances are formed. This also seems to be the case as will be discussed in section 5.5.

The DOC values for Trelleborg were already very low to start with. This material is also quite different from the other two so it should not necessarily behave in the same way. The low initial DOC might also make it behave differently.

Table 9 shows a comparison between TOC in the solid material and in the eluate (DOC after the 0.45 µm membrane). It shows that the leachable part of TOC decreases during treatment for MBA 1 and MBA 2. The first values for MBA 1 are not very reliable since the first two TOC values are strange, but it is clear that there is a decrease. For Trelleborg this part is extremely low to start with, so the detected increase is very small in absolute terms and can probably be ignored.

Table 9 TOC in waste samples compared to DOC in the eluate

Material (stage in treatment)	TOC in solids [g/kg DM]	DOC in eluate < 0.45 µm [g/kg DM]	DOC/TOC [%]
MBA 1 (0 week)	185	36	20
MBA 1 (2 week)	196	28	14
MBA 1 (6 week)	127	3.0	2.4
MBA 1 (9 week)	115	1.8	1.6
MBA 2 (Input)	219	7.0	3.2
MBA 2 (Output)	142	3.6	2.5
Trelleborg (Input)	143	0.46	0.32
Trelleborg (Output)	92	0.41	0.44

5.4 Oxygen Demand

The biological and chemical oxygen demands were measured in the eluate after filtration with the 0.45 µm filter. The results are presented in Table 10.

Table 10 Chemical oxygen demand (COD), biological oxygen demand measured over five days (BOD_5) and the BOD_5/COD ratio in eluate from pre-treated waste samples. All samples were filtrated through a 0.45 µm filter before measurement

Material (Stage in treatment)	COD [mg/l]	BOD_5 [mg/l]	BOD_5/COD	Change in ratio [%]
MBA 1 (0 week)	11700	6110	0.52	0
MBA 1 (2 week)	7940	4220	0.53	2
MBA 1 (6 week)	875	47	0.05	-90
MBA 1 (9 week)	586	48	0.08	-84
MBA 2 (Input)	2130	1020	0.48	0
MBA 2 (Output)	993	206	0.21	-57
Trelleborg (Input)	120	13	0.11	0
Trelleborg (Output)	106	4	0.04	-65

Both COD and BOD_5 decrease considerably during treatment as does the BOD_5/COD ratio. The initial oxygen demand in MBA 1 was very high, but after treatment this material has an even lower demand than MBA 2. Trelleborg had very low values, lower than the output from the other facilities, already to start with.

The initial BOD_5/COD ratio was about the same in MBA 1 and MBA 2 (ca 0.5). In Trelleborg it was only 0.1. The ratio decreases with about 80% for MBA 1 and around 60% for MBA 2 and Trelleborg.

These parameters are not limited in the legislation but a low BOD_5/COD ratio indicates a more stable material since that shows that a relatively small part of the organic carbon can be degraded biologically. During pre-treatment in an Austrian facility (Zach, Binner & Latif 2000, results derived from table 1) the initial BOD_5/COD ratio was 0.64; slightly higher than here. After nine weeks of composting the ratio had decreased to 0.18 and after 20 weeks it was 0.05. These results are similar to those found here.

5.5 Humic Acids

The humic acids (HA) were measured with two methods as described above in section 4.1. The results are presented in Table 11. The two methods give similar values, but show different changes in HA, especially for MBA 1. The results from the Institute of Waste Management at the University of Natural Resources and Applied Life Sciences in Vienna show a steady increase in MBA 1 while the results from TUHH show fluctuating results in this material. In wastes from the other two facilities an increase can be seen with both methods.

The sample preparations were different in the two methods and the optic density was measured at different wave lengths which can explain the different results. Smidt, Binner and Lechner (2004) studied composting of different organic wastes. They found increasing HA contents in all samples but one that was stable. This makes the fluctuating content measured at TUHH in the material from MBA 1 seem less likely than the steady increase detected in Vienna. Smidt, Binner and Lechner, however, used the method from Vienna in their study so it is not surprising that there results correspond better to that method. The lab at TUHH does not do this kind of measurement at a regular basis so in all the results from Vienna seem more reliable and will be used in the following discussion.

Table 11 Humic acids in pre-treated waste samples

Material (stage in treatment)	HA [g/kg DM] (TUHH)	HA [g/kg DM] (Vienna)	Change [%] (Vienna)	HA [% of TOM] (Vienna)
MBA 1 (0 weeks)	14	10	0	2.4
MBA 1 (2 weeks)	7	15	+48	3.4
MBA 1 (6 weeks)	19	17	+70	6.2
MBA 1 (9 weeks)	15	20	+95	7.8
MBA 2 (input)	4	9	0	1.9
MBA 2 (output)	21	25	+198	8.9
Trelleborg (input)	22	23	0	7.5
Trelleborg (input leached)	25	28	+22	10.2
Trelleborg (output)	25	27	+19	11.7

The material from MBA 2 had the lowest initial HA content (Table 11). Part of this material had been treated anaerobically before being fed into the composting. Smidt, Binner and Lechner (2004, p. 144) found that anaerobic conditions prevented HA formation; the same could have happened here. They also found that the final HA content was lower in the waste that had an initial period of anaerobic treatment. Here the opposite can be noted; Bassum has the highest formation rate and the final value is in the same range as for the other facilities.

There seems to be an increase in HA content, which shows that the materials are stabilized but the final HA contents are not very high; around 10% of the organic dry matter (see appendix 2, Table 7). Smidt, Binner and Lechner mainly found values above 10% of the organic dry matter in composted wastes. In some cases the HA content was above 25% of the organic dry matter.

Something that might seem strange is that the HA content in the material from Trelleborg is higher after the material has been leached. Some humic substances ought to have left the material with the leachate since it contained organic materials (Karlsson 2006, appendix 5). One possible explanation is that microbial processes took place while the material was leached, forming humic substances, but it can also be the result of some error or the heterogeneity of the waste.

The humic acid contents were also compared to the total organic matter in the wastes. After treatment the HA constitute around 10% of the TOM. In all cases the humic acids constitute a larger part of the organic matter after treatment. This is yet another sign of the increased stability of the treated waste.

The results from the different filtration steps can be seen in Figure 8. Sometimes the HA content seems to increase as the eluate is filtrated through membranes with a smaller cut-off. When interpreting these results it is important to keep in mind that each filtered fraction contains everything that is smaller than the cut-off. For example the fraction smaller than 30 kDa also includes the fraction smaller than 5 kDa. For the concentration of humic substances to increase from a bigger fraction to a smaller it would require a voluminous component (that did not contain humic substances to a significant extent) to be removed. However no important volumes have been unable to pass the membranes. Therefore a higher concentration after filtration through a smaller filter must be considered as an error of some sort, e.g. from the material being contaminated with humic acids or a measuring error. The measurements at TUHH were only done at one wavelength. This is, however, also the case in Vienna. The more thorough extraction procedure and greater experience should lead to more reliable results in Vienna but in the case of the eluate only results form TUHH were available.

When looking at the 0.45 µm fraction from MBA 1 in Figure 8 the HA content in the eluate seems to increase during the first six weeks and thereafter decrease. In the solids the increase continued through the whole treatment. One possible explanation is that the humic acids become bigger than 0.45 µm after six weeks, but the results might also be the cause of measuring errors since the HA measurement at TUHH is not very reliable.

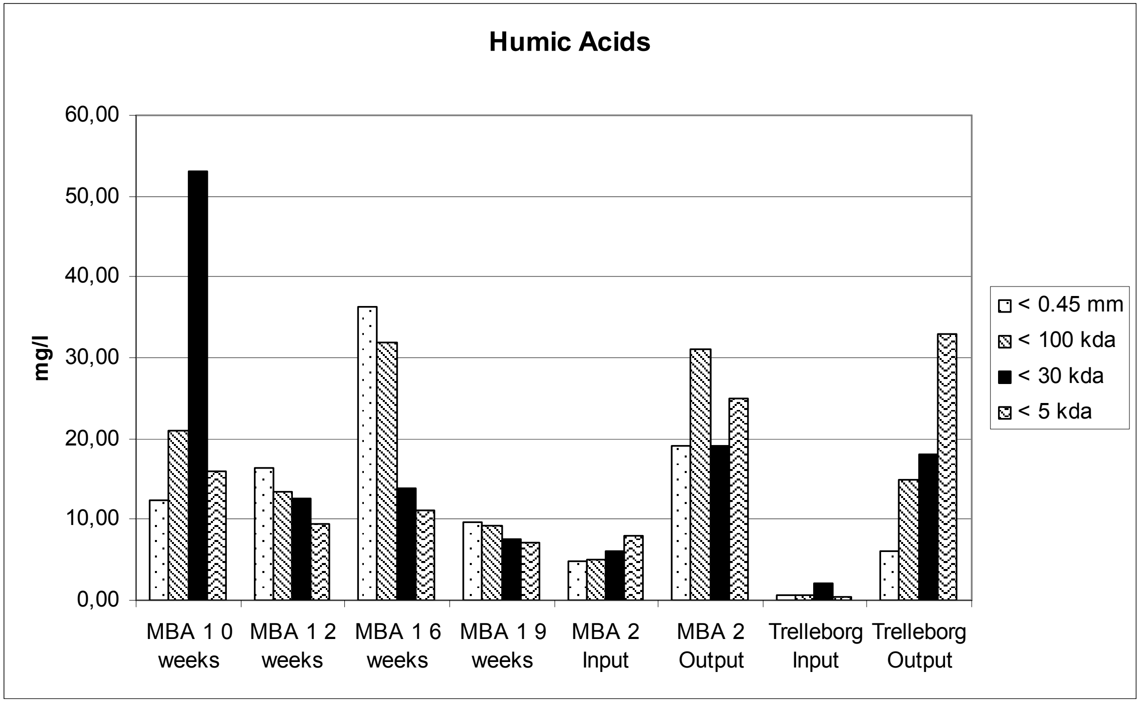

Figure 8 Humic acids in eluted waste samples filtrated through membranes with different cut-offs

To compare the data from the eluate to the solids the results from the biggest cut-off (0.45 µm) was chosen. The comparison is showed in Table 12. The leachable part of the humic acids develop much like the total eluted humic acids; increasing during the first six weeks and then decreasing, but as before the results are not very reliable. However, it is clear that only a small part of the humic acids is actually eluted, only around one percent. The eluate was filtrated with a 0.45 µm membrane before measurement. Humic substances can be bigger than that and considering the data available here it is not impossible that a big amount of humic substances could exist as suspended matter in the leachate.

Compared to the DOC the humic acids are present at relatively low concentrations in the eluate (Table 12). This comparison is not completely relevant since the humic substances contain many other elements except for carbon, but compared to the total dissolved organic matter the HA part would be even lower.

Table 12 Comparisons of humic acids (HA) in solid pre-treated waste (measured at TUHH and in Vienna) and its eluate (studied only at TUHH). The eluate is filtrated through a 0.45 µm membrane

Material (stage in treatment)	HA in eluate/HA in solids [%] (Vienna)	HA in eluate/DOC [%]
MBA 1 (0 weeks)	1.20	0.3
MBA 1 (2 weeks)	1.09	0.6
MBA 1 (6 weeks)	2.09	12
MBA 1 (9 weeks)	0.49	5.4

MBA 2 (input)	0.56	0.7
MBA 2 (output)	0.75	5.3
Trelleborg (input)	0.03	1.5
Trelleborg (output)	0.22	15

In aquatic systems the concentration of humic substances range from 0.1 (sea water) to 10 mg/l and more in boggy areas; in rivers it is typically around 3.5 mg/l (Van den Bergh 2001, p. 5). Compared to those values the eluates in this study have high HA contents, especially considering that other types of HS should be present as well. In many cases the concentrations exceed the values that can normally be found in natural waters. The exception is the input material in Trelleborg. The material from Trelleborg consists to 75% of materials that should have a very low humic acid content; fresh building waste and sewage sludge (as mentioned in above in this section anaerobic degradation does not seem to be favourable for HS formation). Is also has a much lower DOC content than the other materials (see section 5.3). The elution method used here is supposed to achieve maximum concentrations of the eluted compounds and humic substances are not considered harmful. Therefore it is probably not alarming that the HA values in the eluate are higher than in natural waters.

Humic substances are not regulated in Sweden nor Germany.

5.6 Heavy Metals

The heavy metal contents of the different solid materials are presented in Table 13. For MBA 1 the content of all metals increase by 50 to almost 1000% during treatment. An increase is to be expected since the organic matter is degraded and lost as CO_2 but the metals remain. Unfortunately information about the weight-loss during treatment was not available for comparison. Increasing metal concentrations, although not as big (maximum 140%), was also noted for Trelleborg with the exception of zinc. An increase of heavy metal concentrations during composting was also found by Ciawatta et al. (1993, p. 150) and Bhattacharyya et al. (2004, p. 183). For MBA 2, however, it is the other way around. Here a decrease in all metals except for zinc can be noted. There can be a considerable variation in the input material. This might explain these seemingly contradictory results.

Table 13 Heavy metals in solid waste samples

Material (stage in treatment)	Cd [mg/kg]	Cr [mg/kg]	Cu [mg/kg]	Pb [mg/kg]	Ni [mg/kg]	Zn [mg/kg]
MBA 1 (0 weeks)	1.4	709	472	289	331	587
MBA 1 (2 weeks)	11	797	1789	389	428	886
MBA 1 (6 weeks)	17	1060	1544	352	574	1320
MBA 1 (9 weeks)	15	1100	904	436	605	2020
MBA 2 (input)	2.1	871	1630	337	484	552

MBA 2 (output)	1.3	828	873	160	366	1700
Trelleborg (input)	0.85	843	159	193	347	1010
Trelleborg (input leached)	0.87	1080	304	515	571	828
Trelleborg (output)	1.0	1120	379	218	458	659
Trelleborg (output, previous study)	1.0	38	425	171	18	711

When the material from Trelleborg was leached a decrease in the metal content in the remaining solids could be expected since some metals were found in the leachate (Karlsson 2006, appendix 5). However, for all metals except for zinc an increase can be seen (Table 13), in some cases quite large (up to 170%). The input material and the leached input material both originate from the same batch so there is really nothing to explain these strange results.

The metal concentrations in the eluates are presented in Figure 9 to Figure 14. In MBA 1 the final content of all metals except for cupper is lower than the initial content but what happens between these occasions varies as will be discussed later in this section.

All metals except for cadmium seem to be affected by filtration; the filtration removes some metals from the eluate. It should not be possible for the metal concentration to increase when the sample is filtrated (se also section 5.5 where this is discussed for humic substances), so these cases should be considered errors. Large parts of the dissolved metal species however seem to be smaller than 5 kDa, with the exception of lead.

Jensen and Christensen (1999, p. 2144) fractionated landfill leachate. They found an important part of the heavy metals in the colloidal fraction (1.2-0.001 μm). This means that there could be a lot of metals in the fraction removed by the 0.45 μm filter and thus never detected in this study. Interestingly they also noticed that cadmium was mainly present in the truly dissolved fraction (<0.001 μm). This study also indicated that cadmium species are generally smaller since that metal was the least affected by filtration.

There are big differences between the trends in the solid and the eluted waste samples. But generally the decrease is bigger or similar in the eluate showing a decreasing or unchanged leachability as can be seen in Table 14.

The cadmium content in the solid waste from MBA 1 increased during treatment except for a small drop at the end. In the eluate the cadmium concentration triples during the first two weeks to drop to half of the initial concentration after six weeks (Figure 9). Initially six percent of the cadmium was eluted (Table 14). After two weeks only three percent was eluted and towards the end of treatment this dropped to less than one percent. Nickel behaves very similarly to cadmium.

Copper behaved a bit differently in the solid material from MBA 1 compared to the other metals, starting with an increase to finally drop to almost its initial concentration. In the eluate it behaves similarly (Figure 11). The part of the copper that is eluted is less than one percent. In spite an initial decrease the part is the same at the end of treatment (Table 14).

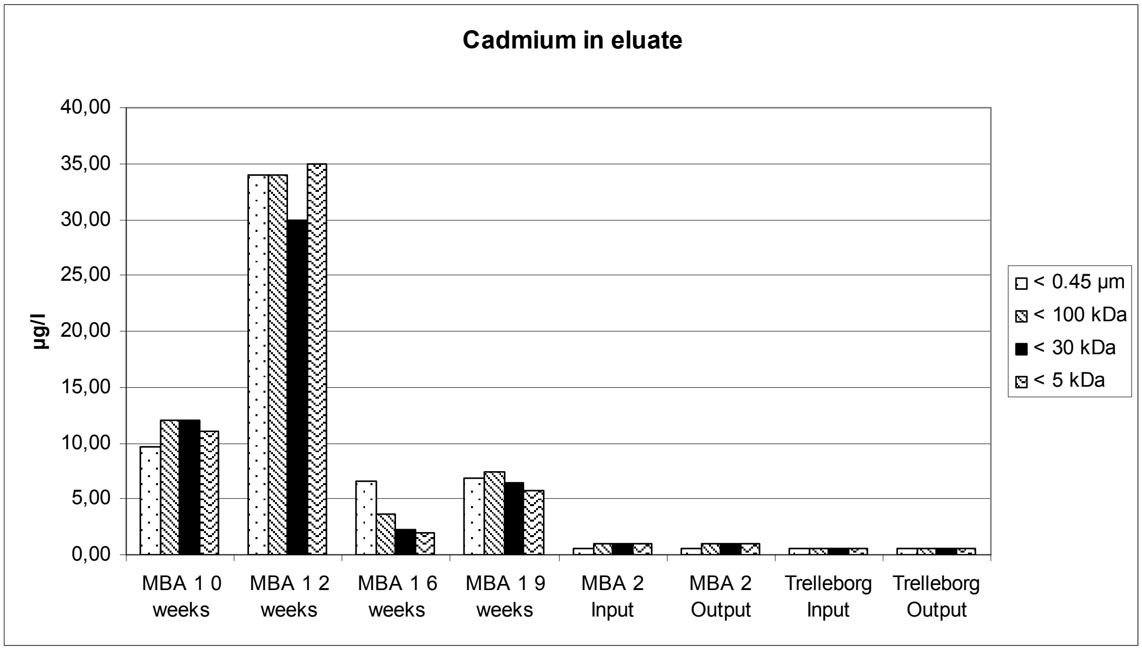

Figure 9 Cadmium in eluted waste samples

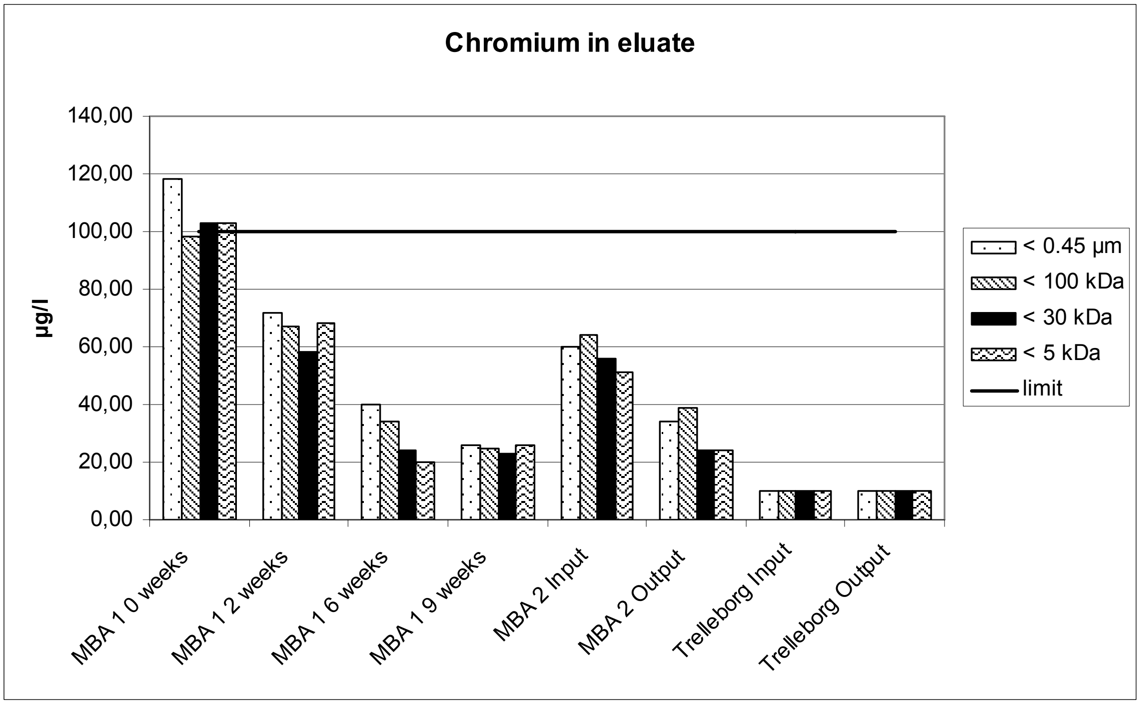

Figure 10 Total chromium in eluted waste samples. The limit value for Cr (VI) for German class II landfills is included

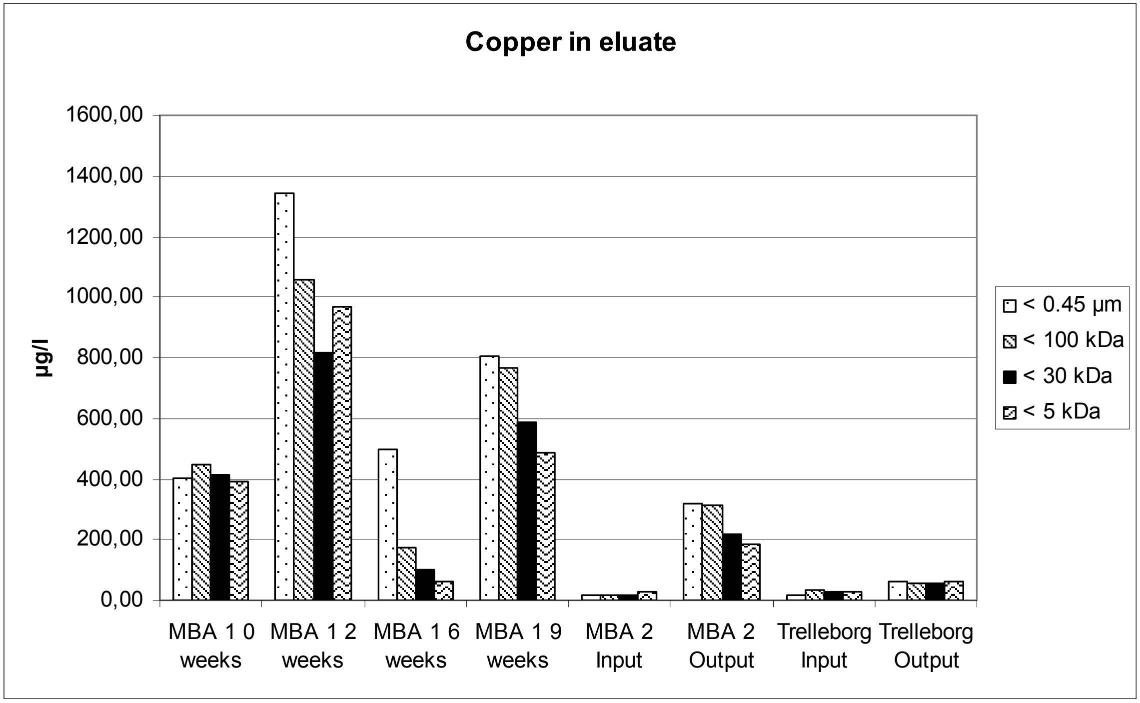

Figure 11 Copper in eluted waste samples

Chromium, lead and zinc all increase in the solid material from MBA 1 but decrease in the eluate; i.e. the eluted part decreases. Initially a relatively high part (23%) of the Zinc in MBA 1 was eluted but at the end less than one percent of the zinc was eluted, as for the other metals (Table 14).

