

Doctoral Thesis

**In-depth analysis of degradation processes in old MSW landfills
under different oxygen and water regimes**

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Dissertation

**Detallierte Analyse der Abbauprozesse in alten Hausmülldeponien
unter verschiedenen Sauerstoff- und Wasserregimen**

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Father... father, the sleeper has awakened!

David Lynch

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Abstract

Despite global initiatives on prevention, reuse and recycling of waste, landfilling will remain a substantial part of solid waste management all around the world. This implies that the overall amount of waste “stored” at landfills will continuously increase, and thus proper management of landfill processes becomes even more important in future with respect to environmental protection. A reliable assessment of the future landfill emission potential is difficult, as it is influenced by various interdependent factors, such as waste composition, climatic conditions, presence and types of microorganism and landfill operation, of which many are hardly determinable. A possible way to decrease the future landfill emission potential is the method of in-situ aeration. By initiating aerobic degradation processes the microbial turnover rate and thus waste mineralization is accelerated. As this remediation method is comparably new, a long-term assessment of landfill emissions after applying in-situ aeration is yet to be accomplished.

It is therefore the goal of this work to provide the basis of an improved assessment of future landfill emissions by giving new insights in the aerobic degradation process. The conduction of a two year lab-scale municipal solid waste degradation experiment featuring a unique experimental design allowed for drawing previously unnoticed conclusions. By operating aerated landfill simulation reactors under differing water regimes, the influence of water on aerobic waste degradation could be examined. It was shown, that water addition only exerted a minor effect on the carbon balance in the experiment, but had a strong impact on the nitrogen balance. The TOC-pool was reduced by 35 % of the initial pool for all aerated treatments and the total Nitrogen

discharge amounted to 17-18 % of the initial N load present for the aerated dry reactors with water addition, and only to 7.5-13 % without.

As detailed information about the waste composition prior to landfill aeration represents a prerequisite for evaluating the overall impact of this measure, a multilinear statistical model has been established, that allows predicting solid waste composition (mainly water content, TOC, TN, NH₄-N, COD and BOD₅) based on a few key variables (loss on ignition, pH, electrical conductivity and Cl) measured. Finally, aerobic waste degradation was compared to the degradation of organic matter in a natural system (beech litter, *Fagus sylvatica* L.) and communalities were investigated. For instance, the decomposition constants ($k \sim 1 \text{ a}^{-1}$) and the specific amount of microbial biomass were similar for both systems. For the beech litter system drastic microbial changes were observed in the first few weeks, which might also be valid for the aerobic degradation of MSW.

The present work represents an important step towards a better understanding of the landfill metabolism during aerobic conditions and will thus contribute to a better design and operation of future landfill in-situ aeration projects.

Kurzfassung

Trotz globaler Initiativen zur Vermeidung, Wiederverwendung und Recycling wird das Deponieren von Abfällen global ein substantieller Anteil der Abfallwirtschaft bleiben. Das impliziert, dass die Gesamtmenge an in Deponien „eingelagerten“ Abfällen kontinuierlich zunehmen wird. Daher wird die Kontrolle und Steuerung von Deponieprozessen in Bezug auf den Umweltschutz an Bedeutung zunehmen. Eine belastbare Prognose des zukünftigen Emissionspotentials von Hausmülldeponien ist schwierig, da es von verschiedenen miteinander in Beziehung stehenden Faktoren wie der Abfallzusammensetzung, klimatischen Bedingungen, Präsenz und Art der vorhandenen Mikroorganismen, sowie von der Deponietechnik abhängt, die oft kaum quantifizierbar sind. Ein möglicher Weg, um das zukünftige Emissionspotential damit auch das von Deponien ausgehende Umweltrisiko zu reduzieren, ist die in-situ Belüftung. Durch Zufuhr von Sauerstoff werden aerobe Abbauvorgänge initiiert wodurch die mikrobiellen Umsatzraten und damit die Mineralisation der biologisch abbaubaren Substanz beschleunigt werden. Da diese Deponiesanierungsmethode vergleichsweise neu ist, fehlen Informationen über ihre Auswirkungen auf die Langzeit-Emissionen von Deponien.