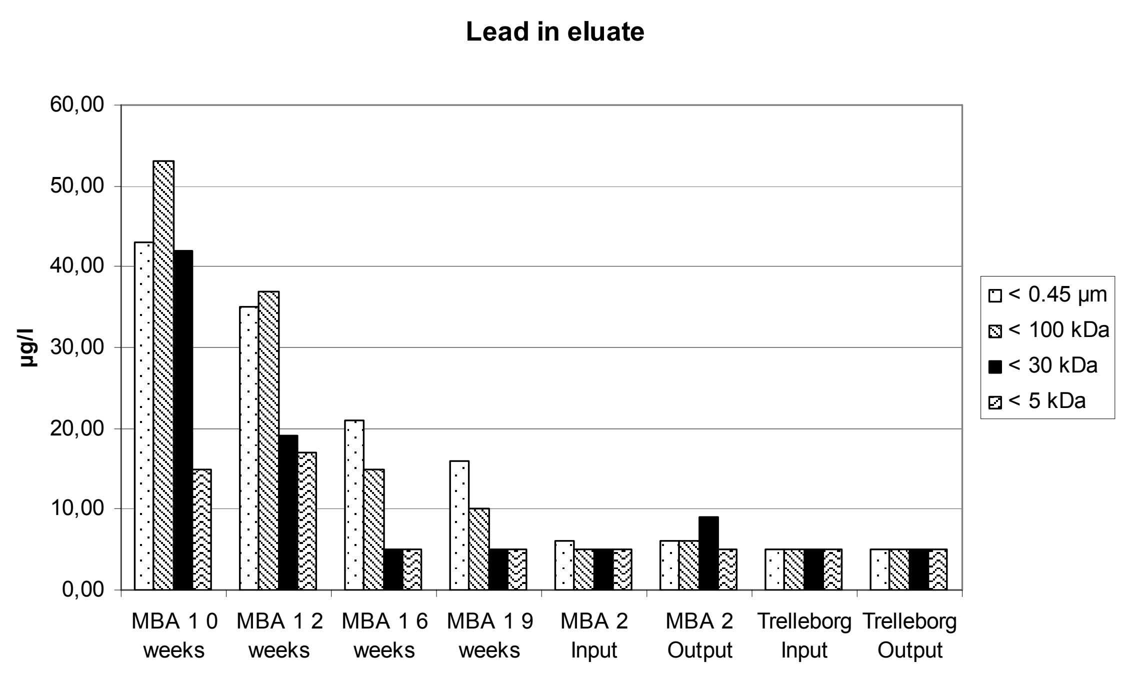

Figure 12 Lead in eluted waste samples

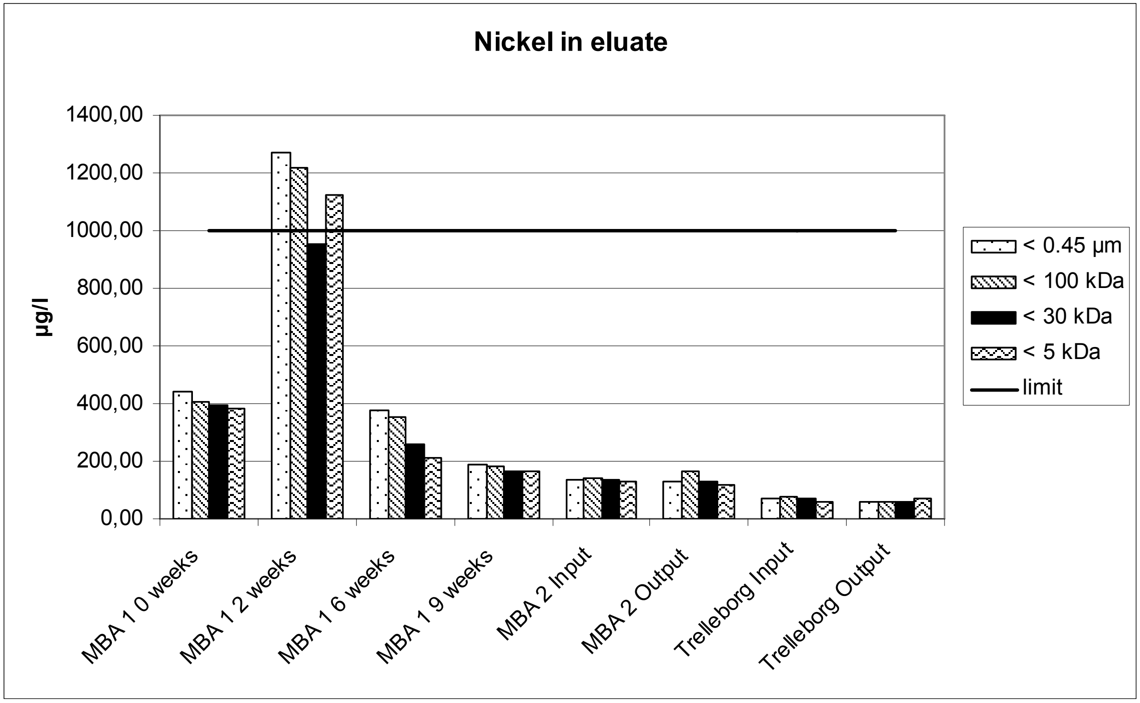

Figure 13 Nickel in eluted waste samples. The limit value for German class II landfills is included

MBA 2 has much lower metal concentrations than MBA 1. The change in concentration in the eluate from MBA 2 is very small for all metals except for chromium. The zinc and copper concentrations increase from input to output. The eluate from Trelleborg generally had the lowest metal concentrations and small changes during treatment. The leachability in this material is also more or less unaffected by treatment, but it was very low to start with.

Table 14 Leachability of heavy metals. The concentration in solid waste samples as part of the content in eluate filtrated through a 0.45 µm membrane

Material (stage in treatment)	Cd in eluate [%]	Cr in eluate [%]	Cu in eluate [%]	Pb in eluate [%]	Ni in eluate [%]	Zn in eluate [%]
MBA 1 (0 weeks)	7	0.2	0.9	0.15	0.2	23
MBA 1 (2 weeks)	3	0.1	0.8	0.09	0.09	7
MBA 1 (6 weeks)	0.4	0.04	0.3	0.06	0.04	0.5
MBA 1 (9 weeks)	0.5	0.02	0.9	0.04	0.02	0.3
MBA 2 (input)	0.2	0.07	0.01	0.02	0.07	0.3
MBA 2 (output)	0.4	0.04	0.4	0.04	0.04	0.7
Trelleborg (input)	0.6	0.01	0.1	0.03	0.01	0.3
Trelleborg (output)	0.50	0.01	0.3	0.02	0.01	0.4

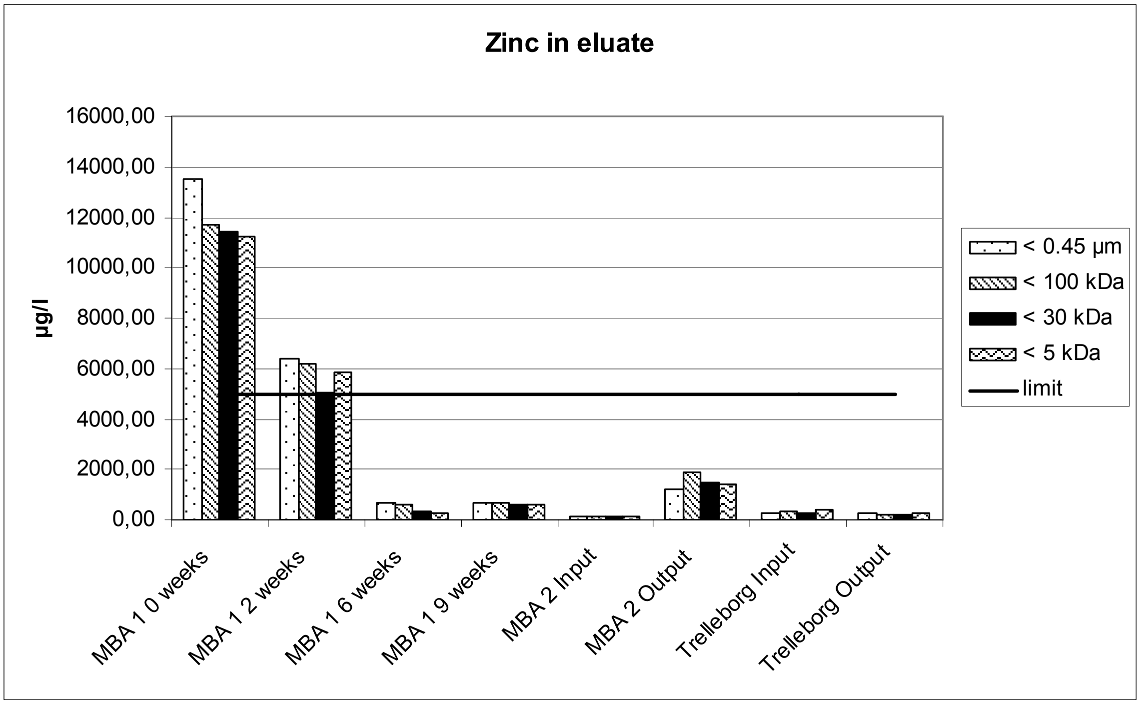

Figure 14 Zinc in eluted waste samples. The limit value for German class II landfills is included

In MBA 1 all metals except for copper are harder to leach after treatment but the changes are in some cases very small. Zinc in the other hand is 99% less leachable after treatment. In MBA 2 and Trelleborg it goes both ways but the eluted part was small to start with and the changes are very small. The decreasing leachable part is interesting since the leachate is the most important source for heavy metal emissions. At least in the case of MBA 1 it seems that the treatment makes the metals less mobile which is a positive effect.

It would be interesting to know whether the metals are associated to the humic substances or other organic matter. The behaviour of the metals indicates that they are bound to molecules that are stopped by the different filters. This is most likely some kind of organic matter. A large part of the metals are smaller than the 5 kDa membrane, but this is true for the DOC as well, so an association is still possible. The results from the filtration of humic acids are hard to interpret, but it is possible that a large part of the HA are smaller that 5 kDa as well. Considering these results it is at least not possible to rule out an important association between HA and heavy metals.

The values after filtration with the 0.45 µm membrane are used for comparison with the legislation. For the material from MBA 1 the German legislation will apply. After treatment the concentrations of all metals were lower even than the stricter limits for class I landfills. For cadmium, copper and lead this was true even before treatment. The values for chromium are not really relevant since they are for total chromium and the legislation only have limits for Cr(VI). If all chromium in the sample was Cr(VI) the input material could not be landfilled in Germany, but at the end of treatment it could even be landfilled in class I. The input values for zinc would not allow the material to be landfilled but after six weeks the concentration has decreased very much and does not pose any problems.

The eluate from the input material from MBA 2 has very low concentrations; all metal concentrations comply with the class I limits even before treatment, except for chromium. After treatment, however, this metal is at least below the class II limit.

The metal concentrations in the material from Trelleborg comply with all possible limits before and after treatment with the exception for the nickel concentration that exceeds the limit for inert waste in Sweden. The values correspond quite well with those found by Karlsson (2006, p. 329). He found that all metal concentrations in the output material were below the limits for inert waste. The values in this study are all slightly above his values except for copper but he used a different method to produce the leachate. This makes his values more relevant for Swedish conditions since the percolation method is prescribed in the Swedish legislation. The German elution method generally gives higher values.

5.7 Nitrogen

The total nitrogen (T-N) in the solid material is listed in Table 15. It was measured in the finely ground material. This material was dried for more than 24 hours in 105°C before the measurement. The drying will cause NH_4^+ to be lost since it is in equilibrium with NH_3 which is a gas at temperatures over -33°C. At high temperatures and high pH values the equilibrium will be shifted towards NH_3 (Körner & Stegmann 2002, p. 144). To see how big influence the evaporation of NH_3 will have on the total nitrogen the NH_4^+ content in the wet material was measured. The results can be found in Table 15. How much of the ammonium that will evaporate is not possible to tell, so the values can not simply be added, but if all available ammonium evaporated 9-18% of the total nitrogen was lost. The T-N values measured in the dried material will be used knowing that they might not represent the entire content.

The NH_4-N content in the solid waste from Trelleborg was not analysed here but in a previous study (Karlsson 2006, appendix 3) it was found to be 0.049 g/kg. This is a much smaller part than for the other materials, but this measurement seems to have been made with a dried sample that had probably already lost a considerable amount of its NH_4-content.

Table 15 Total N, NH_4-N and C/N ratio in composted waste material

Material (stage in treatment)	Total N [g/kg DM]	NH_4-N in solid waste [g/kg DM]	C/N ratio
MBA 1 (0 weeks)	9.9	1.6	19
MBA 1 (2 weeks)	10.0	2.2	20
MBA 1 (6 weeks)	8.4	1.8	15
MBA 1 (9 weeks)	7.8	0.8	15
MBA 2 (input)	7.4	1.0	30
MBA 2 (output)	8.2	1.3	17
Trelleborg (input)	8.6	Not measured	17

Trelleborg (input leached)	7.0	Not measured	13
Trelleborg (output)	6.8	Not measured	11

There are no limit values for N in solid waste so the values in Table 15 can only be compared to those found in other studies. Norbu, Visvanathan and Basnayake (2005, p. 998) found T-N contents around 10 g/kg in the dry raw waste. This is comparable to the input values found here. Tognetti, Mazzarino and Laos (2007, p. 1070) also found N-contents in this range.

Since there was no leaching during treatment the only way for nitrogen to leave the waste would be through evaporation of ammonia or loss of other gaseous N-compounds such as N_2. The exception from this is Trelleborg since this material was exposed to rain. An increase of total N can be possible due to enrichment as other compounds are mineralized and lost (e.g. organic compounds lost as CO_2). Generally these processes combined lead to an initial increase in T-N later followed by a decrease (Körner & Stegmann 2003, p. 382). In this study some of the measured changes during treatment are too small to confirm statistically but there seems to be a small decrease in T-N for MBA 1 and Trelleborg. In MBA 1 the NH_4^+ content also decreases towards the end of treatment. The materials after six and nine weeks of treatment in MBA 1 both had pH over eight, something that might favour loss of ammonium, which might add to the decrease. pH values between 7.5 and 8.5 also favour nitrification of ammonium to nitrate (Environmental Biotechnology 2004, p. 35). There are many processes that could contribute to the decreasing NH_4^+ content in the waste from MBA 1.

The T-N in MBA 2 has increased after treatment, but what has happened during treatment is unknown. Tognetti, Mazzarino and Laos (2007, p. 1069) studied municipal organic waste composts and found a decrease in T-N in some but not in others, so this increase is perhaps not that strange.

There should be a significant ammonification during treatment as organic molecules are degraded. Körner and Stegmann (2002, p. 149-150) carried out a series of composting experiments and found a significant ammonia/ammonium production in most, commonly between 40-70%. No large increase in ammonium content can be seen here. The ammonia will be incorporated in growing microbial biomass which can explain that no increase could be detected even though a considerable mineralization ought to have taken place. As stated above, nitrogen can also be lost as gaseous compounds. Körner and Stegmann (2002, p. 153) found important but varying nitrogen releases via exhaust air in their composting experience. Other composting experiences have found a decrease in NH_4-N during composting (Tognetti, Mazzarino & Laos 2007, p. 1069).

The C/N ratios for the studied wastes can be found in Table 15. They are calculated using the T-N and TOC values in the finely ground material. According to Norbu, Visvanathan and Basnayake (2005, p. 1000) a suitable C/N ratio for composting would be 20-25. They seem to be using the ratio of total C and total N in dried waste. 25-30 is also suggested as the optimum (Environmental Biotechnology, p. 69). How this value should be calculated is unclear. The MBA 1 and Trelleborg values seem a little low in comparison to these recommendations. The waste from Trelleborg is a mixture of natural compost, digested sewage sludge and construction waste. The compost and the sludge should have relatively low C/N ratios while the construction waste probably contains a lot of wood that has a very high ratio (Environmental Biotechnology, p. 69). MBA 2 also contains digested material but still has a higher ratio than MBA 1 which ought to be the least stable material. This possibly strange result might be explained by the big uncertainty in the results and the big variations in waste material.

After composting the C/N ratio should have decreased to at least less than 20 but preferably less than 15 (Iglesias Jiménez & Pérez García 1992, p. 265). All materials in the study show a decreasing ratio and thus an increasing stability. MBA 2 still has a rather high ratio after treatment, but this material also had a higher initial ratio. Tognetti, Mazzarino and Laos (2007, p. 1070) calculated the C/N ratio in municipal organic waste compost using TC and TN ratios. They found a decrease during treatment, starting at values between 15 and 30 and achieving values from 12 to 23. If the TOC would have been used, as here, these values would have been slightly lower and very similar to those found in this study.

The NH_4-N in the eluate is presented in Figure 15. It seems to increase during the first part of treatment in MBA 1 and decrease during the later part. Microbial degradation of proteins most likely accounts for the increase. The decrease can have the same reasons as the potential decrease in T-N, i.e. evaporation and, in the case of Trelleborg, leaching. NH_4^+ can also be incorporated in growing biomass and in humic substances and degraded lignin molecules.

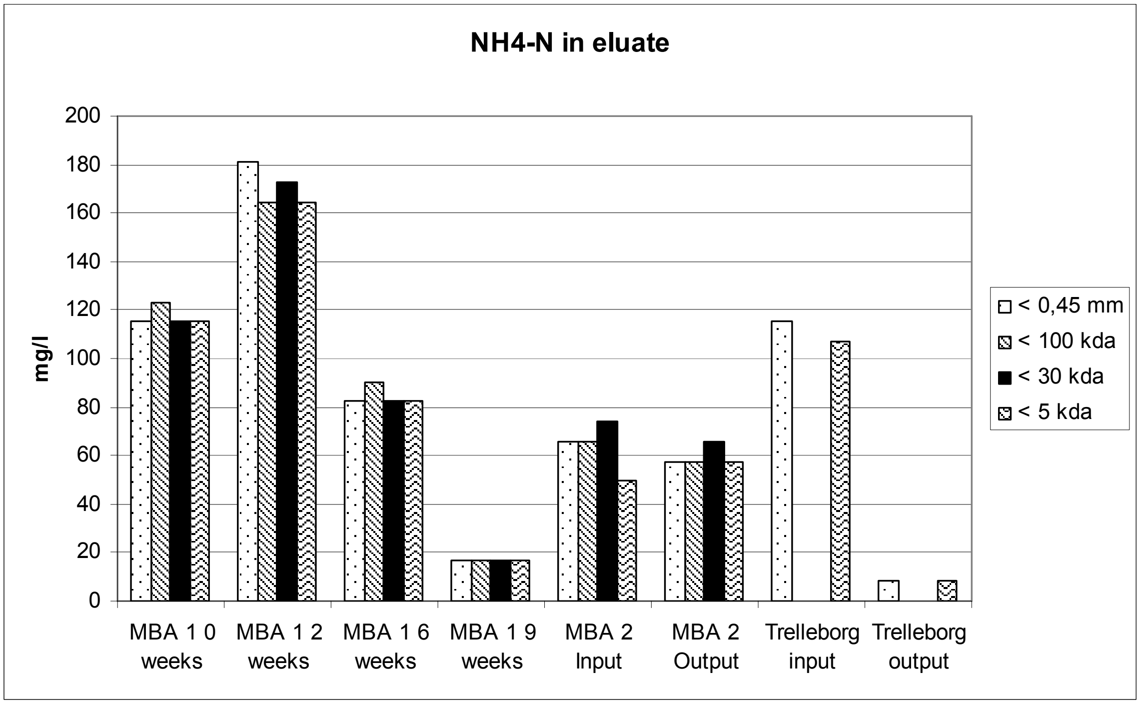

Figure 15 NH_4-N in eluate from mechanically-biologically pre-treated waste

As can be seen in Figure 15 filtration does not influence the concentration. NH_4^+ is a small and soluble compound and dissolved it will pass all membranes. Microbial cells should be removed by the first filtration step, but humic acids are range from 1 to 1000 kDa and could be removed step by step by the different membranes. Unfortunately no reliable results from the filtration of humic acids could be achieved (se discussion in chapter 5.5), but the fact that the filtration had no effect on the NH_4^+-concentration indicates that it is not bound to humic substances to any large extent.

The decrease in dissolved ammonium in MBA 1 from week two to week nine is 1.7 g/kg DM (Figure 15) and the total N in the solids decrease 3.2 g/kg DM (Table 15). From this data it is impossible to show that any ammonium is incorporated in biomass, but all growing biomass will need nitrogen to build nucleic acids and proteins so this process is there even if it cannot be detected from the data present.

In Table 16 the NH_4-N in the eluate is compared to the T-N and the NH_4^+ in the solid material. The part of the T-N and NH_4^+ in the solids that became eluted follows the same pattern of increase and decrease as the NH_4-N content in the eluate. The interesting part of this is that less NH_4^+ appears in solution at the end of treatment. This opposes the conclusion above that the decrease of NH_4^+ in the eluate is not the cause of absorption to organic molecules. If the dissolved NH_4^+ is incorporated into biomass or evaporates it should not be found in the solid material either. It is possible that some NH_4^+ is attached to organic molecules smaller than 5 kDa, but this can not be said for certain.

Table 16 Total N and NH_4-N found in solid materal and eluates from waste treatment plants

Material (stage in treatment)	NH_4-N in eluate <0,45 µm [g/kg DM]	NH_4-N in eluate/T-N [%]	NH_4 in eluate/NH_4 in solids [%]
MBA 1 (0 weeks)	1.15	12	72
MBA 1 (2 weeks)	1.81	18	83
MBA 1 (6 weeks)	0.82	10	46
MBA 1 (9 weeks)	0.16	2	21
MBA 2 (input)	0.66	9	65
MBA 2 (output)	0.58	7	44
Trelleborg (input)	1.15	13	N/A
Trelleborg (output)	0.08	1	N/A

Allocation criteria exist for ammonium-N in the eluate. I Germany the limit is 200 mg/l for landfills class II (both MBT waste and other); well below the values found in this study. In Sweden there are no relevant criteria.

5.8 Biological Activity

In Figure 16 the effect of treatment on the respiration activity (RA_4) is clearly visible. The activity decreases significantly during treatment. The decrease for MBA 1 is bigger (95%) than the other materials (less than 90%). The reason for this is probably the high initial activity (more than double that of MBA 2) which depends on the material being very fresh compared to the others which were partly treated already.

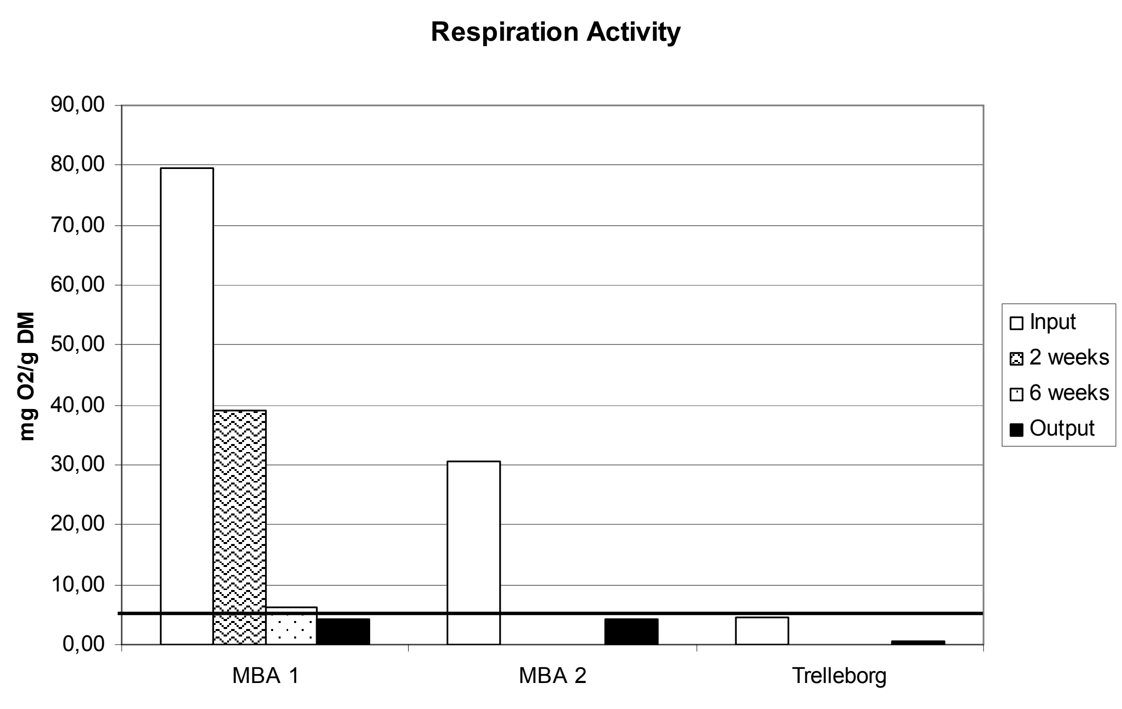

Figure 16 Respiration activity (RA) in pre-treated waste samples. The German limit value of five mg O_2/g DM show in the picture

The German limit is 5 mg O_2/g dry matter (AbfAblV, annex 2 nr. 5). All materials are below the limit after treatment. The material from Trelleborg is below already before treatment but the respiration activity still decreased about 90%.

The leached input material from Trelleborg had a RA_4 of 3.3 mg O_2/g DM, i.e. a 73% decrease of the respiration activity. A decrease was expected since the leachate from the colon tests contains organic material (Karlsson 2006, p. 15). When the output material was leached the resulting RA_4 was 0.8 mg O_2/g DM which actually is a small increase. This should depend on some error. The amount of sample used was very low considering the low activity. The absolute difference is also very low. The results are not very reliable since a small amount of sample will increase the effect of the inhomogeneous waste samples.

The material from Trelleborg was also analysed with different dry matter contents to investigate the effect of the water content on the activity. The results are presented in Figure 17. Three samples with three replicates each were measured except for the dry conditions where only one sample was measured using three replicates. Especially when measuring the respiration activity in the materials drier than optimal, the difference in dry matter content was too small to get very good results (dry matter contents in Table 3). Earlier experiments have shown that the dry matter content significantly affects the degradation rate. Heerenklage and Stegmann (1995) showed that the highest degradation took place at 60% of the maximum water holding capacity of the material which in their case was a dry matter content of 66%. Higher or lower water content meant decreasing degradation.

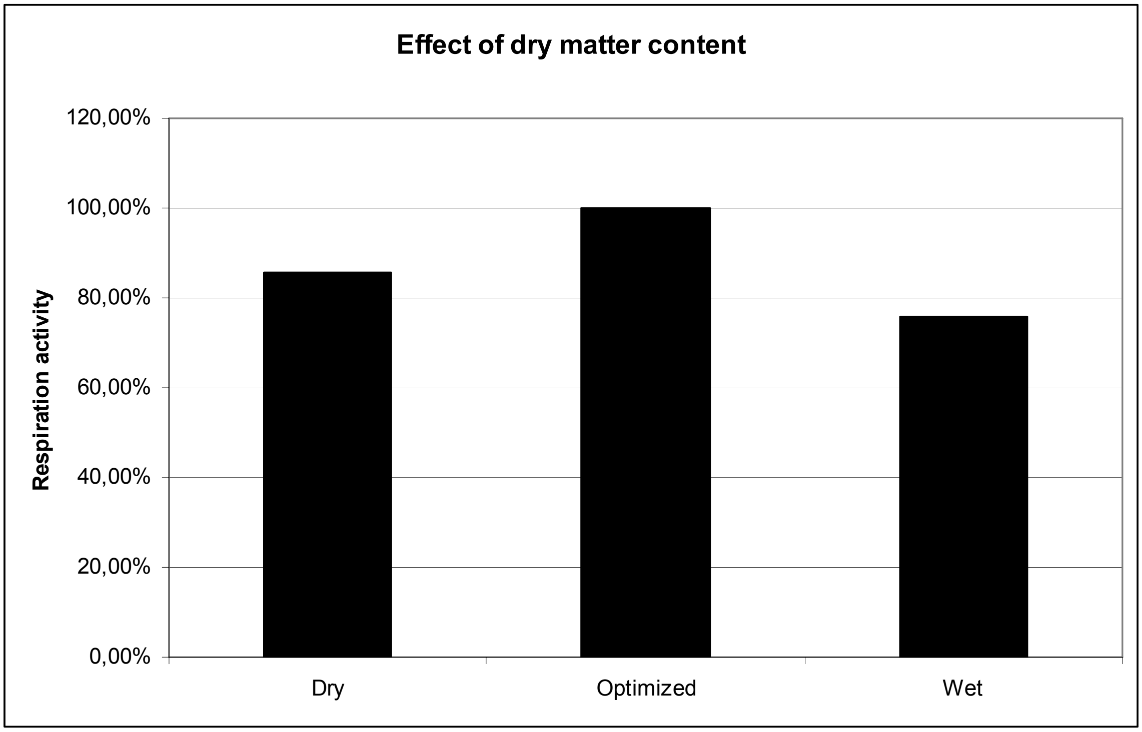

Figure 17 The effect of water content on respiration activity (RA_4). The respiration activity is presented as a percentage of the activity at optimised water content.

Like in the case of respiration activity the anaerobic gas potential decreases during treatment (see Figure 18). The decrease was 97% for MBA 1 and 87% for MBA 2. The results are very similar to those for the respiration activity. The limit value in Germany is 20 Nl/kg DM for pre-treated waste (AbfAblV, annex 2 nr. 5). All output materials comply with the limit.

No results where obtained for the material from Trelleborg. The gas production of the material was very low, and the inoculum sludge used in that experiment had a higher gas production than normal. Therefore it was not possible to measure the production from the sample. It was however clear that all samples from Trelleborg that were supposed to be measured (input, output, leached input) were well below the limit value.

The decrease in respiration activity is faster in the beginning of the treatment. 54% of the decrease occurs during the first two weeks of treatment. The period from week two to six account for 43% of the decrease while the last three weeks only represent three percent of the decrease. The gas potential decreases faster in the middle of the treatment period. 70% of the decrease takes place from week two to six. During last three weeks only 5% of the decrease happens. The respiration activity was not low enough after six weeks but the gas potential was, and only one of these parameters need to comply with the criteria in order for the waste to be landfilled.

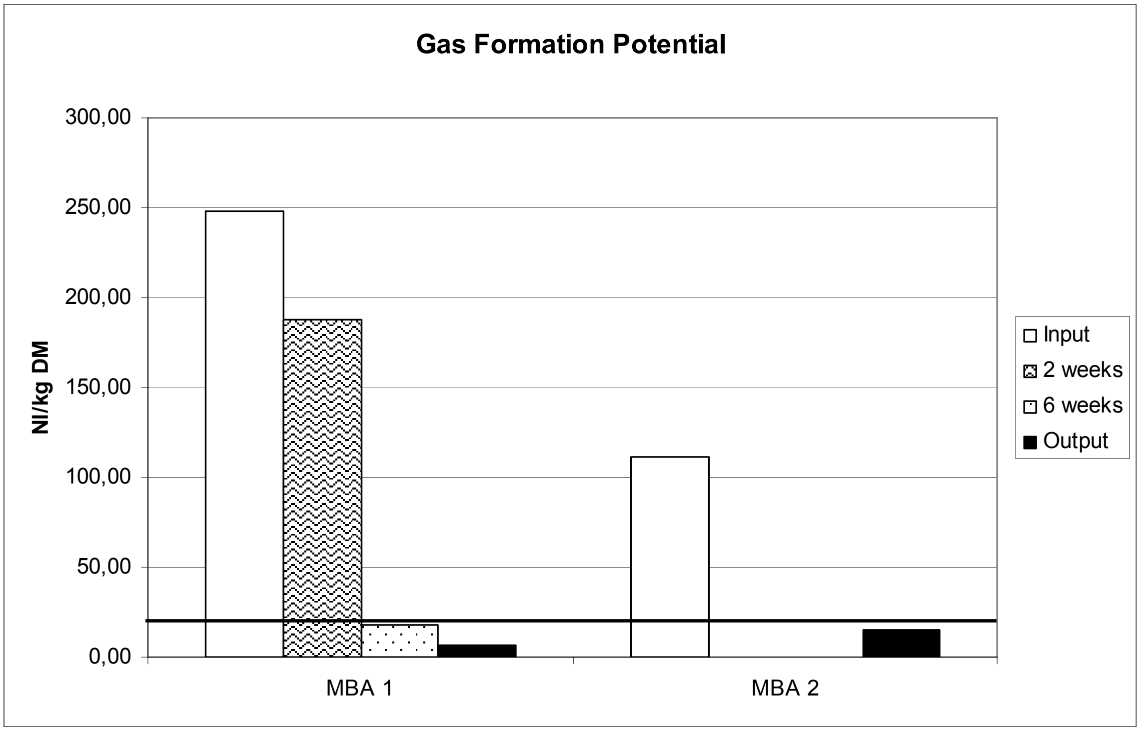

Figure 18 Gas formation potential in pre-treated waste. The limit value of 20 Nl/kg DM show in the figure

The material from Trelleborg was not frozen after sampling but only refrigerated. One possibility is that the low activities in this waste would be the cause of degradation during storage. However the organic components correspond quite well to those measured in the previous study. It is more likely that the low activities depend on a low input of degradable components and, in the case of the output material, a long treatment period.

5.9 FT-IR Spectroscopy and Thermal Methods

The FT-IR investigation of the samples resulted in Figure 19 to Figure 21. The spectrums give information about important functional groups and chemical structures in the samples and will thus help to describe the materials and their stability. Some peaks will e.g. shrink during pre-treatment. The figures together with explanations can also be seen in appendix 5 which was received from the Institute of Waste Management at the University of Natural resources and Applied Life Sciences in Vienna. The discussion of the data is exclusively done using appendix 5 and no extensive analysis has been done in the scope of this thesis.

The peaks at 2920 cm^{-1} and 2850 cm^{-1} representing methylene and at 1720-1740 cm^{-1} representing C=O bonds in several different molecules are among those that should decrease as the material degrades. Especially the first ones are clearly shrinking as can be seen in the figures, thus indicating increasing stability. Other peaks should increase, e.g. carbonate at 875 cm^{-1} and 1420 cm^{-1}. This is also visible in the figures. All three materials show an increasing stability (see also appendix 5). Interestingly the peaks at 2920 and 2859 are higher in the material that was treated two weeks at MBA 1 than the material that was only treated once. This corresponds to the TOC and TOM measurements that showed higher organic content in the 2 weeks material than in the input.

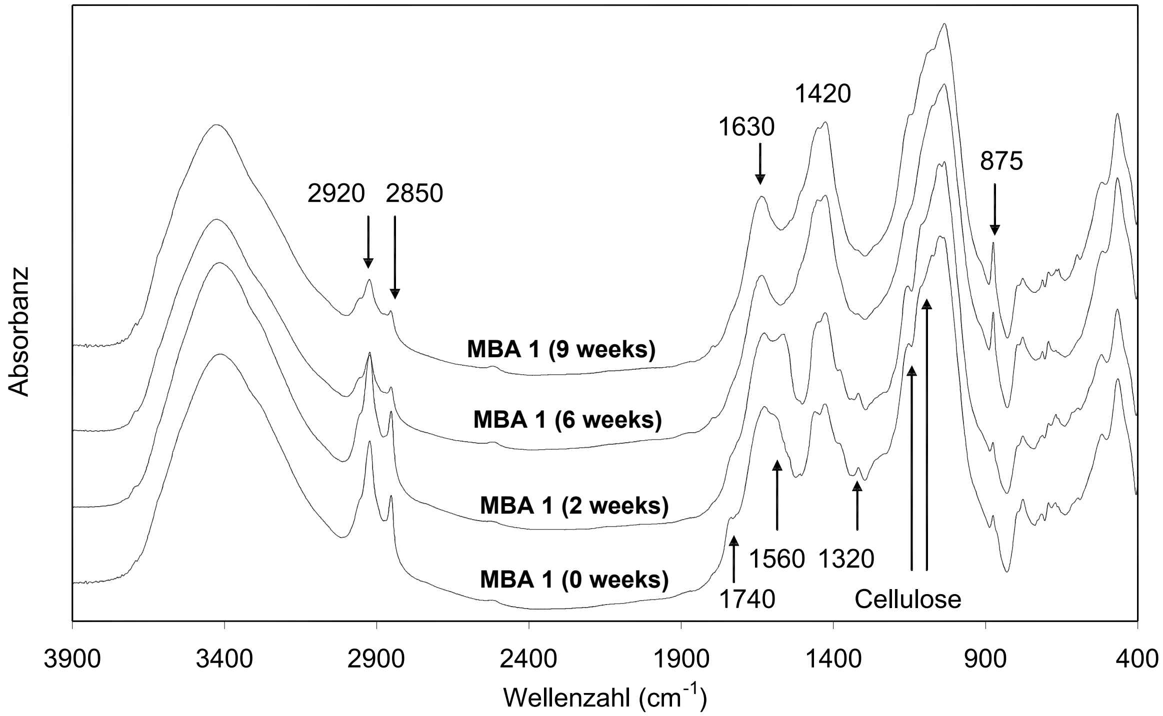

Figure 19 Absorbance in waste material measured with FT-IR spectroscopy

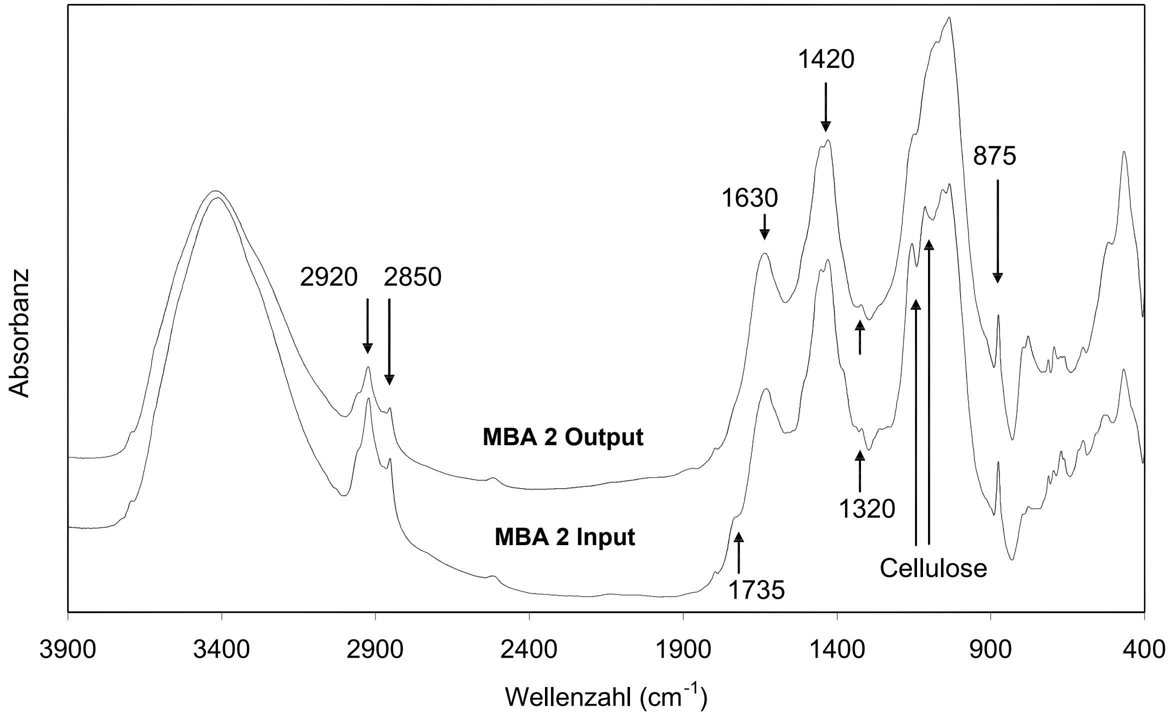

Figure 20 Absorbance in waste material measured with FT-IR spectroscopy

In the sample from Trelleborg (Figure 21) the plaster rich building waste probably affects the spectrum. Sulphate might cause the peaks around 600-700 cm^{-1}. Gypsum carton, which is a likely content in building waste, has a fitting peak around 1200 cm^{-1} (see spectrum in appendix 5).

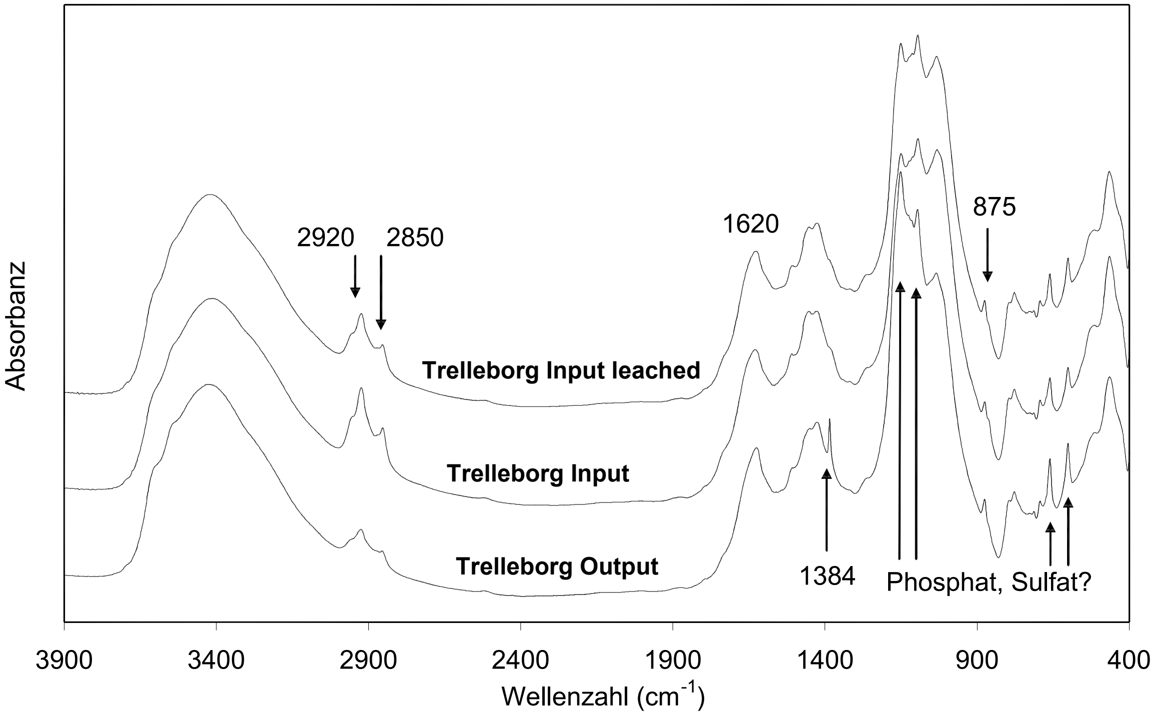

Figure 21 Absorbance in waste material from Trelleborg measured with FT-IR spectroscopy

The samples from MBA 1 were also examined with thermal methods. The behaviour at high temperature can reveal properties such as stability of wastes. Three measurements will be presented here; loss of mass per minute, CO_2 ion flux and heat flux.