Das Ziel dieser Arbeit ist es daher, Wissensgrundlagen für die Prognose zukünftiger Emissionen von belüfteten Deponien zu erarbeiten. Dazu wurden zweijährige Laborexperimente zur Erforschung des biologischen Abbaus von Abfall durchgeführt. Konkret wurden aerobe Deponiesimulationsreaktoren mit verschiedenen Bewässerungssystemen betrieben, anhand derer der Einfluss von Wasserzugabe auf den aeroben Abbau von Abfall untersucht werden konnte. Die Ergebnisse der Untersuchungen zeigten, dass Wasserzugabe die Kohlenstoffbilanz nur gering

beeinflusst, wohingegen die Stickstoff-Bilanz wesentlich vom Wasserhaushalt bestimmt wird. Der anfängliche TOC-Pool wurde etwa um 35 % bei allen belüfteten Reaktoren reduziert, während der gesamte Stickstoff-Austrag rund 17-18 % des anfänglichen Pools bei den aeroben bewässerten Reaktoren betrug, und 7 -13 % bei den trocken belüfteten.

Nachdem detaillierte Informationen über die Abfallzusammensetzung und die räumliche Verteilung der Abfallzusammensetzung eine wichtige Voraussetzung für die Konzeptionierung und auch für die Bewertung des Erfolgs von Deponiebelüftungsmaßnahmen darstellen, wurde ein multilineares statistisches Modell erstellt, das die Vorhersage wichtiger Abfallparameter (im Wesentlichen Wassergehalt, TOC, TN, NH₄-N, CSB und BSB₅) erlaubt. Dabei sind lediglich wenige Schlüsselparameter (Glühverlust, pH, elektrische Leitfähigkeit und Chlorid-Konzentration im Eluat) des Abfalls zu analysieren. Außerdem konnte die Vergleichbarkeit des aeroben Abbaus von Abfall mit dem aeroben Abbau in natürlichen Systemen gezeigt werden (Buchenstreu, *Fagus sylvatica* L.). So waren beispielsweise die Abbaukonstanten ($k \sim 1 \text{ a}^{-1}$) und die spezifische Menge an Mikroorganismen von einer vergleichbaren Größenordnung. Im Buchenlaub Experiment konnten bereits in den ersten Wochen drastische Veränderungen in der mikrobiellen Gemeinschaft festgestellt werden, was auch für den aeroben Abbau von Abfall gelten könnte.

Insgesamt stellt die vorliegende Arbeit einen wichtigen Schritt zum zunehmenden Verständnis vom Metabolismus einer Deponie unter aeroben Bedingungen dar, und wird daher zu einem verbesserten Design und damit Durchführung von zukünftigen Belüftungsprojekten beitragen.

Author's contribution to the submitted articles

Article #1

Using multivariate regression modeling for sampling and predicting chemical characteristics of mixed waste in old landfills

C Brandstätter, D Laner, R Prantl, J Fellner

For this article, I mainly coordinated the solid sampling campaign as well as the chemical analyses for landfill A. I also elaborated the statistical model.

Article #2

Carbon pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes

C Brandstätter, D Laner, J Fellner

To assess the carbon pools and flows for this article, I conducted and partly supervised the lab-scale experiment and coordinated the chemical analyses. I also performed the necessary data analyses and calculations.

Article #3

Nitrogen pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes (submitted)

C Brandstätter, D Laner, J Fellner

To assess the nitrogen pools and flows for this article, I conducted and partly supervised the lab-scale experiment and coordinated the chemical analyses. I also performed the necessary data analyses and calculations.

Article #4

A closeup study of early beech litter decomposition: potential drivers and microbial interactions on a changing substrate

C Brandstätter, K Keiblinger, W Wanek, S Zechmeister-Boltenstern

For this article I personally conducted most of the chemical and statistical analyses. The data analysis and interpretation was mainly conducted in collaboration with the Co-authors, particularly with Katharina Keiblinger.

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1. Introduction

On a global scale the environmental pressure induced by solid waste management is likely to increase, since municipal solid waste (MSW) generation is expected to rise in the coming years, coupled with the growing consumption of goods (Karak et al. 2012). The amount of MSW generated is estimated to nearly double from 1.3 billion tons in 2012 to 2.2 billion tons until 2025 (Hoornweg and Bhada-Tata 2012). Even if the exact figures are debatable, a booming trend for MSW generation on a global scale is expected without much doubt.

Landfilling remains a major disposal path even in the European Union (Mazzanti and Zoboli 2008), where the strategy of banning landfilling of untreated MSW is continuously pursued, starting with the introduction of the landfill directive 1999 (European Union, 1999). Nonetheless, even if landfilling is decreasing in Europe, only in Austria ~5,300 abandoned sites are registered at the moment, with an estimation of 7,400 existing old waste disposal sites (Valtl and Granzin, 2015). At least 300 Mm³ of MSW are deposited in old Austrian landfills larger than 25,000 m³ (Laner et al. 2008).