Loss of mass per minute related to the increasing temperature can be seen in Figure 22. The first peak around 100°C is the evaporation of water. The two following peaks (around 290°C and 470°C) are caused by burning of the organic material. The bigger the peaks the more organic material was present. The fourth peak (around 660°C) is due to the breakdown of carbonates. The intensity of this peak will increase with increasing amount of inorganic components. As the organic stability of the samples increases the peaks will be shifted to the right (higher temperatures). (Smidt, s.a., pp. 4-5)

At the second and third peak in Figure 22 the input sample (0 weeks) and the sample after two weeks show a bigger intensity than the samples that had been treated longer. This shows that organic materials have been degraded. The fourth peak shows a greater mineralization in the materials with longer treatment. A shift of the peaks to the right can also be seen. All these facts show that degradation and stabilisation have taken place. The two more fresh materials behave similarly and the two materials with longer treatment are also much like each other. This could be an indication that most of the degradation is taking place between two and six weeks of treatment. As stated above the activities show similar results, at least only a very small part of the activity decrease takes place during the last two weeks. The third peek exhibit the same relationship between the input material and the material after two weeks of treatment as the TOC, TOM and FT-IR measurements, i.e. the two weeks old material has a lower organic content. The second and the fourth peaks however indicate the opposite.

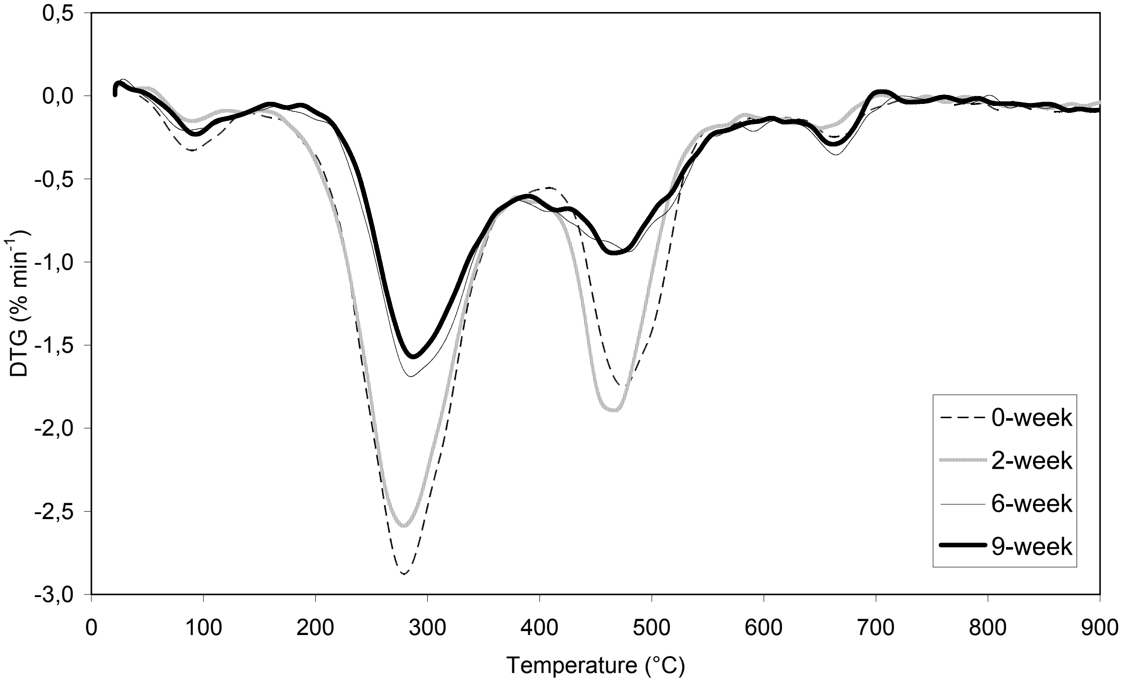

Figure 22 This thermogram of pre-treated waste (MBA 1) shows loss of mass per minute as the sample is burned with increasing temperature

The ion flux shown in Figure 23 confirms the results from the thermogram. The combustion of organic materials leads to a high flux of CO_2 at the same temperatures as the combustion peaks in the thermogram. Both dominating peaks in the ion flux graph correspond to the previous findings that the input has a lower organic content than the material that was treated for two weeks.

The heat fluxes during combustion were measured calorimetrically and the results are shown in Figure 24. The heat flux is the entire time positive, i.e. no net endothermic processes take place in this case. The two peaks representing combustion of organic material visible in the thermogram can also be seen here as exothermic peaks. The more degraded the material is the less intense the peaks are. The two weeks material is once again showed to have a higher organic content than the input. The total energy in the system (the area under the graphs) also increases as the material is mineralized, just like it should (Smidt s.a., p. 9). Most organic wastes show these two exothermic peaks, but e.g. soil lacks them entirely (Smidt s.a., p. 10). Even though the material from MBA 1 has undergone a considerable mineralization it is not yet really soil-like in this respect.

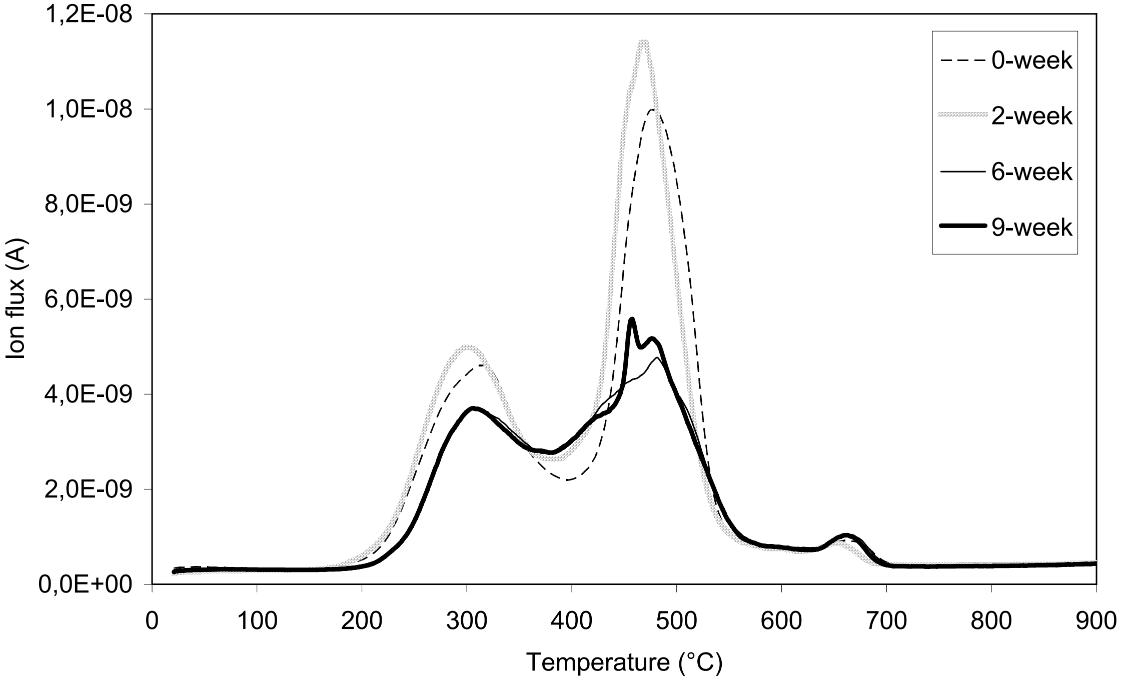

Figure 23 CO_2 ion flux during combustion of pre-treated waste (MBA 1) samples at increasing temperatures

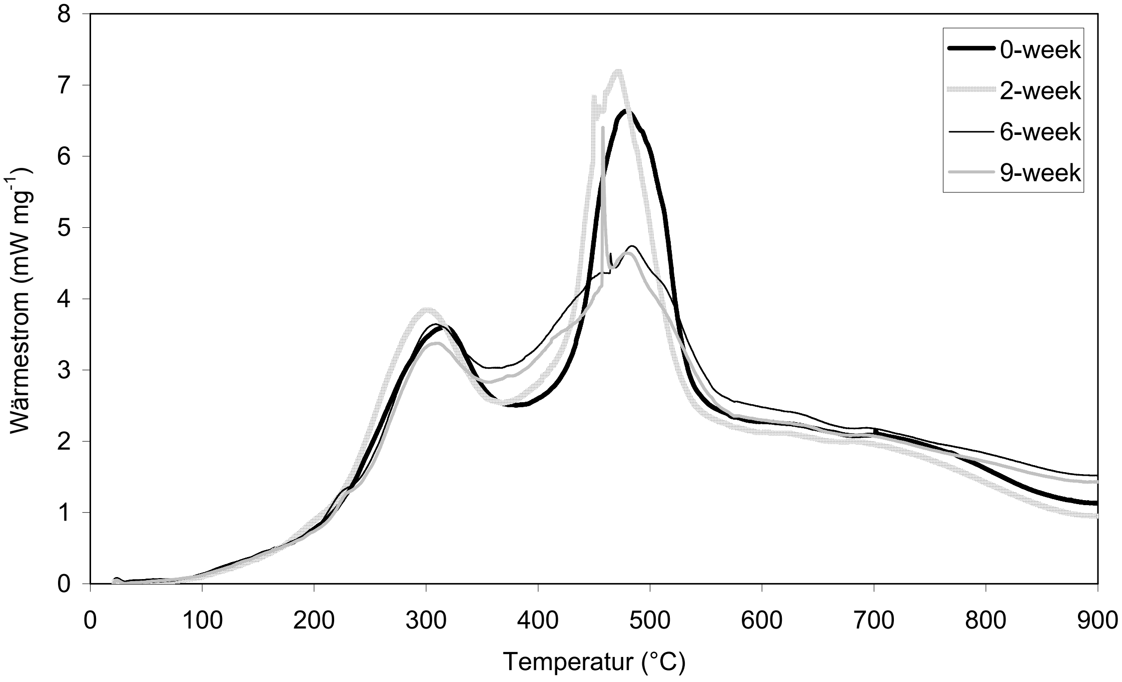

Figure 24 Heat flux during combustion of pre-treated waste (MBA 1) samples at increasing temperatures

5.10 Landfill Simulators

The four bioreactors that were used to simulate landfilling of the output material from MBA 1 are shown in Figure 25. The raw data for the bioreactors are presented in appendix 4. In this section the results are discussed. The data is not good enough to allow a quantitative analysis; therefore the following discussion will be mainly qualitative.

Figure 25 Four bioreactors used for landfill simulation. From right to left: Reactor 1, aerobic, reactor 2, anaerobic with leachate recirculation, reactor 3, anaerobic and reactor four, anaerobic dry

The CO_2 production in the aerated reactor one can be seen in Figure 26. It is high in the beginning of the experiment but decreases and after 36 days it seems to stabilize at a level of about 25% of the initial production. At the end of the experiment the measurements were not as frequent so the results are not as certain. The sudden dips in the production are probably due to sharp variations and uncertainties in the flow rate measurement and do most likely not represent real dips in CO_2 production.

The biogas composition in reactor two, three and four is showed in Figure 27 to Figure 29. For all three anaerobic reactors there was ten to twenty percent of carbon dioxide in the gas before the gas production started. This means that the carbon dioxide values presented in the graphs are higher than the actual production, especially initially. When the reactors were opened and then flushed with CO_2 and N_2 at day 15 the CO_2 concentration decreased in reactor two and three. This is not a real change in the composition of the produced biogas. A conservative guess is that the gas composition did not change at all and this was used to even out the curves. The gas composition in reactor four was not as strongly affected by the opening of the top and in that case the graph was left unchanged.

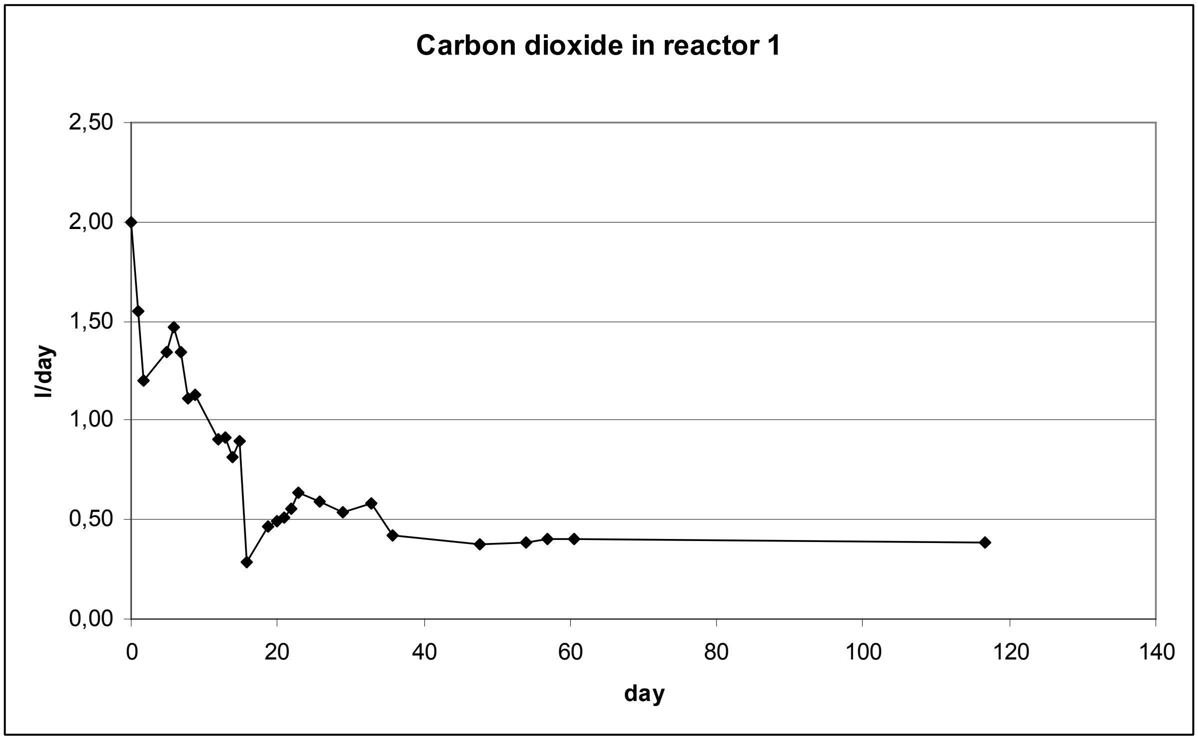

Figure 26 CO_2 production in an aerobic bioreactor

In reactor two and three the CO_2 production was high already after a few days (Figure 27 and Figure 28) and it culminated around the 25th day. The methane production followed a similar pattern but with a lag phase of around three weeks. The graphs are very similar to that for a typical landfill (Figure 1) but the lag phase is shorter. Naturally there will be no aerobic phase since the oxygen was removed before the experiment. Since most of the easily degradable material had already been removed the acidic phase could also become less important. When the first leachate sample was taken after nine days the pH value was seven, and the methane concentration in the gas was still only one percent of the total. This indicated that the lag phase was not the result of an important acidic phase but it can not be ruled out. Comparison with a similar experiment using fresh waste showed big differences. Sanphoti et al. (2006) experienced a long acidic phase (about 200 days) with low methane production (mainly below five percent) and pH just below six. The experiments are not exactly comparable, but it is clear that the lag phase for methane production is longer with untreated waste. If the acidic phase can be avoided this could reduce the emissions from the landfill since the leachate is normally more harmful during this phase (Kjeldsen et al. 2002, p. 301).

As can be seen in Figure 29 the biogas formation in the dry reactor was much more modest than in the reactors with optimized water contents. The methane concentration was especially low; it never reached above two percent of the biogas. A surprising fact was that this reactor had oxygen levels around two percent the first two weeks compared to around one percent in the other reactors, and also later on in the experiment the oxygen levels were higher (see raw data in appendix 4). The reactors should in fact be oxygen free, but some oxygen will always contaminate the gas at sampling. There is no explanation to why more oxygen should enter the samples from reactor four. One possible explanation is that the oxygen did not enter at sampling but that more oxygen was trapped in the waste in reactor four. The other anaerobic bioreactors where saturated with water and did not contain much free space, but in the dry waste in reactor four there was room for quite a lot of oxygen. The fact that the water content, and thus the microbial activity, was so low in reactor four can also have lead to a slower depletion of oxygen.

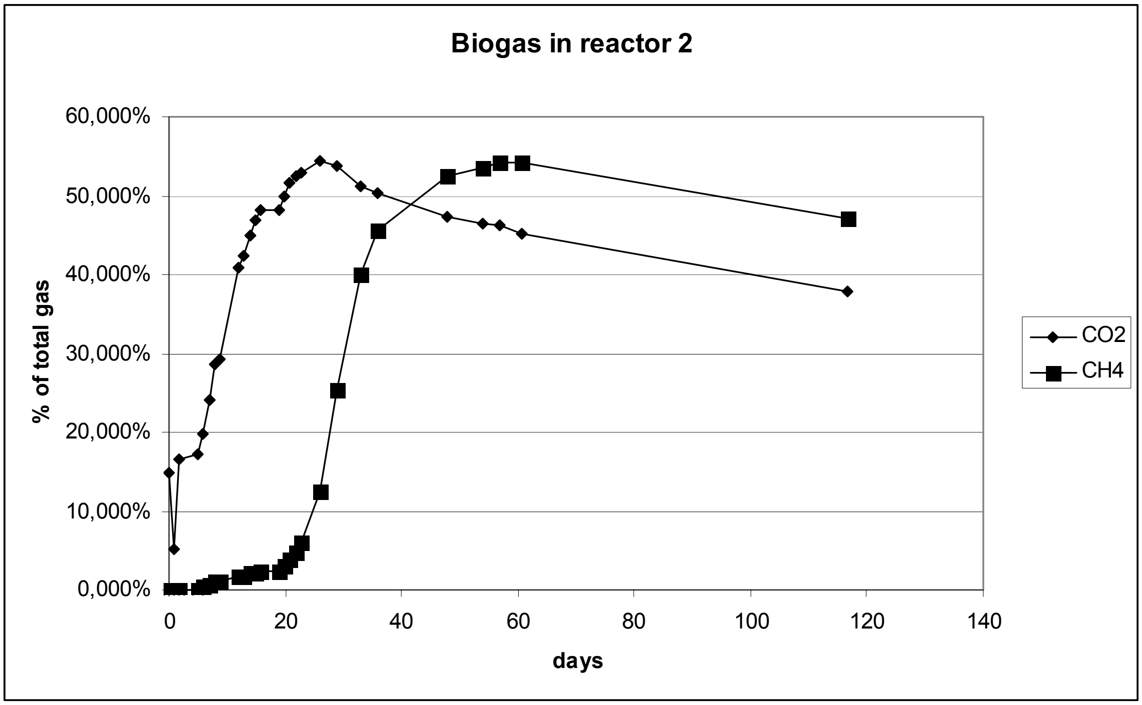

Figure 27 Biogas composition in an anareobic bioreactor with leachate recirculation and filled with pre-treated waste

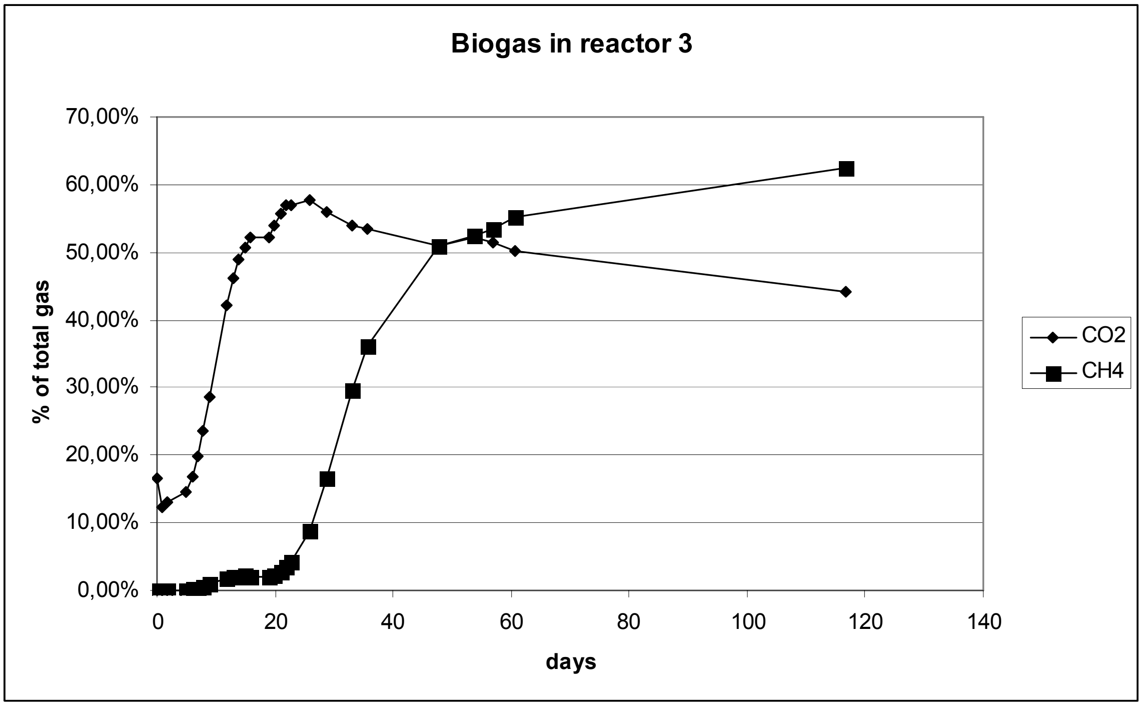

Figure 28 Biogas composition in an anaerobic bioreactor with pre-treated waste

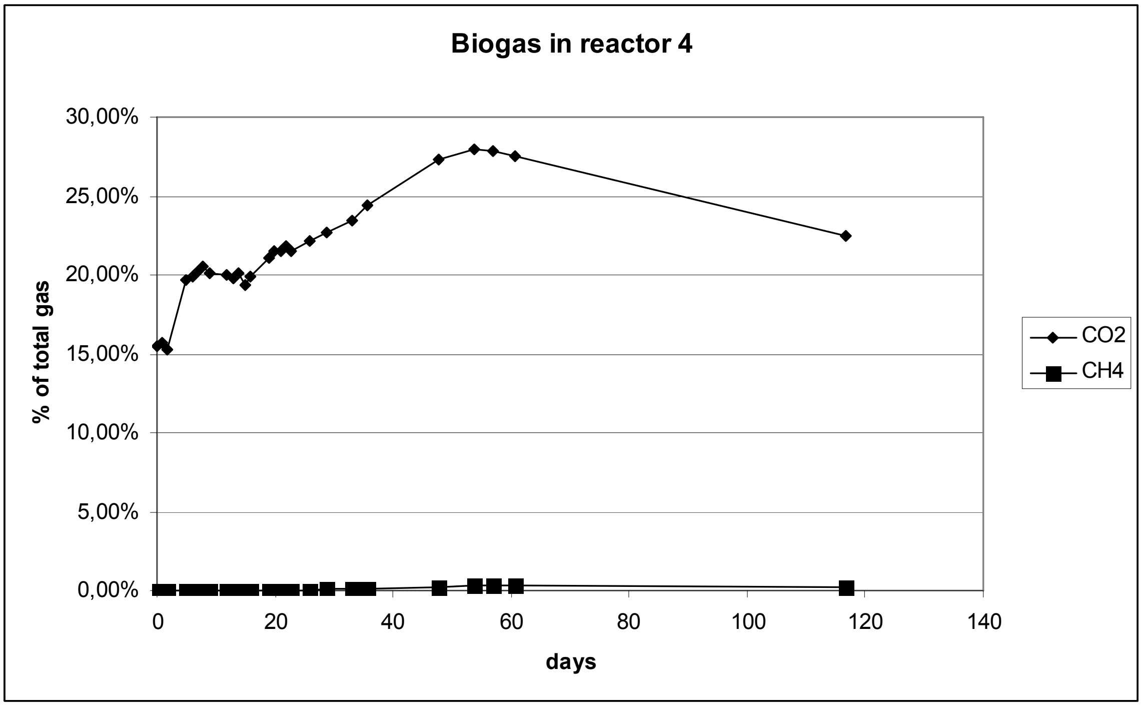

Figure 29 Biogas composition in a dry anaerobic bioreactor

The accumulated gas volumes produced in the three anaerobic reactors are presented in Figure 30. After the entire 117-day-long experiment the total volumes that had been measured were six litres in reactor two, 16 litres in reactor three and one litre in reactor four. These data are not very accurate due to some problems with the method but it is clear that there were big differences between the gas volumes.