Globally, lower income countries are more dependent on direct landfilling because of the comparably low disposal costs (Hoornweg and Bhada-Tata 2012). Landfills mainly pose a threat to human health and environment, e. g. by the production of CH₄ or emitting a high NH₄ load in the landfill leachate (EI-Fadel et al. 1997), especially if the waste was not treated beforehand. Currently decreasing trends in landfilling are only observed in Europe and slightly in North America (mean/continent, Fig. 1).

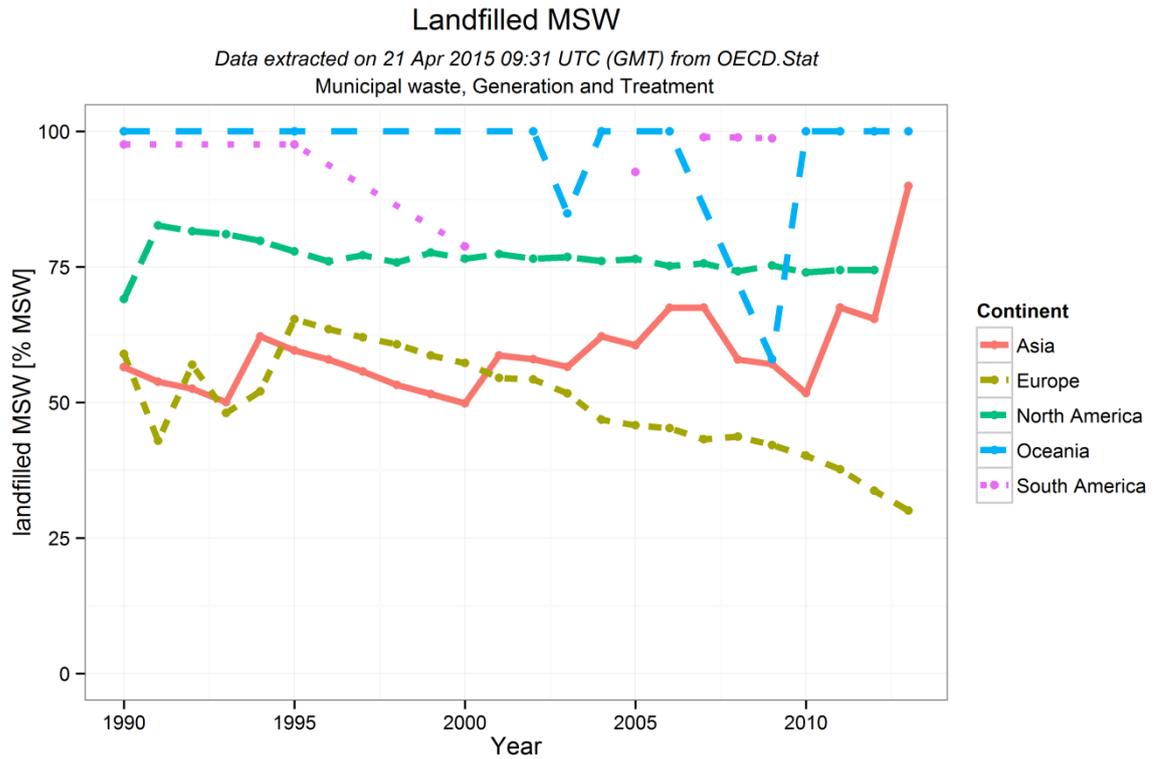


Fig. 1 Global trends in landfilling of MSW

The main purpose of waste treatment prior to landfilling is the reduction of the organic fraction in terms of mass and reactivity, leading to reduced landfill emissions and thus environmental hazards (Salati et al. 2013). Typical ways of waste treatment prior to landfilling would be either waste incineration, to achieve thorough mineralization of the MSW and energy recovery, or the mechanical biological treatment (MBT), where valuable waste fractions (e.g. metals, paper, plastics) are separated for recycling or thermal utilization and easily degradable organic fractions get reduced during the composting process. Nonetheless, these treatment ways, even if beneficial from an environmental point of view, are rarely feasible on a global scale mainly due to higher costs (Hoornweg and Bhada-Tata 2012) and most of their final products would require landfilling as well. In this thesis only landfills of untreated MSW are considered.