The dry reactor (reactor four) is extreme, both in the respect that it has much lower gas production and that the methane part of the biogas is almost negligible. The lack of water is obviously an important limiting factor for anaerobic degradation.

Reactor two had a much lower accumulated gas production than reactor three. The only difference in reactor setup between these reactors was that reactor two had leachate recirculation. Leachate recirculation can in fact enhance methane formation by creating a better water supply. In this case the waste was already at its optimal water content, but recirculation can have other positive effects, such as redistributing substrates and nutrients and helping micro-organisms to colonize new parts of the waste mass (Sanphoti et al. 2006, p. 28). The potential effect is a faster degradation and faster stabilization. This should show as a higher gas formation rate earlier in the experiment. In this case however, this can not be seen. The gas composition in reactor two and three are very similar and the methane production has its peak the same day for both reactors. The only important difference in gas composition is that for reactor three the methane concentration continues to increase towards the end of the experiment. This is however only shown by one measurement and is therefore not very reliable. The positive effects of leachate recirculation could not be detected here, but the potential effect was not that big since the waste was already saturated. The leachate was replaced with fresh water at two occasions to simulate rainfall. Since the leachate contained a lot of suspended matter this means that a part of the organic matter was removed this way so the gas formation potential in the waste was lowered. This is the most likely explanation to the low amounts of gas formed in reactor two.

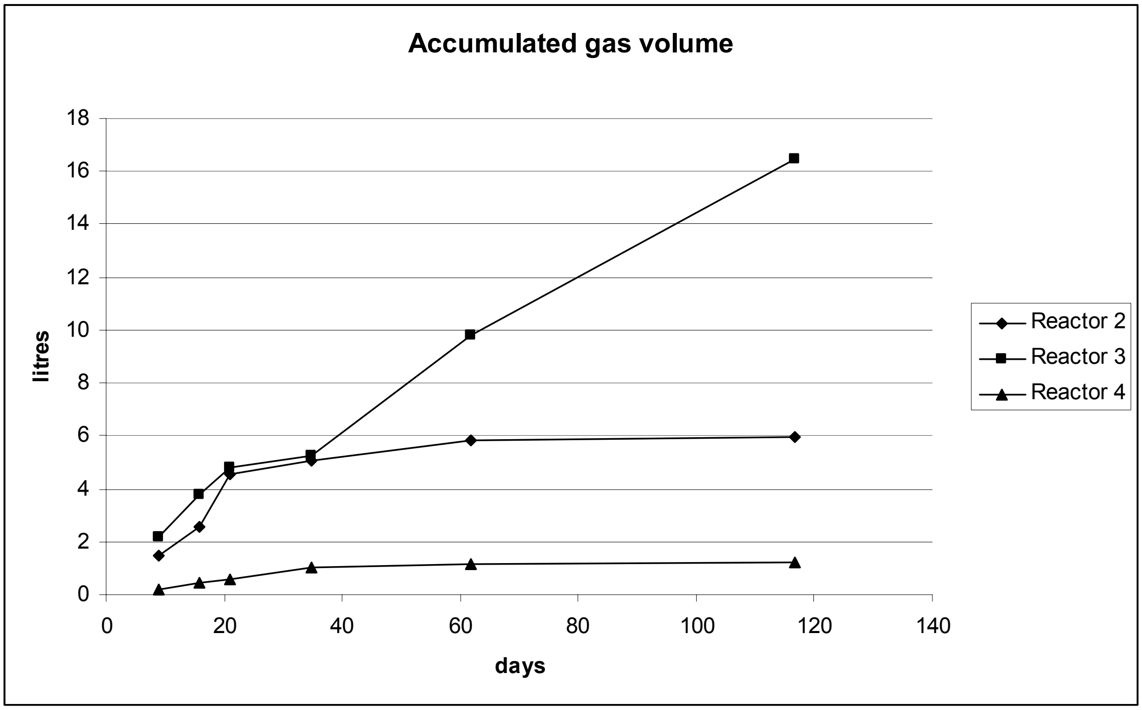

Figure 30 Accumulated biogas formation in anaerobic bioreactors filled with pre-treated waste and operated under different conditions

In Table 17 and Table 18 the different measurements done in the eluate from the solid samples are presented and compared to the output material from MBA 1; i.e. the input material to the reactors. The sampling was done after 16 days and the results do therefore not represent the output material. As can be seen from the tables the two anaerobic reactors at optimal water content behave similarly in most cases and differ from the other two reactors.

Table 17 Measurements in pre-treated waste before and after 16 days in four different bioreactors

Sample	pH	EC [mS/cm]	DOC [mg/l]	COD [mg/l]]	BOD_5 [mg/l]	BOD_5/ COD	HA [mg/l]	NH_4 [g/l]
Input	8.11	5.19	181	585	48	0.08	9.7	0.02
Reactor 1	8.08	4.66	122	415	26	0.06	12.3	<0.01
Reactor 2	8.09	2.53	233	566	55	0.1	42.4	0.04
Reactor 3	8.09	2.67	235	625	56	0.09	52	0.04
Reactor 4	7.94	5.38	172	489	25	0.05	15.9	0.03

The pH values are all similar to the initial pH around eight. This does however not mean that the pH never changed; the pH in the leachate from reactor two was around seven after nine days. The EC decreases in reactor two and three, to around half of the initial value. The DOC on the other hand increases almost 30% in reactor two and three, so in this case the emission potential seems to increase. The aerobic reactor has a decrease in DOC and probably also a small decrease in conductivity.

The COD seems to decrease in reactor one and four and the BOD_5 definitely does. The BOD_5/COD ratio also seems to decrease. For the anaerobic reactors the opposite seems to happen, but these smaller changes can also be caused by the heterogeneity of the material.

There seems to have been a formation of humic acids in all reactors, but absolutely most in reactor two and three. This speaks against the hypothesis presented in section 5.5 that anaerobic conditions prevent HA formation. It is possible that the formation in the aerobic reactor was even bigger but that the acids aggregated and were removed by filtration and therefore do not show in the analysis. This is not possible to confirm since no analyses of the solid waste was done. This HA analysis was also done with the less reliable method. The samples were taken when the methane production was still quite low, so the samples are not typical for methanogenic conditions.

The anaerobic reactors seem to have higher NH_4^+ concentration after 16 days. The aerobic reactor has lost some of its NH_4^+. The aeration might have increased the loss of this gaseous compound, but there may also be other explanations for this difference. As stated above in section 5.7 the NH_4^+ content is influenced by a large number of factors and the data here is really too limited to draw any conclusions.

The metal content in the eluate after 16 days can be seen in Table 18. As for the other parameters reactor two and three are similar to each other and reactor one and four are also similar with the exception of zinc. In some cases reactor two and three have lower values after the experiment and in other cases one and two have the lowest values. Nickel and lead seem to have become more leachable after having spent 16 days in an anaerobic landfill, but there is no telling what will happen later on.

Table 18 Heavy metals in pre-treated waste before and after 16 days in four different bioreactors

Sample	Cd [µg/l]	Cr [µg/l]	Cu [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [µg/l]
Input	7	26	806	191	16	692
Reactor 1	5	17	647	141	7	275
Reactor 2	2	27	209	414	35	192
Reactor 3	2	30	168	455	60	474
Reactor 4	6	20	759	178	11	437

The fact that the dry anaerobic reactor was more similar to the aerobic reactor than to the other anaerobic ones might be because some oxygen was trapped in the reactor and there might actually have been some access to oxygen. The anaerobic reactors often seemed to have a higher emission potential than the aerobic after 16 days. At this point the methanogenic phase had not really started so this should not be considered as evidence that anaerobic treatment increases the emission potential.

For the output material after the full 117 day experiment there is a limited amount of data, presented in Table 19. The respiration activity has decreased further, especially in the aerobic reactor. For DOC there are no significant changes except for a decrease in the aerobic reactor. This shows that anaerobic treatment is more efficient to reduce the biological activity and organic content of the waste.

Table 19 Parameters in the input and output material from bioreactors simulating landfills

Sample	RA_4 [mg O_2/g DM]	DOC [mg/l]
Input	4.1	181
Reactor 1	1.1	94
Reactor 2	2.6	190
Reactor 3	3.4	220
Reactor 4	2.2	200

5.11 Summarising Discussion

The organic content in all three waste materials decreased during treatment. The parameters that indicate biological stability all clearly show an increasing stability; the respiration activity and gas potential decreased around 90%, the BOD_5/COD ratio decreased, the humic acid content increased, the C/N ratio decreased and the FT-IR spectra and thermal methods showed increasing stability. The leachability of the pollutants also decreased in most cases; in MBA 1 the DOC/TOC ratio decreased by 90%, smaller portions of the humic acids and ammonium were leached and in many cases the heavy metals showed a much lower potential of leaching after treatment. For MBA 2 a bigger part of the metals seemed to be eluted after treatment, but the leachability of the metals was very small to start with and the change was small. For Trelleborg more humic acids were eluted after treatment but they are naturally occurring, stable compounds that should cause little harm. In all the emission potential of the wastes was lowered; much less landfill gas will be produced and the leachates will contain less pollutants.

Even though the emission potential was lowered considerably it was not zero after treatment. The landfill simulation showed that the waste could be further degraded after landfilling. Some pollutants will also possibly be leached. It is important to know that the emission potential does not disappear after treatment even if it is lowered.

MBA 1 had the highest initial potential as could be seen from most of the measurements. After treatment MBA 1 did not show a higher emission potential than the others. Since the input material from MBA 1 is so wet and fresh it risks forming anaerobic zones when stored before treatment. The low pH values found in the input material indicate that this had happened. Formation of anaerobic zones can lead to emissions of greenhouse gases and odorous compounds.

The analyses of the leached material from Trelleborg showed some contradictory results. The RA_4, T-N, TOM and TOC decreased as would be expected. The effects are not as big as for the treatment process. The humic acid content increased which might be explained by degradation going on during leaching. The metal concentration (except for zinc) increases after leaching which seems impossible and no good explanation to this behaviour has been found.

It was clear that only small parts of the metal content in the wastes were leachable. Except for the initial leachability of Zinc and Cadmium (23 and 7% respectively) only around one percent or less of the heavy metals were leached.

Not all regulated parameters were measured in this study but if it was only a matter of the parameters measured here the materials from MBA 1 and Trelleborg could be landfilled as MBT waste in German class II landfills. The material from Trelleborg could be landfilled in Germany even before treatment. The material from MBA 2 has a too high DOC content and cannot be landfilled. The Swedish criteria are generally harder to comply with. MBA 1 and MBA 2 could not be landfilled at all in Sweden since the DOC and TOC values exceed the limits. For Trelleborg the Swedish TOC limit causes problems, but if the material could be classified as non-hazardous waste the exception from the ban on landfilling organic waste with a TOC smaller than 10% could be used and the waste could be landfilled. Karlsson (2006, p. 28) measured more parameters in the material from TOC but still found that the DOC was the biggest problem for the material from Trelleborg.

Since the input materials were so different it is hard to compare the methods and say that one is more successful than another. The high final DOC value in MBA 2 speaks against that method, but this was only shown by one sample and might be a temporary problem.

The allocation criteria are generally stricter in Sweden, but other parts of the legislation enable landfilling of waste with a relatively high emission potential. As long as the waste can be classified as non-hazardous there are no allocation criteria, but organic waste must not contain more than 10% TOC. However, if there is not enough treatment capacity in the region the waste can be landfilled with no treatment at all. This is not supposed to be a permanent solution, but still happens.

The Swedish legislation is clearly not adapted for MBT-treated waste in the landfills, unlike the German legislation. The German legislation is not perfectly adapted either, but has become more so with the new higher DOC limit. If the goal is to allow MBT technology as an alternative before landfilling the German legislation is undoubtedly better adapted. The question will then be if MBT treatment is a good way to treat waste before landfilling.

There are big advantages of landfilling MBT waste compared to untreated waste. These are however not the only alternatives. The waste could e.g. also be incinerated, or treated biologically with the end product being used instead of landfilled. One advantage of MBT treatment over incineration that has been mentioned in the literature (EPEA 2004, p. 6) is that the carbon is stabilized in the waste instead of being released as CO_2. However, if the energy from the incineration plant is used it could replace other energy sources such as coal, thus leading to a smaller net release of fossil CO_2. To assess if incineration or MBT treatment has a better CO_2 balance is a big task and not possible to do within the scope of this thesis. Greenhouse gas emissions are not the only problem. In both cases valuable components such as nutrients in the waste are lost as the waste cannot be further used. The leachate also has to be controlled but comparing the leachate from MBT treated waste with leachate from incinerator ashes is yet another big task.

The TOC values are often limiting for landfilling in Sweden, so an interesting question is whether TOC is really relevant as an allocation criterion. The emission potential of organic waste in landfills is related to the potential release of greenhouse gases and leaching of organic matter. If the activity of the material is low, this shows that there will be a small potential of greenhouse gas emissions. The potential for leaching of organic matter can be assessed by the DOC value. The TOC value in the solid material is related to those parameters but not directly related to the emission potential. The DOC/TOC ratio decreased during treatment. The relation between TOC and the activities also changed. This shows that the TOC value will not be a reliable source to tell how much carbon that will be leached or transformed into gas. The relevance of the DOC limit is also important to discuss. It will depend on the emission potential of the organic matter that constitutes the DOC. In this study a relatively small part seems to be humic acids, so there must be other important components as well. Once they are known the relevance of the DOC criteria should be possible to assess.

The degradation will be optimal at certain water content. In the experiment less water in the sapromat led to a lower activity. The same was observed in the dry bioreactor; the gas formation was much lower than for the other reactors. It is impossible to completely avoid organic matter in landfills and the material present will eventually degrade. If very little water is present the gas production rate will be lower but the gas formation potential will remain longer. This might lead to that the landfill has to be monitored for a longer period of time.

The landfill simulation showed that the aerobic reactor reduced the biological activity more efficiently. For the anaerobic reactors the acidic phase seemed to have been made less important by the pre-treatment. This might reduce the emissions via the leachate.

MBA 1 had a low organic content in the input material at the sampling date for some reason. This shows from the TOM and TOC measurements. Most of the data from the FT-IR and thermal investigations also confirm this fact. The organic material present in the input sample was, however, fresh and had a much higher respiration activity and gas potential than the material that had been treated for two weeks. This shows that it is important to look at the activity of the material and not blindly at the carbon content. It also indicated that the FR-IR and thermal methods correspond better to the measurements of organic content and not so much to the activity methods. This raises the question whether these methods are relevant as maturity indicators.

5.12 Statistical Evaluation

From MBA 1 and MBA 2 sampling was done according to the German legislation. For Trelleborg the sample was mixed from twelve samples taken at the same time. Waste material is extremely heterogeneous and one sample is not always representative for the whole batch. There can also be variations in the input material over time. Even if one sample is representative for the input material present at sampling it is not necessarily representative for the average input material. Variations in the process can introduce further differences over time.

As small samples were used for the analyses the impact from heterogeneity increased. The analyses were done with one to three replicates as specified above in chapter 4. In the cases of filtrate and the finely ground material one sample was prepared and then divided to do more than one measurement. The methods themselves introduce yet another source for uncertainty. The margin for error was however less than five percent in most cases. Different ways to verify some of the results are presented in this section.

The total organic matter and the total organic carbon changes at approximately the same rate with the exception of Trelleborg, and can thus verify each other to some extent. In the case of Trelleborg the results can be controlled with a previous study. Karlsson (2006, calculated from appendix 3) found a TC/TOM rate of 48% in the output material from Trelleborg; in this study this value was found to be 49%.

For TOC the mean value for the last 50 measurements in MBA 1 is known to be 14.7%. All of those values lie between 9.8% and 18%; the 80% percentile is 15.9[4]. The value at 11.5% obtained here is among the lowest values. It was expected at least not to be in the higher range since some of the previous measurements were done during a reconstruction period that affected the treatment results. The total carbon in the material from Trelleborg has previously been found to be 10.7% (Karlsson 2006, appendix 3). This corresponds well to the total carbon found in this study which was 11.2% (see appendix 2). Karlsson (2006, appendix 3) found a TOM of 22.2% in the output from Trelleborg and here it was found to be 22.7%. All these facts put together indicate that the TOC and TOM data are rather reliable.

The metal samples are given as the mean of the two measurements. The values for copper in the solid material from MBA 2 (input as well as output) varied more than 10% even after the analysis had been redone.

The metal content in the output material from Trelleborg has been studied before (Karlsson, 2006). A comparison could verify the values found here. As can be seen in Table 13, the results are in the same range except for chromium and nickel where the difference is 97% and 96%, respectively. The values that are very different from the previous measurement still fit well together with other measurements in this study. It is not clear how the previous measurement was performed. Perhaps differences in methods could explain the deviations.

A previous measurement of the total N in the output from Trelleborg was 9.7 mg/kg (Karlsson 2006, appendix 3). This is higher than the value of 6.8 found here but still in the same range, so there is reason to believe that the measurement did not introduce any large errors in this case. The C/N ratio in Trelleborg was here found to be 11. This can be confirmed by a previous study (Karlsson 2006, appendix 3) that found the same ratio.

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[4] The information about previous measurements was received in an e-mail from Jörn Heerenklage, Institute for Waste Resource Management, TUHH 2006-12-20.

The respiration activity and gas potential in MBA 1 has been analyzed by the Institute for Waste Resource Management, TUHH[5] many times before. The median RA_4 value in the 52 last output values including the sample examined in this study is 3.45. The 80% percentile is 4.4. The sample measured in this study is well within the percentile.

The median GP_{21} value in the 49 last output values for MBA 1 measured at the Institute for Waste Resource Management, TUHH including the sample examined in this study is 9.9 l/kg[6]. The 80% percentile is 14.0. The sample at hand has an activity that is lower than the median while the RA_4 is higher. The correlation between RA_4 and GP_{21} is however not always exact and since this material does not deviate from what is normal there is no reason to suspect any problems with the results.

The results from GP_{21} and RA_4 also confirm each other since they behave similarly; MBA 1 has higher values to start with but decreases rapidly and at the end both materials have similar values.

MBA 1 had a low organic content in the input material at the sampling date. This is shown by the TOM and TOC measurements. Most of the data from the FT-IR and thermal investigations also confirm this fact.

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[5] E-mail from Jörn Heerenklage, Institute for Waste Resource Management, TUHH 2006-12-20.

[6] Se previous footnote.

6 Conclusions and Recommendations

During treatment the humic acid content in the waste increased and the BOD_5/COD ratio decreased. The respiration activity and the gas formation potential decreased with up to more than 90%. All these changes show an increasing biological stability.

The organic material clearly changes during treatment. The biological stability was notably increased, and the leachability of the pollutants decreased. These changes reduce the emission potential. Over all the treatment seem to have made the materials much better adapted for landfilling.

With few exception in the input materials one percent or less of the heavy metals could be leached.

The parameters measured in MBA 1 and Trelleborg comply with the limit values and these materials could be landfilled in Germany after treatment if no other parameters are too high. Trelleborg could be landfilled Trelleborg already before treatment. MBA 2 did not comply with all criteria. None of the German output materials could be landfilled in Sweden and Trelleborg can only be landfilled if it can be classified as non-hazardous waste. The Swedish limits are generally stricter than the German ones and the most limiting criterion is TOC.

Although the Swedish limit values are very strict, exceptions in the legislation enable landfilling of waste with high emission potential. A better solution is to create a legislation that is possible to comply with to avoid having to make exemptions and allowing untreated waste to be landfilled.

TOC is not the most relevant parameter to assess the emission potential of waste being landfilled. It could be replaced by activity measurements like RA_4 or GP_{21} together with measurements of DOC.