If none of the pretreatment options are feasible, or if the respective landfill contains untreated MSW, alternative ways of reducing gaseous landfill emissions could be applied during and after landfill deposition; be it the collection of landfill gas (LFG) for the purpose of energy usage (thermal or electrical), or biological or thermal methane oxidation for mitigation of greenhouse gas emissions. For mitigating environmental damage from landfill leachate, the leachate should be collected and treated on-site or off-site. However, due to the long lasting emission potential of landfill leachate (e.g. Belevi and Baccini 1989; Ehrig and Brinkmann 1998; Krümpelbeck 2000; Laner 2009; Laner et al. 2011) all of these measures would require sound, long term technical landfill management measures, thereby significantly increasing overall costs for landfilling and impairing the principle of sustainability.

Sustainable landfilling, as contradictory these two terms might seem, was defined as landfills releasing emissions up to a controlled and environmentally acceptable level, with waste residues not posing an unacceptable risk and the post closure care not being passed to future generations (Reinhart et al. 2002). This definition is similar to the concept of the **final storage**, where fluxes in the environment should not alter the latter in the long- and short-term (Baccini 1989; Brunner 1992).

For achieving all these goals, enhanced emission reduction measures are required, since MSW landfills containing preliminarily untreated MSW typically show high emission levels, even centuries after closure depending on the aftercare strategy (e.g. Ehrig and Brinkmann 1998; Krümpelbeck 2000; Laner et al. 2012).

A possible way to shorten the long lasting landfill aftercare period would be the method of in-situ aeration (Ritzkowski et al. 2006). During the process of in-situ aeration, air and consequently oxygen is injected into a landfill transforming the

anaerobic environment into an anoxic and subsequently aerobic state (Fig. 2). With the increasing application of landfill in-situ aeration projects an increasing amount of attention was paid to the aerobic degradation of old MSW (e.g. Chong et al. 2005; Cossu et al. 2003; Hrad et al. 2012; Prantl et al. 2006b; Ritzkowski et al. 2006). Various technical implementations are available, the most common being the low pressure in-situ aeration, where air is introduced at relatively low rates over a period of several years (Ritzkowski and Stegmann 2012). Aeration leads to increased microbial carbon turnover rates and mineralization of organic matter and thus is supposed to reduce the future landfill emission potential.

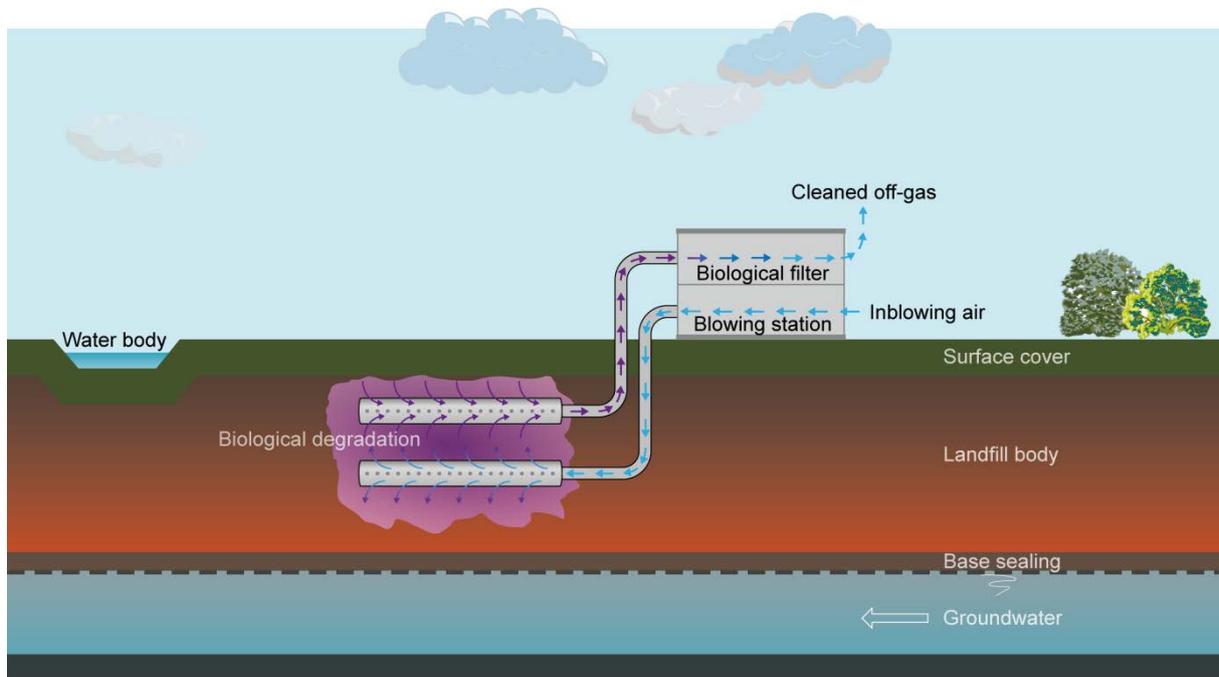


Fig. 2 Schematics of a typical in-situ aeration process

So far several lab scale aeration experiments on MSW have been conducted. Typically they were dedicated to gain a better understanding of waste degradation under aerobic conditions and were applied to predict the amount of biodegradable content in the waste material (Hrad et al. 2013; Prantl et al. 2006b; Ritzkowski et al.

2006), to consequently assess the degradation process in the field. Some of the experiments have been conducted also with regards to determining a rational time point for termination of the air injection (Ritzkowski and Stegmann 2012).

A central issue arising from performing lab-scale experiments on aerobic waste degradation is the transferability of the observed results. Even if the biodegradable content of the waste material can be assessed, the question how representative such results are for the field situation remains crucial. For properly upscaling laboratory results to the field scale, certain knowledge of the composition of the landfilled waste body is indispensable for a reliable comparison (Fellner et al. 2009; Kylefors et al. 2003). Until now, the necessary assessment of the solid waste composition of landfills prior the application of in-situ aeration is rarely performed since waste sampling and analyzing involves high costs. In providing a statistical tool for assessing the solid body composition of landfilled waste, these costs could be reduced, as well as increasing the information gain.

In addition, even though numerous lab-scale in-situ aeration studies were conducted (e.g. Borglin et al. 2004; Hrad et al. 2013; Prantl et al. 2006b; Ritzkowski et al. 2006, Shao et al. 2008), until now comprehensive balances from aeration experiments were largely missing. This is especially unfavorable, as during the aerobic degradation of landfilled MSW previously bound substances, inaccessible for microbes under anaerobic conditions, are released. For a comprehensive assessment of the remediation method of in-situ aeration such balances are required as a basis to evaluate the long-term behavior of the waste material after aeration.

2. Objectives

The main goal of this thesis is to improve the **performance evaluation** of in-situ aeration measures. Done in a comprehensive way, this involves mainly discussing the scalability of the experimental laboratory results and providing an improved understanding of the in-situ aeration process including main conditions (e.g. presence and mobility of water) influencing the performance of in-situ aeration.

The following questions are addressed in this thesis:

- i) In view of landfill heterogeneity, how can the knowledge about the **spatial distribution of organic substances** in the landfill be increased to improve the transformation of lab-scale results to the field scale?
- ii) What are the net **carbon-** and **nitrogen-** losses during the in-situ aeration process in relation to the anaerobic default landfill scenario and what are the long-term implications from these balances?
- iii) How can the aerobic degradation process of MSW be related to microbial degradation occurring in **natural ecosystems**?

These questions are addressed on the basis of four peer reviewed articles (Appendix).

To provide an outline for the following thesis, first the available literature concerning the composition of the solid landfill body and the process of in-situ aeration will be presented (Chapter 3). In the following chapters the performed analyses and experiments are described (Chapter 4) and their results are discussed (Chapter 5). Finally, the references (Chapter 7) as well as the peer reviewed articles themselves (Appendix I-IV) are included.

3. Scientific Background

3.1. Solid composition of MSW landfills

The assessment of solid body composition of landfills is important both for landfill owners and municipalities, since landfill emissions derive from the solid body (Barlaz et al. 1990). However, Chiampo et al. (1996) stated that only limited data on landfill waste characteristics are available and this still applies nearly 20 years later. Even though it is well known that the (gaseous) emission potential of MSW highly depends on its composition (Jokela et al. 2002), and though landfill exploration came progressively into focus with the increasing application of landfill mining projects in recent years (Quaghebeur et al. 2013), chemical solid body analyses of full scale MSW landfills were conducted relatively rarely in a scientific context (Attal et al. 1992; Baldwin et al. 1998; Bogner 1990; Hogland et al. 2004; Hull et al. 2005; Mor et al. 2006b; Östman et al. 2006; Sormunen et al. 2008; Suflita et al. 1992; Xiaoli et al. 2007).

Generally it has to be distinguished, whether only the types of waste fraction were analyzed or the chemical composition was assessed (see Table 1), as both types of analysis are subsumed under “characterization”. It becomes obvious, that the scientific understanding of the solid body composition of a MSW landfill is formed by only few exploration studies. The generalized information deducted from these studies is also listed in Table 1. The significance of the organic fraction was pointed out in each of these studies, and selected findings are presented in the following paragraphs.