Aerobic conditions lowered respiration activity and DOC more efficiently than anaerobic conditions in the landfill simulation.

The water content in the landfill will affect the degradation rate for aerobic as well as anaerobic degradation. Anaerobic processes need a higher water content to function optimally and will, therefore, be affected earlier. A slower degradation will cause organic matter to have a longer lifetime in the landfill.

7 Recommendations for Further Studies

Several questions remain unanswered. The association of the metals to the humic acids and other organic material could not be properly assessed here and deserves more attention. The DOC and its contents should be further studied to get a better knowledge about its emission potential.

Since the emissions happen via the leachate this is more relevant to study than the solid material, but can be interesting to study the solid material as well to be able to relate the concentrations in the eluate to those in the solids.

Before deciding to filter the samples the goal of that method should be clearly defined since this method consumes a lot of time and cleaning chemicals. A faster filtration method should be preferred compared to the one used in this work.

If the goal is to study the effects of treatment it is better to follow one batch of material through treatment and take samples from that at different times rather than to sample at different stages at the same day. This will at least eliminate the influence from differences in input material.

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List of Abbreviations

Abbreviation	Explanation
BOD_5	Biological oxygen demand measured over 5 days
COD	Chemical oxygen demand
DM	Dry matter content
DOC	Dissolved organic carbon
EC	Electrical conductivity
FA	Fulvic acids
IR	Infrared
FT-IR	Fourier Transform Infrared
GP_{21}	Gas formation potential measured over 21 days
HA	Humic acids
HS	Humic substances
kDa	kiloDalton, i.e. a thousand atomic mass units
LOI	Loss on ignition
MBT	Mechanical-biological pre-treatment
RA_4	Respiration activity measured over 4 days
TC	Total carbon
TIC	Total inorganic carbon
T-N	Total nitrogen
TOC	Total organic carbon
TOM	Total organic matter
TUHH	Hamburg University of Technology

Appendix 1 Methods

This appendix contains a list of all examined parameters and the methods and apparatus used to assess them. When standardised procedures have been used the names of the standards has been given.

Tabell 1 List of parameters measured in the solid waste and the methods used to assess them

Parameter	**Method**	**Apparatus**	**Standard**
Dry matter content	Drying in 105°C	Drying cupboard WTE (Binder, Tuttlingen, Germany)	DIN 38414 - S2
Organic substances	Ignition loss		DIN 38 414, part 3
pH	Lixiviation of probe in 0,01 mole/l $CaCl_2$; measuring pH with single-rod measuring cell	Single-rod pH measuring cell of type E50, pH-mV-Meter pH 90 (WTW, Hamburg, Germany)	DIN 38-404-C5 and Metodbook for the analyses of compost (Federal Compost Quality Assurance Organiziation, Cologne, 2004)
TOC	Removal of inorganic carbon and IR measurement.	Leco CNS analyser	
Respiration activity, RA_4	Breathing activity measured over 4 days with Sapromat.	Sapromat D12 with data collection unit DDES 12-48 (VOIT GmbH, Heidenheim, Germany)	Ordinance on Environmentally Compatible Storage of Waste from Human Settlements (AbfAblV, BGBl. I S. 205), annex 2 nr. 5.
Gas potential, GP_{21}	Gas formation potential measured over 21 days	Eudiometer	Ordinance on Environmentally Compatible Storage of Waste from Human Settlements (AbfAblV, BGBl. I S. 205), annex 2 nr. 6.
Heavy metals (Cd, Cr, Cu, Pb, Ni, Zn)	Homogenised and boiled with aqua	PE-Elan 6000 ICP-MS or PE-Optima	

	regia and measured spectrometrically	2000 DV ICP-OES	
Total N		Büchi N-analyser	
NH_4	Water vapour distillation, back filtration	PE-Elan 6000 ICP-MS or PE-Optima 2000 DV ICP-OES	
Humic acids	Mixed with NaOH/Na oxalate solution and measured photometrically	Shimaxdu UV-VIS Spectral photometer	
Humic substances	Extraction, centrifugation and photometric measurement.	Centrifuge, photometer	Modified Danneberg method
Spectral analysis	FT-IR Spectroscopy	Bruker Equinox 55 FTIR-Spectrometer, range 4000 400 cm^{-1}, transmission mode, resolution 4 cm^{-1}, 32 scans per spectrum (average)	
Thermal methods	Thermogravimetry, Dynamic differential calorimetry, Mass spectrometry	Thermal weighing machine, Calorimeter, Mass spectrometer STA 409 CD Skimmer from Netzsch GmbH	

Table 1 List of parameters measured in the leachate and the methods used to asses them

Parameter	**Method**	**Apparatus**	**Standard**
pH	Measuring with single-rod measuring cell	Single-rod pH measuring cell of type E50, pH-mV-Meter pH 90 (WTW, Hamburg, Germany)	38404 - C5
Conductivity	Conductometry	Conductivity meter LF 539, measuring cell (electrode)	38404 - C8

		Tetracon 96 (WTW, Hamburg)	
Biological Oxygen Demand (BOD_5)	Dilution method (Nitrificationinhibitor N-Allylthiourea in dilution water)	Oximeter OXI 2000, Oximatic EO 200 (WTW, Hamburg)	38409 - H51
Chemical Oxygen Demand (COD)	Oxidation with potassium dichromate in the presence of silver sulphate (catalyst), mass analytical determination of residual potassium dichromate with ammomium ferric (II) sulphate solution.	Digester (GERHARDT, Bonn), Titration with: TR156, T100, TA20 (SCHOTT, Hofheim)	38409 - H41
Total Organic Carbon (TOC)	Thermic oxidation of carbon compounds to CO_2, IR spectroscopic measurements of CO_2 (TC); removal of the inorganic carbon (TIC) as CO_2 with phosphoric acid, IR spectroscopic measurement of CO_2	Analyzer C-mat 5500 A2, TOC-Sampler-Unit, Software C-mat 5500 (STRÖHLEIN, Kaarst)	38 409 - H3
Humic Acids	Dissolved in NaOH/Na oxalate solution and measured photometrically	Shimadzu VU-VIS	
Heavy metals	Boiled with HNO_3 and measured spectrometrically	PE-Elan 6000 ICP-MS or PE-Optima 2000 DV ICP-OES	
NH_4	Shaken with $CaCl_2$, filtrated and measured spectrometrically		

Table 2 List of parameters measured in the gas from the landfill simulators and the methods used to assess them

Parameter	**Method**	**Apparatus**
N_2, O_2, CO_2, CH_4	Gas Chromatography	Instrument: HP 5890 (Agilent) Detector: TCD Column: HayeSep N, 2m, 1/8’’, 80-100 Mesh Molsieve 13X, 2m, 1/8’’, 60-80

		mesh (Agilent) Software: HPChemStation (Agilent)
Gas volume	Collection in gasbags and volume measurement in gas clock.	Gas clock from Ritter.

Appenix 2 Results summary

This appendix contains all results used in this the study except for the data that concerns bioreactors. The data presented is not processed or compensated for dry matter content or disturbing substances that have been removed prior to measurements. The exception from this is the RA_4 and GP_{21} data. For these parameters calculations according to AbfAblV, annex 2 nr 5 and 6 has been performed.

Table 1 Dry matter content for pre-treated waste materials

Material (stage in treatment)	Dry matter content [%]
MBA 1 (0 weeks)	54
MBA 1 (2 weeks)	54
MBA 1 (6 weeks)	67
MBA 1 (9 weeks)	66
MBA 2 (input)	67
MBA 2 (output)	81
Trelleborg (input)	61
Trelleborg (input leached)	53
Trelleborg (output)	60
Trelleborg (output leached)	55

Table 2 Disturbing substances removed prior to grinding dried, pre-treated waste materials

Material (stage in treatment)	Disturbing substances removed [%]
MBA 1 (0 weeks)	10.4
MBA 1 (2 weeks)	9.2
MBA 1 (6 weeks)	17.9
MBA 1 (9 weeks)	17.8
MBA 2 (input)	12.6
MBA 2 (output)	17.7
Trelleborg (input)	16.1
Trelleborg (input leached)	8.7
Trelleborg (output)	10.1

Table 3 pH in pre-treated waste materials and their eluates

Material (stage in treatment)	pH in solid material	pH in eluate for different filtration cut-offs				
		Before filtration	0.45 µm	100 kDa	30 kDa	5 kDa
MBA 1 (0 weeks)	5.5	5.8	5.9	5.9	6.0	6.1
MBA 1 (2 weeks)	6.9	6.7	7.3	7.1	6.8	6.8
MBA 1 (6 weeks)	7.9	7.2	8.2	7.9	8.1	7.8
MBA 1 (9 weeks)	7.5	7.3	8.1	7.6	7.7	7.5
MBA 2 (input)	7.3	6.9	7.4	7.8	7.9	8.0
MBA 2 (output)	7.7	7.3	7.7	8.4	8.2	8.3
Trelleborg (input)	Not measured	Not measured	7.6	7.5	7.5	7.8
Trelleborg (output)	7.3	Not measured	7.6	7.5	7.6	7.8

Table 4 Electrical conductivity in eluted waste samples

Material (stage in treatment)	Electrical conductivity [mS/cm]				
	Before filtration	0.45 µm	100 kDa	30 kDa	5 kDa
MBA 1 (0 weeks)	6.52	6.57	6.72	6.55	6.36
MBA 1 (2 weeks)	6.69	6.83	6.54	6.61	6.63
MBA 1 (6 weeks)	4.15	4.18	4.05	4.00	3.86
MBA 1 (9 weeks)	4.94	5.19	4.95	5.08	4.97
MBA 2 (input)	4.34	3.96	4.14	4.13	4.02
MBA 2 (output)	4.60	4.53	4.53	4.51	4.35
Trelleborg (input)	Not measured	3.55	3.36	3.47	3.38
Trelleborg (output)	Not measured	3.09	2.96	2.98	3.02

Table 5 Organic parameters in pre-treated waste samples

Material (stage in treatment)	Loss on ignition [%]	TIC [g/kg]	TC [g/kg]	TOC [g/kg]
MBA 1 (0 weeks)	47.5	34	242	207
MBA 1 (2 weeks)	48.9	57	273	216
MBA 1 (6 weeks)	34.1	41	196	154
MBA 1 (9 weeks)	31.1	36	176	140
MBA 2 (input)	51.3	49	299	251
MBA 2 (output)	34.6	29	201	172
Trelleborg (input)	35.9	35	206	171

Trelleborg (input leached)	30.1	46	148	101
Trelleborg (output)	25.2	44	124	80

Table 6 Chemical and biological oxygem demand in eluted waste samples. Prior to measurement the samples were filtrated with a cut-off of 0.45 µm

Material (stage in treatment)	COD [mg/l]	BOD_5 [mg/l]
MBA 1 (0 weeks)	11729	6105
MBA 1 (2 weeks)	7943	4216
MBA 1 (6 weeks)	875	47
MBA 1 (9 weeks)	586	48
MBA 2 (input)	2129	1016
MBA 2 (output)	993	206
Trelleborg (input)	120	13
Trelleborg (output)	106	4

Table 7 Humic substances in pre-treated waste samples measured at Technische Universität Hamurg-Harburg (TUHH) and at the Institute of Waste Management at the University of Natural resources and Applied Life Sciences in Vienna

Material (stage in treatment)	HA [g/kg DM] (TUHH)	Humic Acids [OD/g org DM]	Fulvic Acids [OD/g org DM]	Humic Acids [% org DM]
MBA 1 (0 weeks)	16	127	145	2.4
MBA 1 (2 weeks)	8	207	142	3.4
MBA 1 (6 weeks)	23	442	247	6.2
MBA 1 (9 weeks)	18	574	275	7.8
MBA 2 (input)	5	79	66	1.9
MBA 2 (output)	25	666	229	8.9
Trelleborg (input)	26	550	362	7.5
Trelleborg (input leached)	27	779	424	10.2
Trelleborg (output)	28	900	325	11.7

Table 8 Heavy metals in solid pre-treated waste samples

Material (stage in treatment)	Cd [mg/kg]	Cr [mg/kg]	Cu [mg/kg]	Pb [mg/kg]	Ni [mg/kg]	Zn [mg/kg]
MBA 1 (0 weeks)	1.56	791	527	322	369	655

MBA 1 (2 weeks)	12.5	878	1970	428	471	976
MBA 1 (6 weeks)	20.1	1285	1880	429	699	1610
MBA 1 (9 weeks)	18.4	1335	1100	530	736	2460
MBA 2 (input)	2.37	997	1860	386	554	632
MBA 2 (output)	1.62	1006	1061	194	444	2070
Trelleborg (input)	1.01	1005	189	230	414	1200
Trelleborg (input leached)	0.95	1185	333	564	625	907
Trelleborg (output)	1.12	1240	421	243	509	733

Table 9 Cadmium in eluted and filtrated waste samples

Material (stage in treatment)	< 0.45 µm [µg/l]	< 100 kDa [µg/l]	< 30 kDa [µg/l]	< 5 kDa [µg/l]
MBA 1 (0 weeks)	9.7	12	12	11
MBA 1 (2 weeks)	34	34	30	35
MBA 1 (6 weeks)	6.6	3.7	2.2	2
MBA 1 (9 weeks)	6.9	7	6.4	5.8
MBA 2 (input)	<0.5	1	1	1
MBA 2 (output)	<0.5	1	1	1
Trelleborg (input)	<0.5	<0.5	<0.5	<0.5
Trelleborg (output)	<0.5	<0.5	<0.5	<0.5

Table 10 Copper in eluted and filtrated waste samples

Material (stage in treatment)	< 0.45 µm [µg/l]	< 100 kDa [µg/l]	< 30 kDa [µg/l]	< 5 kDa [µg/l]
MBA 1 (0 weeks)	401	448	413	389
MBA 1 (2 weeks)	1340	1060	815	969
MBA 1 (6 weeks)	498	173	98	62
MBA 1 (9 weeks)	806	769	588	488
MBA 2 (input)	18	17	18	27
MBA 2 (output)	320	314	218	187
Trelleborg (input)	18	32	29	27
Trelleborg (output)	62	58	57	64

Table 11 Chromium in eluted and filtrated waste samples

Material (stage in treatment)	< 0.45 µm [µg/l]	< 100 kDa [µg/l]	< 30 kDa [µg/l]	< 5 kDa [µg/l]
MBA 1 (0 weeks)	118	98	103	103
MBA 1 (2 weeks)	72	67	58	68
MBA 1 (6 weeks)	40	34	24	20
MBA 1 (9 weeks)	26	25	23	26
MBA 2 (input)	60	64	56	51
MBA 2 (output)	34	39	24	24
Trelleborg (input)	10	10	10	10
Trelleborg (output)	10	10	10	10

Table 12 Nickel in eluted and filtrated waste samples

Material (stage in treatment)	< 0.45 µm [µg/l]	< 100 kDa [µg/l]	< 30 kDa [µg/l]	< 5 kDa [µg/l]
MBA 1 (0 weeks)	444	403	395	382
MBA 1 (2 weeks)	1270	1215	952	1125
MBA 1 (6 weeks)	377	355	261	213
MBA 1 (9 weeks)	191	181	164	164
MBA 2 (input)	133	139	133	132
MBA 2 (output)	131	162	127	118
Trelleborg (input)	72	75	69	58
Trelleborg (output)	56	56	59	69

Table 13. Lead in eluted and filtrated waste samples.

Material (stage in treatment)	< 0.45 µm [µg/l]	< 100 kDa [µg/l]	< 30 kDa [µg/l]	< 5 kDa [µg/l]
MBA 1 (0 weeks)	43	53	42	15
MBA 1 (2 weeks)	35	37	19	17
MBA 1 (6 weeks)	21	15	5	5
MBA 1 (9 weeks)	16	10	5	5
MBA 2 (input)	6	<5	<5	<5
MBA 2 (output)	6	6	9	<5
Trelleborg (input)	<5	<5	<5	<5

Trelleborg (output)	<5	<5	<5	<5

Table 14 Zinc in eluted and filtrated waste samples

Material (stage in treatment)	< 0.45 µm [µg/l]	< 100 kDa [µg/l]	< 30 kDa [µg/l]	< 5 kDa [µg/l]
MBA 1 (0 weeks)	13500	11700	11400	11200
MBA 1 (2 weeks)	6390	6185	5050	5875
MBA 1 (6 weeks)	667	608	326	291
MBA 1 (9 weeks)	692	702	620	581
MBA 2 (input)	152	159	159	164
MBA 2 (output)	1200	1897	1459	1390
Trelleborg (input)	269	340	245	380
Trelleborg (output)	268	171	202	258

Table 15 Nitrogen in pre-treated waste

Material (stage in treatment)	Total N [g/kg]	NH_4 [g/kg WM]
MBA 1 (0 weeks)	11	1.055
MBA 1 (2 weeks)	11	1.424
MBA 1 (6 weeks)	10.2	1.461
MBA 1 (9 weeks)	9.5	0.627
MBA 2 (input)	8.5	0.825
MBA 2 (output)	10	1.283
Trelleborg (input)	10.2	1.055
Trelleborg (input leached)	7.7	1.424
Trelleborg (output)	7.6	1.461

Table 16 Dissolved NH_4 in eluted and filtrated waste samples

Material (stage in treatment)	< 0.45 mm [µg/l]	< 100 kDa [µg/l]	< 30 kDa [µg/l]	< 5 kDa [µg/l]
MBA 1 (0 weeks)	0.14	0.15	0.14	0.14
MBA 1 (2 weeks)	0.22	0.20	0.21	0.20
MBA 1 (6 weeks)	0.10	0.11	0.10	0.10
MBA 1 (9 weeks)	0.02	0.02	0.02	0.02
MBA 2 (input)	0.08	0.08	0.09	0.06
MBA 2 (output)	0.07	0.07	0.08	0.07

Trelleborg (input)	0.14	Not measured	Not measured	0.13
Trelleborg (output)	<0.01	Not measured	Not measured	<0.01

Table 17 Respiration activity (RA$_4$) and gas formation potential (GP$_{21}$) in pre-treated waste samples

Material (stage in treatment)	**RA$_4$ [mg O$_2$/mg DM]**	**GP$_{21}$ [Nl/kg DM]**
MBA 1 (0 weeks)	79.42	248.37
MBA 1 (2 weeks)	38.98	187.59
MBA 1 (6 weeks)	6.28	17.82
MBA 1 (9 weeks)	4.14	6.46
MBA 2 (input)	30.56	111.78
MBA 2 (output)	4.22	15.01
Trelleborg (input)	4.58	None detected
Trelleborg (input leached)	3.34	None detected
Trelleborg (output)	0.51	None detected
Trelleborg (output leached)	0.80	Not measured

Table 18 Respiration activity in pre-treated waste samples measured to assess the impact of dry matter content on the activity

Material (stage in treatment)	**RA$_4$ [mg O$_2$/mg DM]**
Trelleborg (Output)	0.51
Trelleborg (Output)	0.37
Trelleborg (Input)	4.58
Trelleborg (Input)	4.72
Trelleborg (Output. second test)	0.58
Trelleborg (Output. second test)	0.71
Trelleborg (Output. second test)	0.54

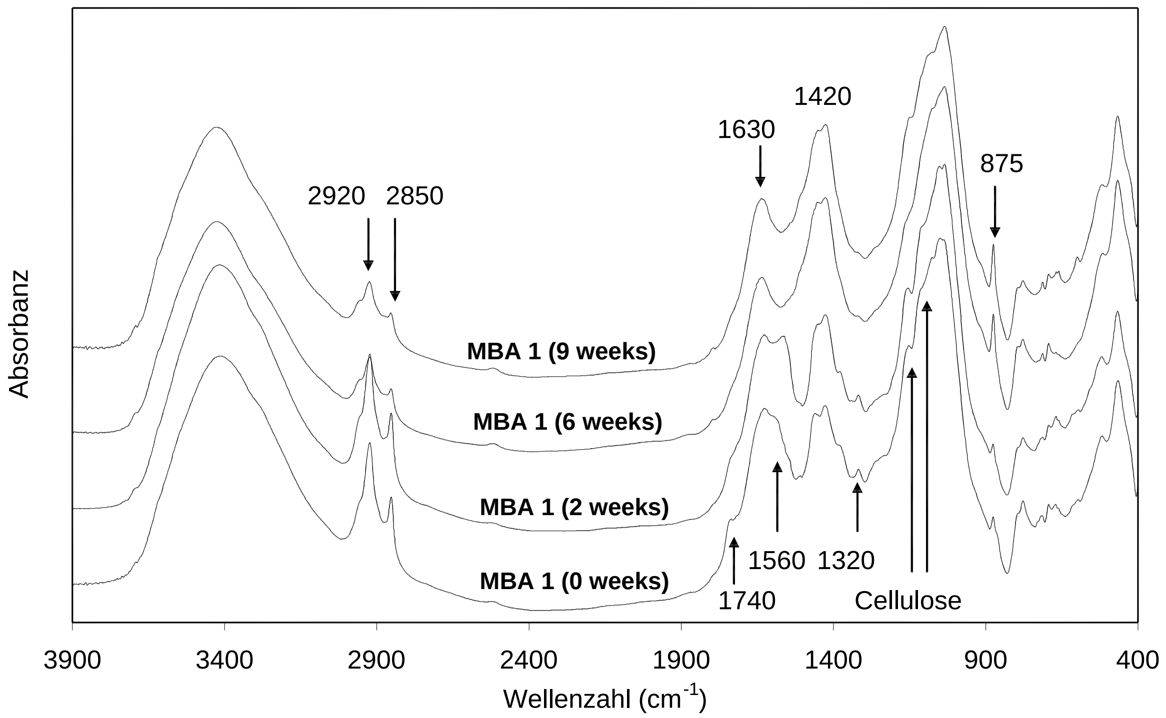

Figure 1 Absorbance in pre-treated waste material from MBA 1 measured with FT-IR spectroscopy