Table 1 “Recently” Published MSW landfill studies focusing on solid landfill characterization

Source	Landfill size	Samples taken	Waste fractions assessed	Measurements conducted	Reasoning behind study	Selected highlights
Unit		[#]	Yes/No			
Bogner 1990	3 landfills, details not indicated (USA)	3*6	Yes	BMP, TS, VS, CNP, K, Fe, Zn, Ni, extractable bases	Assessing the adaptability of BMP assays from water treatment for landfills	Moisture decreases variability in gas production. Actual landfill practice hinders gas production.
Attal et al. 1992	Still active landfill; 30 ha (France)	2*6	Yes	BMP, VFA, CH ₄ , CO ₂ , H ₂ , N ₂	Finding a reliable sampling procedure for determining the methane potential	Variable sample sizes found in the literature. Landfills show strata in relation to landfill age (found in a still active landfill).
Sufita et al. 1992	67 mio m ³ (USA)	47	Yes	T, selected enzymes, BMP, SO ₄ , Cellulose, Lignin, VS, degradable organic matter	Decrease the knowledge gap in microbial landfill processes in a multidisciplinary way	Moisture influences biodegradation. Sulphate might originate from gypsum. Cellulose/Lignin ratio is a promising indicator for microbial decomposition. Much readily degradable organic material was found to be persistent in landfills. Viruses and protozoa most likely do not survive under landfill conditions.
Chiampo et al. 1996	500.000 t (test cell, Italy)	2 x 8-10	Yes	TS, VS, COD, TOC, RedOx	Testing sampling procedures	Spatial variation of the analyzed variables in depth.
Baldwin et al. 1998	data not given; 3 landfills with different climatic conditions (USA)	44 * 7 + 4*20	Yes	Mass loss, Moisture content, Holocellulose, Lignin	Explore the degradability of differing sample substrate qualities in a litterbag study	Cellulose main degradation constituent and negatively affected by lignin. Moisture content increased decomposition. Temperature was crucial for decomposition.
Hogland et al. 2004	2 landfills, size not accurately indicated (Sweden)	Not indicated	Yes	Grain size distribution, TS, ash, caloric value, CNHP, Metal contents	Assessing landfill mining potential	Caloric value sufficient for incineration.
Hull et al. 2005	22 ha, max. height 40 m (USA)	98	Yes	TS, VS, T, Grain size distribution, High heating value, Bulk density,	Investigating potential for site reclamation.	High amount of fine fraction in older landfills, Waste age was predictive for TS, VS.
Mor et al. 2006	3.6 mio m ³ (India)	25	Yes	TS, pH, Volatile solids, Loi, K, P, S, CHNS	Estimating gas potential	LFG models robust; high potential in Indian landfills.
Östman et al. 2007	7.5 mio m ³ (Sweden)	58	No	pH, RedOx, Loi, TC and TN, K, Na, S, P, various metals	Future metal release	Two distinguished vertical layers in the landfill; metals associated with organics
Xiaoli et al. 2007	~ 24 mio m ³ (China)	16	No	pH, TOC, CEC, organic matter, TN, COD, NH ₃ -N, Ni, Cr, Cd, Zn, Pb, Cu	Investigating the abundance and mobility of heavy metals	Heavy metal concentrations were highest in residues. Metal concentrations were not dependent on waste age. Heavy metal concentrations were high, but remained stable under ordinary landfill conditions.
Sormunen et al. 2008	2 landfills: 7.4 mio and 3.2 mio m ³ (Finland)	44 + 24	Yes	TS, VS, TN, pH, BMP, NH ₄ , COD	Feasibility study of landfill sampling in view of future monitoring	Results from one landfill not easily transferable to another.

Notes: BMP biochemical methane potential, CEC cation exchange capacity, COD chemical oxygen demand, Loi loss on ignition, T Temperature, TOC total organic carbon, TS total solids (inverse to water content), VS volatile solids.

In each of these studies landfill heterogeneity was discussed and the sampling procedures and sizes also largely differed. Difficulties in transferring the results of one landfill sampling to another site were reported (Sormunen et al. 2008), even if both landfills were situated in the same country. This was explained by differences in sample and landfill size, on-site pre-treatment in one landfill and differing landfill age.

Low moisture content was considered to limit biodegradation (Bogner 1990; Suflita et al. 1992) and methanogenesis could be related to moisture content (Suflita et al. 1992). Samples were placed in lysimeters for determining the gas potential and samples with higher moisture content showed higher gas production. Generally vertical, but not horizontal trends could be observed for selected variables, like TN or volatile solids in certain landfills (Chiampo et al. 1996; Sormunen et al. 2008), as well as for $\text{NH}_4\text{-N}$ and Cl (Hogland et al. 2004), or for water content (Östman et al. 2006), temperature (Hull et al. 2005) and CH_4 -content (Attal et al. 1992). The observation of these depth gradients could be either attributed to differing waste age in different horizontal layers in a still active site (Attal et al. 1992), or possibly to leachate transport downwards along the gravity gradient. The trends in depth however were not consistent; roughly, younger landfills seem to have the regions of high reactivity on top (e.g. Attal et al. 1992; Chiampo et al. 1996) and older landfills on the bottom (Sormunen et al. 2008).

A more common approach to characterizing landfills with respect to its current and future emission potential is the investigation of the landfill leachate. Numerous landfill leachate characterization studies were conducted (e.g. Baun and Christensen 2004; Berge et al. 2006; Brad et al. 2008; Butt and Oduyemi 2003; Chian and DeWalle 1977; Chu et al. 1994; Eggen et al. 2010; Fellner et al. 2009; Matejczyk et al. 2011;

Mor et al. 2006a; Öman and Junestedt 2008). Sampling of leachate is, in comparison to solid waste sampling, much easier to conduct and landfill leachate is also of high interest because of the threat of groundwater pollution (e.g. Eggen et al., 2010). Like solids, landfill leachate shows high variation depending on its origin as well (Kjeldsen et al. 2002), as for instance younger landfill areas typically manifest leachate with higher concentrations of organic carbon. Spatial variability was even considered an important issue for gaseous N₂O production of mechanical biological treatment (MBT) waste (Harborth et al. 2013).

Furthermore, other than chemical analyses for exploring landfills or investigating leachate emission paths, electrical resistivity/conductivity measurements were applied (e.g. Bernstone and Dahlin 1997; Frohlich et al. 1996). For assessing the quality of the organic fraction, thermography (Belghazal et al. 2013) or FTIR-spectroscopy (Smidt and Meissl 2007; Wu et al. 2011) was applied.

To summarize, in addition to the omnipresent *internal* landfill heterogeneity *external* factors play a crucial role in assessing different landfills: landfill age, technical management, climatic conditions, waste origin, etc. Also the reasons for the various landfill studies differed as did the sampling protocols. The amount of scientific landfill exploration studies is small and many questions remain unresolved. The following commonalities can be observed: cellulose was identified as the main substrate for anaerobic biodegradation, temperature and moisture influenced degradation, and vertical trends are typically observed. The need of knowledge about spatial distribution was pointed out for various reasons: either for predicting gas production, potential landfill mining or future emission potential.

Since the gas production is of major interest for landfill owners, it is not surprising that anaerobic degradation processes in landfills were well studied and numerous degradation models were applied (e.g. Barlaz et al. 1990; Eklund et al. 1998; Farquhar and Rovers 1973; Gioannis et al. 2009; Kamalan et al. 2011; Mahar et al. 2014; Munawar 2014).

Even if the prediction of LFG production and extraction is still not entirely accurate, landfill research mainly focused on anaerobic waste degradation. Studying aerobic degradation is nonetheless well established in the scientific field of waste management, but studies mainly were conducted for the composting process, usually performed in MBT plants (Gómez et al. 2006; Mulbry and Ahn 2014; Sole-Mauri et al. 2007; Zhang et al. 2012), or for methane oxidation processes occurring mainly at the landfill boundaries (Boeckx and Van Cleemput 1996; Bogner et al. 1997; Kightley et al. 1995; Scheutz et al. 2009; Whalen et al. 1990), and to a lesser degree for in-situ aeration, as will be presented in the next chapter.

3.2. In-situ aeration of MSW landfills

In-situ aeration of landfills was introduced as a measure to mainly reduce CH₄-emissions after the production rates decrease below economically feasible utilization (Heyer et al. 1999). Also cost-saving benefits by shortening the landfill aftercare phase were anticipated mainly due to lower nitrogen concentrations in the leachate. Introducing aerobic conditions for enhanced biodegradation was reported to be beneficial in various ways (Ritzkowski et al. 2006), leading to increased carbon discharge in terms of CO₂ instead of CH₄ and reduced leachate concentrations in terms of organic compounds and NH₄-N. Again, the cost saving potential and the relevance of determining an end point for in-situ aeration measures were mentioned.