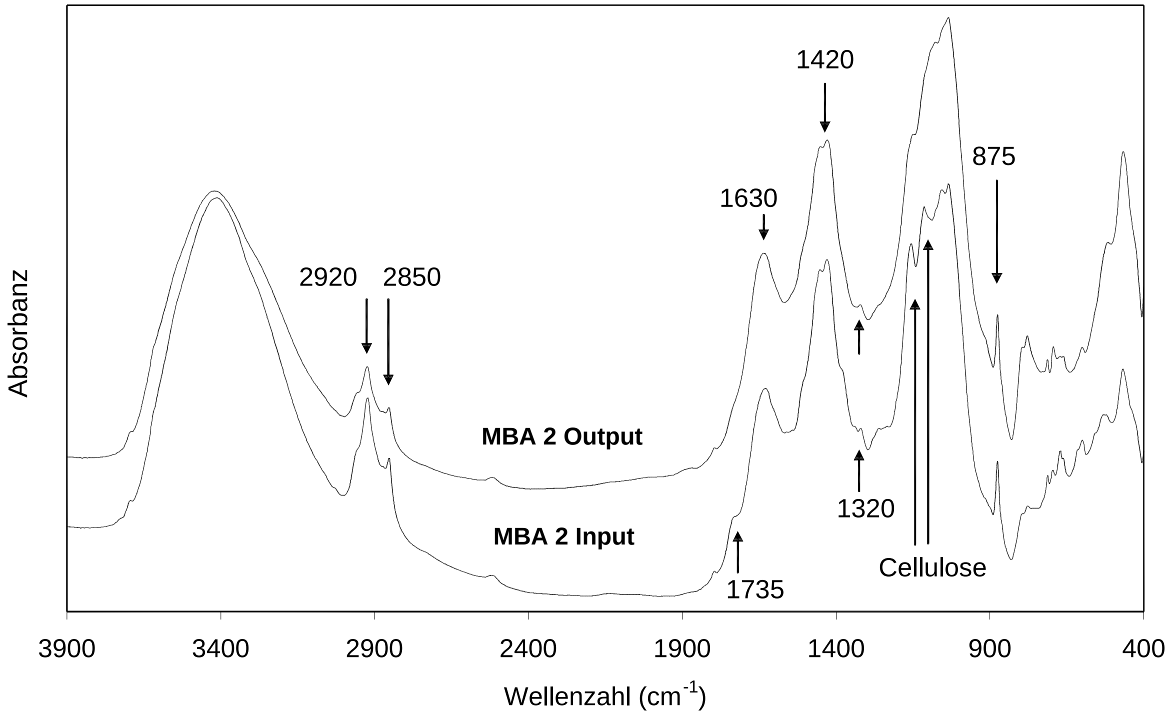

Figure 2 Absorbance in pre-treated waste material from MBA 2 measured with FT-IR spectroscopy

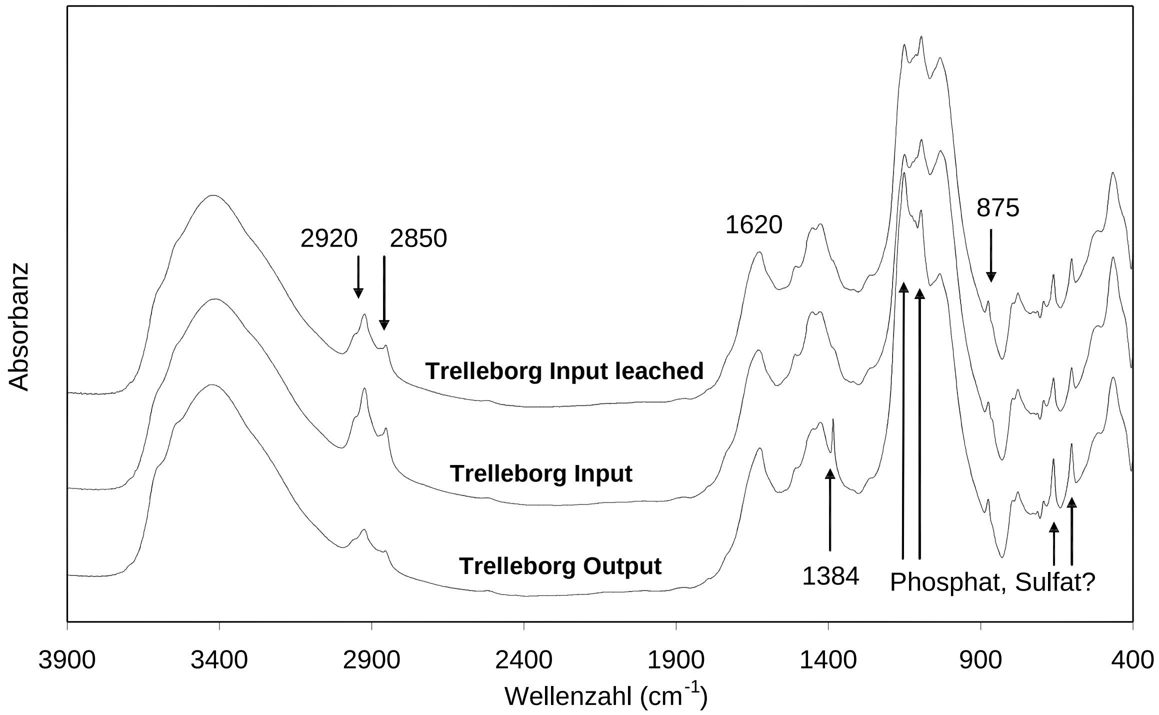

Figure 3 Absorbance in pre-treated waste material from Trelleborg measured with FT-IR spectroscopy

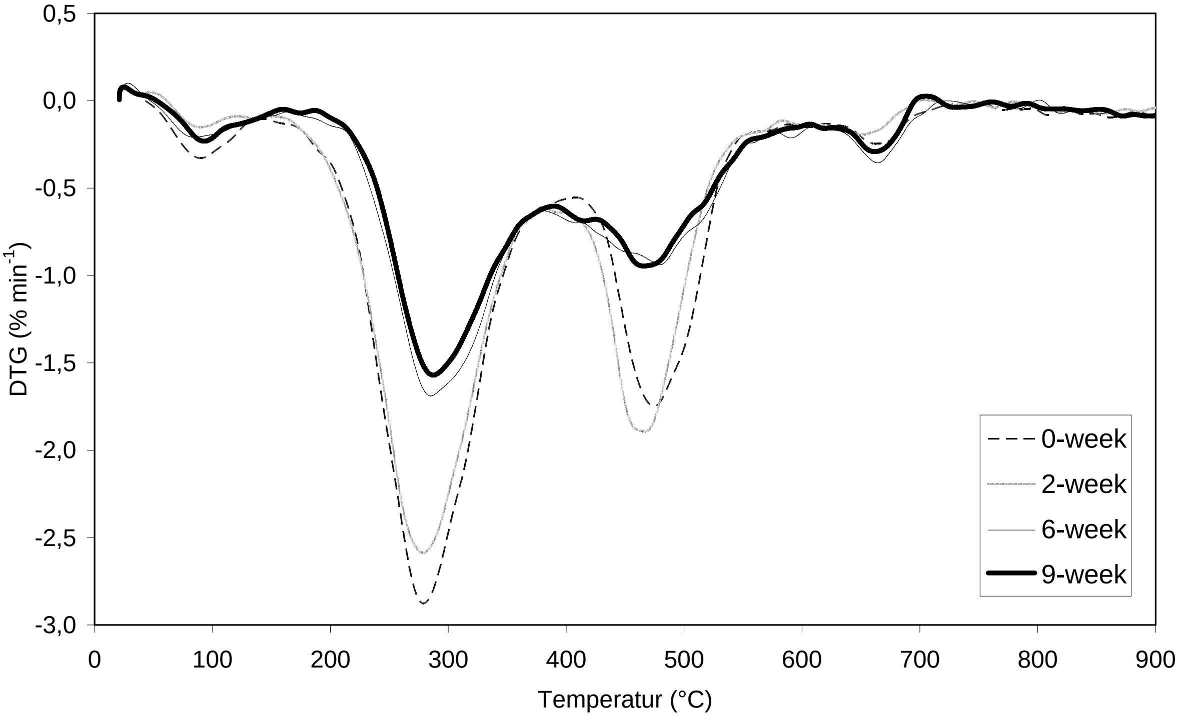

Figure 4 Thermogram of pre-treated waste (MBA 1) showing loss of mass per minute as the sample is burned with increasing temperature

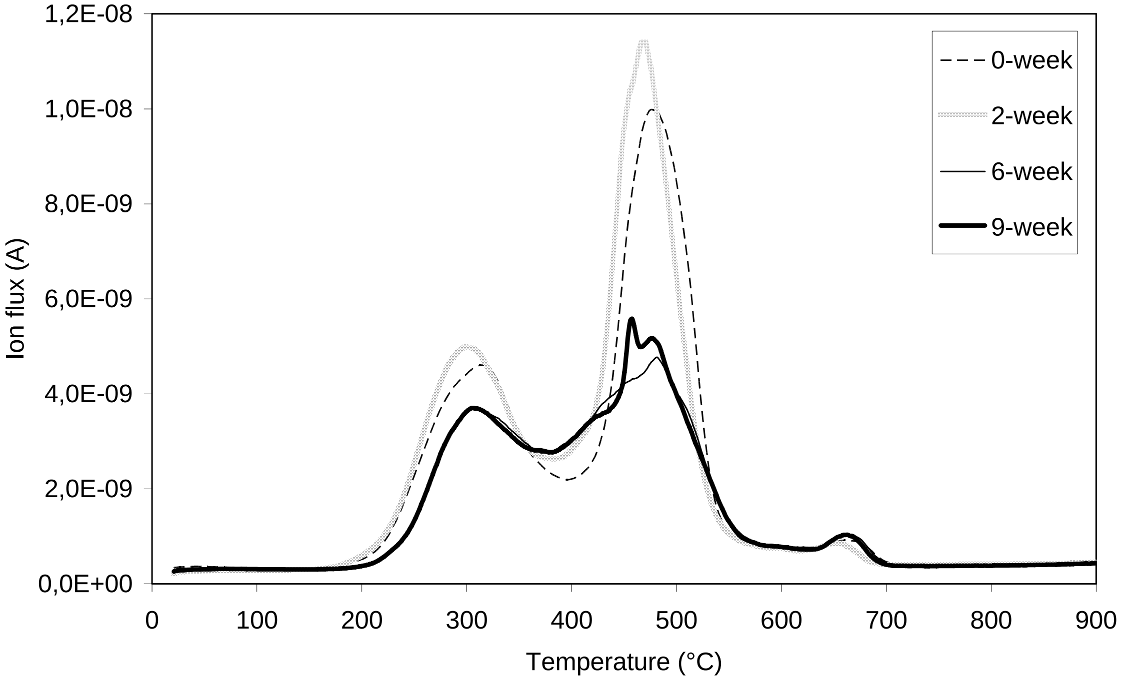

Figure 5. Ion flux of CO_2 in pre-treated waste (MBA 1) during combustion at increasing temperatures.

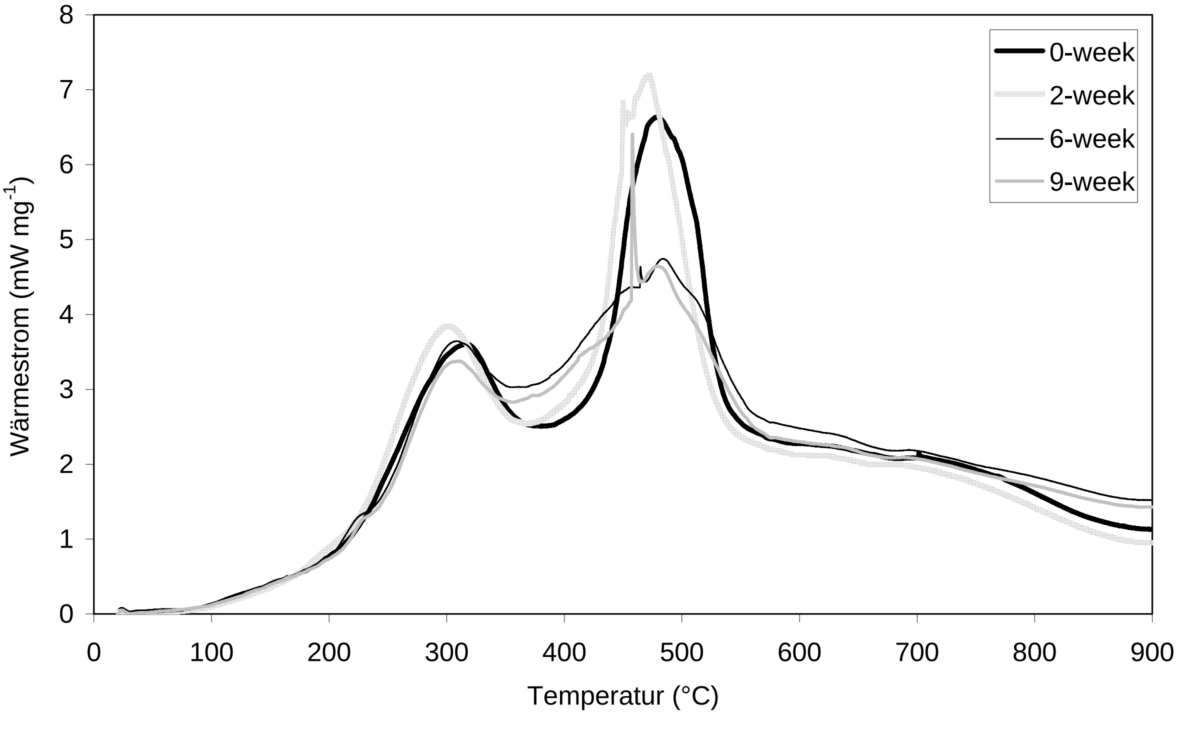

Figure 6. Heat flux in pre-treated waste (MBA 1) during combustion at increasing temperatures.

Appendix 3 Limit values

Table 1 Chosen landfill criteria for landfills in Germany. The criteria for eluate shuold be measured at a liquid to solid ratio of one to ten. Source: AbfAblV, annex 1

Parameter	**Landfill class I**	**Landfill class II**
Ignition loss	≤ 3% by weight	≤ 5% by weight
TOC	≤ 1% by weight	≤ 3% by weight
pH in eluate	5.5-13.0	5.5-13.0
Conductivity in eluate	≤ 10000 µS/cm	≤ 50000 µS/cm
TOC in eluate	≤ 20 mg/l	≤ 100 mg/l
Lead in eluate	≤ 0.2 mg/l	≤ 1 mg/l
Cadmium in eluate	≤ 0.05 mg/l	≤ 0.1 mg/l
Chromium-VI in eluate	≤ 0.05 mg/l	≤ 0.1 mg/l
Copper in eluate	≤ 1 mg/l	≤ 5 mg/l
Nickel in eluate	≤ 0.2 mg/l	≤ 1 mg/l
Zinc in eluate	≤ 2 mg/l	≤ 5 mg/l
Ammunium-N in eluate	≤ 4 mg/l	≤ 200 mg/l

Table 2 Chosen landfill criteria for landfills for mechanically and biologically pre-treated waste in Germany. The criteria for eluate shuold be measured at a liquid to solid ratio of one to ten. Source: AbfAblV, annex 2

Parameter	**Allocation criteria**
TOC	≤ 18% by weight
pH in eluate	5.5-13.0
Conductivity in eluate	≤ 50000 µS/cm
TOC in eluate	≤ 250 mg/l
Lead in eluate	≤ 1 mg/l
Cadmium in eluate	≤ 0.1 mg/l
Chromium-VI in eluate	≤ 0.1 mg/l
Copper in eluate	≤ 5 mg/l
Nickel in eluate	≤ 1 mg/l
Zinc in eluate	≤ 5 mg/l
Ammunium-N in eluate	≤ 200 mg/l
Respiration activity	≤ 5 mg/g
Gas formation potential	≤ 20 l/kg

Table 3 Chosen limit values for landfilling in Sweden. The criteria for eluate shuold be measured at a liquid to solid ratio of one to ten. Source: NFS 2004:10 §§22-23, §§29-30 and §§34-35

Parameter	**Inert waste**	**Non-haz. and haz. waste together**	**Hazardous waste**
Loss in ignition (LOI)	No limit	No limit	10% (TOC can be used instead)
TOC	3%	5%	6% (LOI can be used instead)
pH in eluate	No limit	>6	No limit
DOC in Leachate	500 mg/kg	800 mg/kg	1000 mg/kg
Lead in Leachate	0.5 mg/kg	10 mg/kg	50 mg/kg
Cadmium in leachate	0.04 mg/kg	1 mg/kg	5 mg/kg
Chromium in leachate	0.5 mg/kg	10 mg/kg	70 mg/kg
Copper in Leachate	2 mg/kg	50 mg/kg	100 mg/kg
Nickel in Leachate	0.4 mg/kg	10 mg/kg	40 mg/kg
Zinc in Leachate	4 mg/kg	50 mg/kg	50 mg/kg

Appendix 4 Bioreactor results

Table 1 Gas measurements in bioreactor 1

Time [days]	**N_2 [%]**	**O_2 [%]**	**CO_2 [%]**	**Air flow [l/h]**
0	78.2	20.5	1.3	6.5
1	78.4	20.6	1.0	6.5
2	78.4	20.8	0.8	6.5
5	78.6	20.5	0.9	6.5
6	78.6	20.5	1.0	6.5
7	78.5	20.6	0.9	6.5
8	78.2	21.1	0.7	6.5
9	78.4	20.9	0.8	6.5
12	78.4	21.0	0.6	6.5
13	78.3	21.0	0.6	6.5
14	78.4	21.0	0.7	5.5
15	78.6	20.3	1.1	3.5
16	78.7	19.6	1.7	0.7
19	78.8	18.4	2.8	0.7
20	78.9	18.1	3.0	0.7
21	78.9	18.1	3.1	0.7
22	77.4	20.5	2.2	1.1
23	78.1	21.0	0.8	3.3
26	78.2	21,0	0.8	3.3
29	78.2	21.1	0.7	3.3
33	78.2	20.9	0.9	2.8
36	78.2	21.0	0.7	2.5
48	78.1	21.3	0.7	2.5
54	78.2	21.2	0.7	2.5
57	78.2	21.1	0.7	2.5
61	78.0	21.3	0.7	2.5
117	78.2	21.2	0.7	2.5

Table 2 Gas measurements in bioreactor 2

Time [days]	N_2 [%]	O_2 [%]	CO_2 [%]	CH_4 [%]
0	82.6	2.6	14.8	0.0
1	80.4	14.	5.2	0.0
2	82.9	0.5	16.6	0.0
5	82.4	0.4	17.2	0.0
6	79.3	0.5	19.8	0.4
7	74.8	0.4	24.1	0.7
8	69.9	0.5	28.6	1.0
9	66.7	3.0	29.2	1.1
12	57.1	0.5	40.9	1.6
13	55.1	0.6	42.4	1.8
14	52.4	0.5	45.0	2.1
15	50.4	0.6	46.8	2.2
16	48.7	0.6	48.2	2.4
19	59.4	0.4	38.7	1.4
20	57.1	0.6	40.3	1.9
21	54.7	0.5	42.1	2.8
22	52.7	0.4	43.1	3.8
23	51.2	0.4	43.5	4.9
26	43.5	0.3	44.9	11.3
29	30.9	0.3	44.4	24.4
33	19.2	0.3	41.6	38.9
36	14.3	0.2	40.9	44.6
48	10.6	0.1	37.8	51.5
54	10.3	0.3	36.9	52.4
57	9.9	0.2	36.7	53.2
61	10.7	0.3	35.8	53.2
117	24.8	0.6	28.4	46.1

Table 3 Gas measurements in bioreactor 3

Time [days]	N_2 [%]	O_2 [%]	CO_2 [%]	CH_4 [%]
0	82.9	0.6	16.5	0.0
1	87.1	0.7	12.3	0.0
2	86.2	0.7	13.1	0.0
5	84.7	0.7	14.6	0.0
6	82.5	0.5	16.9	0.1
7	79.4	0.5	19.8	0.3
8	75.4	0.6	23.5	0.5
9	69.9	0.5	28.6	0.9
12	55.5	0.7	42.0	1.8
13	51.6	0.4	46.1	2.0
14	48.5	0.5	48.8	2.1
15	46.5	0.5	50.8	2.2
16	45.2	0.6	52.1	2.1
19	56.8	0.5	41.7	1.0
20	54.4	0.7	43.6	1.2
21	52.5	0.5	45.4	1.6
22	50.8	0.5	46.5	2.3
23	49.6	0.6	46.5	3.3
26	44.7	0.2	47.3	7.8
29	38.9	0.1	45.6	15.4
33	28.0	0.1	43.4	28.4
36	21.9	0.1	43.0	35.0
48	9.6	0.1	40.4	49.9
54	6.8	0.2	41.9	51.2
57	6.4	0.3	41.0	52.4
61	5.8	0.3	39.9	54.1
117	4.7	0.3	33.7	61.3

Table 4 Gas measurements in bioreactor 4

Time [days]	N_2 [%]	O_2 [%]	CO_2 [%]	CH_4 [%]
0	81.4	3.0	15.5	0.0
1	81.4	3.0	15.6	0.0
2	82.1	2.6	15.3	0.0
5	78.4	1.9	19.7	0.0
6	78.0	2.1	19.9	0.0
7	77.8	1.9	20.2	0.0
8	77.5	1.9	20.6	0.0
9	77.6	2.3	20.1	0.0
12	77.6	2.3	20.0	0.0
13	77.9	2.4	19.8	0.0
14	77.8	2.2	20.1	0.0
15	77.9	2.7	19.4	0.0
16	77.6	2.5	19.9	0.0
19	78.0	1.0	21.1	0.0
20	77.7	0.8	21.5	0.0
21	77.7	0.8	21.5	0.0
22	77.4	0.8	21.8	0.0
23	77.4	1.1	21.5	0.0
26	77.1	0.7	22.2	0.0
29	76.6	0.7	22.7	0.1
33	75.6	0.9	23.5	0.1
36	74.6	0.9	24.4	0.1
48	71.7	0.8	27.3	0.3
54	70.9	0.9	28.0	0.3
57	70.8	0.9	27.9	0.4
61	71.1	1.1	27.5	0.4
117	76.0	1.3	22.5	0.2

Table 5 Parameters in bioreactors simulating landfills after 16 days

Sample	pH	EC [mS/cm]	DOC [mg/l]	COD [mg/l]]	BOD_5 [mg/l]	BOD_5/ COD	Humic acids [mg/l]	NH4 [g/l]
Reactor 1	8.08	4.66	122	415	26	0.06	12.3	<0.01
Reactor 2	8.09	2.526	233	566	55	0.1	42.4	0.04
Reactor 3	8.09	2.67	235	625	56	0.09	52	0.04
Reactor 4	7.94	5.38	172	489	25	0.05	15.9	0.03

Table 6 Parameters in bioreactors simulating landfills after 16 days

Sample	Dry matter content [%]	Cd [µg/l]	Cr [µg/l]	Cu [µg/l]	Ni [µg/l]	Pb [µg/l]	Zn [µg/l]
Reactor 1	62	5	17	647	141	7	275
Reactor 2	54	2	27	209	414	35	192
Reactor 3	53	2	30	168	455	60	474
Reactor 4	66	6	20	759	178	11	437

Table 7 Parameters in the output material from bioreactors simulating landfills

Sample	Dry matter content [%]	RA_4 [mg O_2/g DM]	DOC [mg/l]
Reactor 1	63	1.1	94
Reactor 2	53	2.6	190
Reactor 3	56	3.4	220
Reactor 4	66	2.2	200

Table 8 Gas volumes in liters from bioreactors simulating landfills

Sample	Day 9	Day 16	Day 21	Day 35	Day 62	Day 117
Reactor 2	1.5	1.08	1.95	0.524	0.75	0.16
Reactor 3	2.2	1.58	1.05	0.428	4.55	6.65
Reactor 4	0.2	0.24	0.14	0.452	0.1	0.1

Appendix 5 FT-IR

The file that constitutes this appendix was received from the Institute of Waste Management at the University of Natural resources and Applied Life Sciences in Vienna.

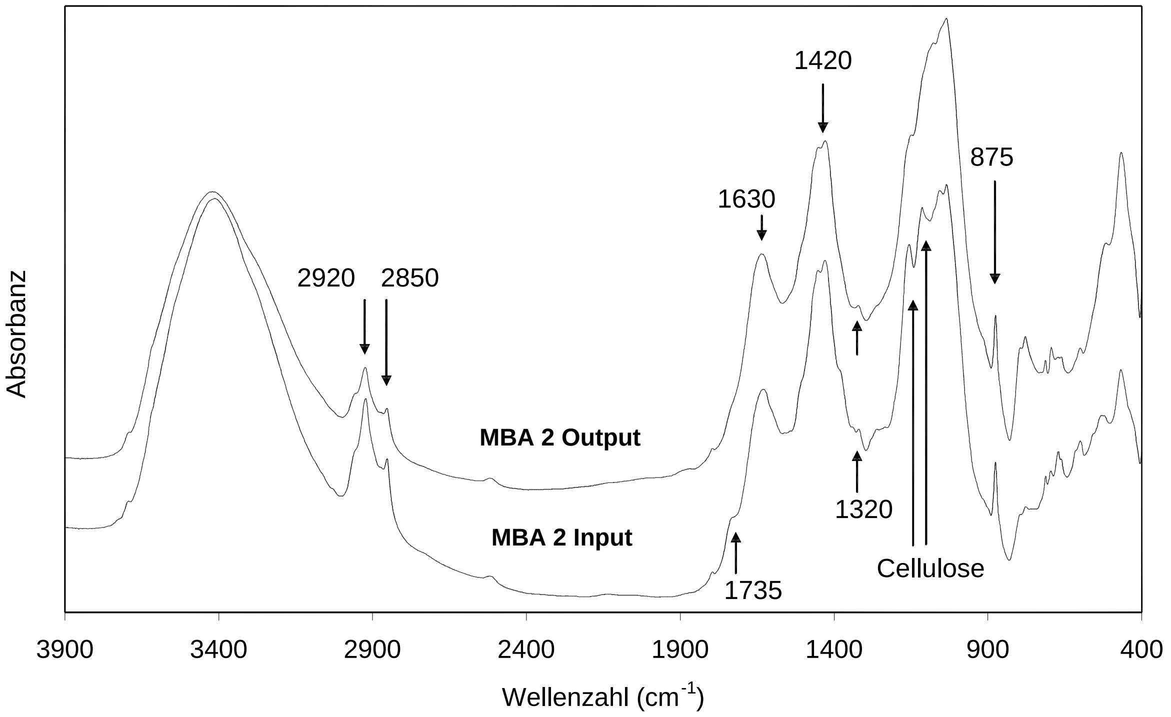

Abb. 1

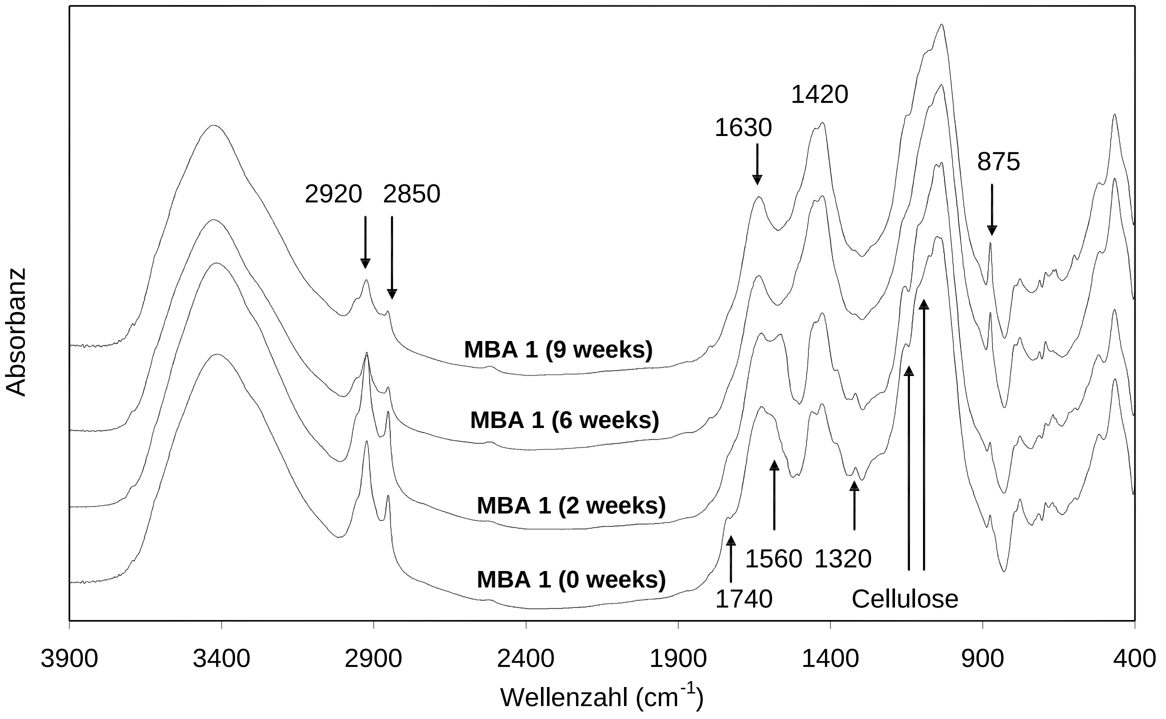

Abb. 2

Bei diesen Probenserie sieht man die Mineralisierung sehr schön: Abnahme der aliphatischen Methylenbanden, Verschwinden der Stoffwechselprodukte (1740, 1560, 1320 cm^{-1}), relative Zunahme von Carbonat (875 cm^{-1}, auch 1420 cm^{-1}).

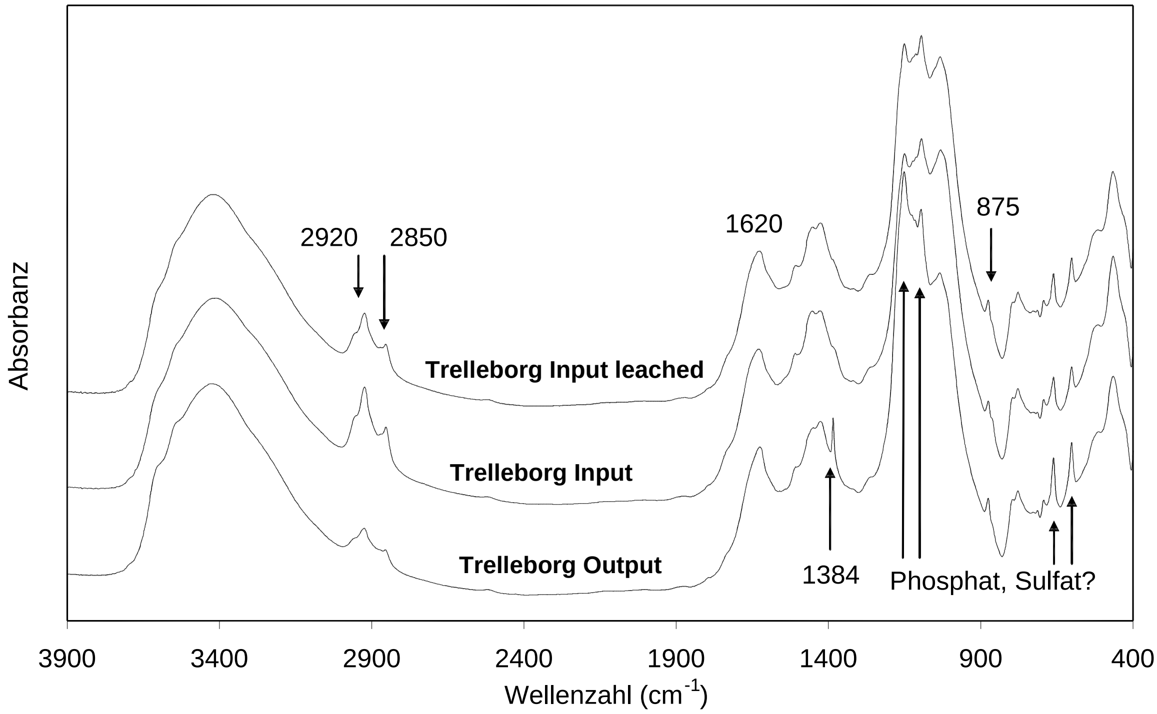

Abb. 3

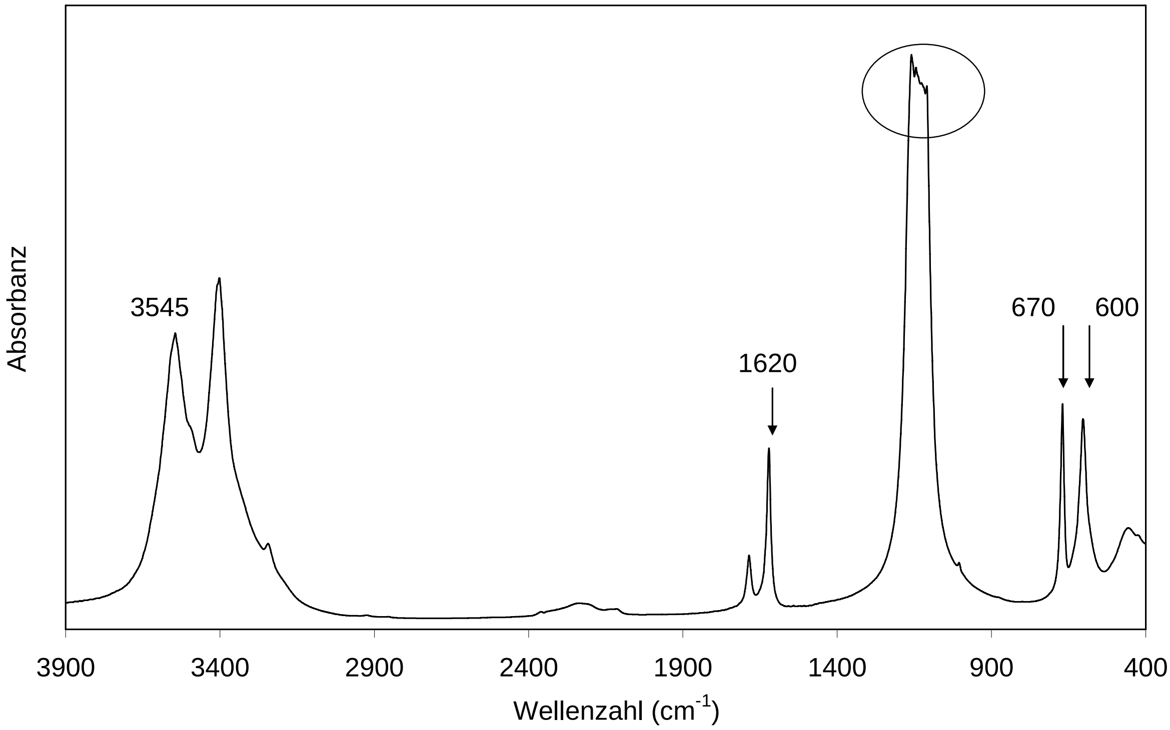

Abb. 4. Infrarotspektrum von Gipskarton

Anschließend ist eine kleine Tabelle (in Englisch) mit den wichtigsten funktionellen Gruppen und Komponenten dargestellt.

Ich habe das Spektrum von Gipskarton dazugestellt (Abb. 4). Bei den Proben SWE kommt auch noch Sulfat in Frage (müsste durch entsprechende Untersuchung, z.B. Zugabe von Sulfat bestätigt werden). Einige Banden (Schulter bei 3545 cm^{-1}, Banden bei 1620, 670, 600 cm^{-1} und die intensive Bande zwischen 1200 und 1000 cm^{-1}) weisen aber stark darauf hin (vielleicht habt Ihr eine Zusatzinformation über den Sulfatgehalt?). Allerdings gibt es bei dem letztgenannten Bereich auch eine Überschneidung mit Cellulose (Abb. 1 und 2), Phosphat und mit Tonmineralen (ca. 1030 cm^{-1}).

wavenumber (cm^{-1})	vibration	compound or functional group	references	development (weeks)	
				<10	>10
3400	O-H stretching	bonded and non-bonded hydroxyl groups and water	Socrates 2001		
2920	C-H stretching	methylene	Smith 1999	↓	→
2850	C-H stretching	methylene	Smith 1999	↓	→
2520		carbonate	Tseng et al. 1996	↑	→
1740-1720	C=O	aldehyde, ketone, carboxylic acids,esters	Ouatmane et al. 2000 Smith 1999, Naumann et al. 1996	↓	
1640	C=O C=C	amide I, carboxylates aromatic ring modes and alkenes	Haberhauer et al. 2000 Naumann et al. 1996 Smith 1999 Ouatmane *et al.* 2000 Smith 1999, Nanny and Ratasuk 2002 Chen and Inbar 1993	↓ ↑	→ →
1635	O-H bending	adsorbed water	Socrates 2001		
1560, 1546	N-H in plane	amides II	Ouatmane et al. 2000 Grube et al. 1999 Smith 1999 Naumann et al. 1996	↓	→
1515 - 1505	aromatic skeletal	lignin	Faix 1991 Ouatmane et al. 2000		
1425	COO^- stretch C-O stretch	carboxylic acids carbonate	Smith 1999 Hesse et al. 1995	↓ ↑	→ →
1384	N-O stretch	nitrate	Smidt et al. 2002 Zaccheo et al 2002 Smith 1999		↑↓
1320	C-N stretch	aromatic prim. and sec. amines	Smith 1999	↑↓	
1260-1240	C-O C-N	carboxylic acids amide III	Smith 1999	↓	
1250-900	C-O-C, C-O, C-O-P	Polysaccharides phosphodiesters	Grube et al. 1999, Tan 1993 Naumann et al. 1996	↓	→
1080		quartz			
1030	Si-O stretch Si-O-Si	Clay minerals silica	Madejova 2003 Smith 1999	↑	→
875	C-O out of plane	carbonate	Bosch Reig et al. 2002	↑	→

Appendix 6 Extraktion und Fraktionierung von Humin- und Fulvosäuren (modifizierte Methode nach Danneberg)

From Institute of Waste Management at the University of Natural resources and Applied Life Sciences in Vienna.

Probe:	luftgetrocknet, gemahlen
Aufbereitung:	Scheibenschwingmühle (Achateinsatz), 4 Min, bei 10.000 U/Min

Prinzip der Arbeitsmethode

Huminstoffe werden mit einer alkalischen Lösung extrahiert und nach ihrem unterschiedlichen Lösungsverhalten im sauren oder alkalischen Milieu fraktioniert. Das Material wird 4x an 4 aufeinanderfolgenden Tagen extrahiert, um eine möglichst vollständige Extraktion der Huminstoffe zu gewährleisten.

Die Humin- und Fulvosäurefraktionen werden photometrisch durch Messung der optischen Dichte bei 400 nm bestimmt. Wegen der besseren Vergleichbarkeit wird die optische Dichte auf 1 g organische Trockenmasse bezogen. Es ist daher notwendig, den Restwasser- und Organikgehalt der lufttrockenen Probe zu bestimmen.

Einige wichtige Hinweise:

Extrahierte Huminstoffe (besonders die Fulvosäurefraktion) reagieren mit Luftsauerstoff. Versuchen Sie daher, die Analysen möglichst zügig durchzuführen und verschließen Sie die Messkolben zwischen den einzelnen Analysenschritten (Huminstoffanalysen werden manchmal sogar unter Stickstoffatmosphäre und bei niederen Temperaturen durchgeführt!).

Drei Fraktionen werden bestimmt: Ausgangsextrakt (unfraktionierter Gesamtextrakt), Fulvosäuren (FS) und Huminsäuren (HS).

Chemikalien und Geräte

- Natriumpyrophosphat (NaPP) $Na_4P_2O_7*10\ H_2O$; 0,1 molare Extraktionslösung
- Konzentrierte HCl (37 %) zum Fällen der Huminsäuren
- 0,1 molare HCl zum Waschen des Huminsäureniederschlages
- NaOH (40 %)
- Pufferlösung:
  - Lösung A: 7,5 g Glycin + 5,8 g NaCl/l H_2O
  - Lösung B: 0,1 molare NaOH
  - Pufferlösung = Lösung A (310 ml) + Lösung B (190 ml)

Photometer zur Bestimmung der optischen Dichte bei 400 nm (OD)

Probenvorbereitung

Das Material wird luftgetrocknet, schonend (ohne Erhitzung des Materials) in einer Scheibenschwingmühle (Achatmühle) gemahlen und < 0,63 mm abgesiebt.

Extraktion

10,0 g des lufttrockenen, gemahlenen und gesiebten Materials werden in 250 ml Kunststoffflaschen eingewogen und mit 50 ml der 0,1 molaren NaPP - Lösung über Nacht auf einem Überkopfschüttler extrahiert. Bei Materialien, die viel Wasser aufnehmen, kann eine größere Menge an Extraktionsmittel notwendig sein.

Herstellung des Ausgangsextraktes

Der Extrakt wird durch Zentrifugation (15 Minuten, 5.000 Upm) vom festen Rückstand getrennt. Der Überstand wird noch einmal zentrifugiert (15 Minuten, 13.500 Upm). Austarieren der Zentrifugenbecher mit NaPP.

Für die zweite Extraktion werden die Rückstände aus der ersten und zweiten Zentrifugation mit 50 ml NaPP versetzt und wieder über Nacht auf dem Überkopfschüttler extrahiert. Die Durchführung der Analysen an den folgenden Tagen erfolgt wie am ersten Tag. Am 4. Tag werden die Zentrifugenrückstände verworfen.

Nach der Zentrifugation wird der Überstand (Extrakt) in 100 ml Messkolben (Glas) gegeben und mit deionisiertem (destilliertem) Wasser bis zur Marke aufgefüllt (= **Ausgangsextrakt**).

Bestimmung der Fulvosäurefraktion (FS)

25 ml des Ausgangsextraktes werden mit 0,3 ml 37 %iger HCl versetzt (0,5 ml, wenn der Carbonatgehalt hoch ist. Bei unbekannten Proben ist es günstig, den pH-Wert zu überprüfen. Er sollte bei 2 liegen, da die Huminsäuren nur bei niedrigem pH-Wert ausfallen). Lassen Sie die Lösung einige Minuten stehen, damit die Huminsäuren ausfallen können. Um sie von der Lösung abzutrennen, wird 5 Minuten bei 7.000 Upm zentrifugiert. Nach der Zentrifugation wird der Überstand in 50 ml Messkolben gefüllt. Der Niederschlag der ausgefällten Huminsäuren wird mit 0,1 molarer HCl gewaschen und noch einmal zentrifugiert (5 Minuten bei 7.000 Upm). (Das Waschen kann entfallen, wenn nur wenig Niederschlag vorhanden ist). Der Überstand wird zu dem ersten hinzugefügt, der Niederschlag (= ausgefällte Huminsäuren) wird verworfen. Da die optische Dichte bei pH-Wert = 10 bestimmt wird, werden 0,5 ml (0,6 ml) 40 %ige NaOH zugegeben. Mit der Pufferlösung wird auf 50 ml aufgefüllt. Dann erfolgt die photometrische Messung dieser Fraktion (= Fulvosäuren).

Bestimmung der Huminsäurefraktion

Die Huminsäurefraktion wird nur rechnerisch durch Subtraktion bestimmt: OD_{400} (HS) = OD_{400} (Ausgangsextrakt = FS+HS) minus OD_{400} (FS).

Bestimmung des nicht fraktionierten Gesamtextraktes

Der erste Gesamtextrakt (Ausgangsextrakt) ist in der Regel sehr dunkel (z.B. Biokompost) und muss daher vor der photometrischen Bestimmung verdünnt werden (mit der Pufferlösung). Der Verdünnungsgrad hängt von der Farbe des Gesamtextraktes ab. Für den Gesamtextrakt des ersten und zweiten Extraktionstages hat sich eine Verdünnung 1:25 bewährt. Später kann die Verdünnung 1:5 betragen. Aber Sie müssen einfach herausfinden, welche Verdünnung für die photometrische Messung ihres Materials günstig ist. Wichtig ist, dass diese Verdünnung bei der Berechnung der optischen Dichte des Gesamtextraktes berücksichtigt wird.

Literatur: Gerzabek M.H., Danneberg O., Kandeler E. Bestimmung des Humifizierungsgrades. In: *Bodenbiologische Arbeitsmethoden.* Schinner F., Öhlinger R., Kandeler E., Margesin R., Eds., Springer Verlag, 1993; 107-109.

Zur Quantifizierung muss eine Kalibration (für ganze Versuchsserien) oder eine gravimetrische Bestimmung der gefällten Huminsäuren gemacht werden.