The method of in-situ aeration was also discussed as a means for reducing landfill gas emissions and leading to CO₂-eq. savings. This saving potential mainly increases with landfill size and depending on the technical control of gaseous landfill emissions (Ritzkowski and Stegmann 2010). More directly related to the degradation process, Prantl et al. (2006b) focused on the stabilization of organic matter during in-situ aeration. The amount of cellulose and TOC was reduced, whereas the amount of humic acids was increased by applying in-situ aeration. Also short-term reactivity was reduced after in-situ aeration in comparison to anaerobic batches and NH₄-N leachate concentrations were lowered upon aeration start. Nonetheless, after aeration of 275 days and a following anaerobic phase an increase in NH₄-N was indicated, but to a lower level. The following chapter will be divided into technical application and process-oriented considerations.

3.2.1. Reported full-scale application of in-situ aeration

Concerning the technical application, different methods of aeration were presented (Ritzkowski and Stegmann 2012). The main differences in various aeration applications arise from the applied pressure; high pressure aeration is targeted to short term amendments in terms of CH₄- and CO₂-removal as well as removal of odorous gaseous compounds mainly for the implementation of landfill mining projects. Low-pressure aeration concepts on the other hand are utilized for increased biological degradation. Different concepts of low pressure aeration are available, like active aeration and off-gas extraction, or passive aeration. Noteworthy is also the semi-aerobic way of in-situ aeration, mainly applied in Japan. In principle, here air is introduced from the bottom utilizing temperature differences through biodegradation for convective transport (Matsufuji 2004), leading in total to higher amounts of gaseous and reduced amounts of leachate emissions. Most full scale European in-

situ aeration projects were targeting enhanced biodegradation and were performed in Germany (Ritzkowski and Stegmann 2012). For the UK, the application of in-situ aeration was at least considered (Rich et al. 2008). In Austria, three landfill aeration projects are currently ongoing; two of them are situated in lower Austria and one in Tyrol.

Data from full-scale applications are increasingly presented in the literature with differing focus and implications (Beatty et al. 2009; Chung et al. 2015; Hrad et al. 2013; Ko et al. 2013; Öncü et al. 2012; Prantl et al. 2006c; Raga and Cossu 2014; Ritzkowski 2005). The application of aerobic ex-situ leachate treatment could reduce $\text{NH}_4\text{-N}$ loadings and induce denitrification to some extent with an observation period of 200-500 days (Chung et al. 2015). Practical difficulties arising from the spatial distribution of air were considered a major drawback of field-scale in-situ aeration (Hrad et al. 2013). The authors also pointed out difficulties with the transferability of lab-scale experiments to the field situation. Difficulties with the air distribution also were reported for a landfill situated in Florida, USA (Ko et al. 2013).

A temperature increase during an intermittent in-situ aeration as well as again difficulties with air distribution were reported shortly after aeration start for a rather big German landfill, closed only in 2009 (Öncü et al. 2012). An increase in electrical conductivity and pH also could be observed in the rather short observation period. In the work of Prantl et al. (2006c), various potential benefits of in-situ aeration are described based on lab-scale data and rather short-term field observations. Difficulties with air introduction were also reported for an Italian landfill (Raga and Cossu 2014), but also some waste stabilization in terms of the (aerobic) respiration index after 4 days (RI_4) could be achieved for solid parameters based on 30 samples

after roughly one year of operation, which was less pronounced for the leachate. For the leachate an increase in the temperature was noticed upon aeration, as well as a decrease in NH_4 (Ritzkowski 2005). However, a solid sampling campaign in the field after 22 months of aeration could not detect a significant decrease in solid contents, like TOC or Loi , but a decrease in RI_4 and residual gas producing potential after 21 days (GP_{21}) based on a smaller amount of samples ($n=6$ for the aeration start and $n=3$ after 22 months).

Finally, from a practical point of view, difficulties in the application mainly arise from controlling the increasing temperature as a result from aerobic degradation, how to achieve a proper air-distribution especially under unfavorable conditions, like a high amount of water in the waste body (Rich et al. 2008) and proper off-gas treatment (Ritzkowski and Stegmann 2012). In Austria, a technical guideline (in German) was created to support municipalities as well as practitioners dealing with the practical implementation of in-situ aeration (Prantl et al. 2006a). The long-term experiences after the application of in-situ aeration are limited. One rare Canadian study (Beatty et al. 2009), of an old aerobic landfill indicates that CH_4 could be eliminated. However, it has to be taken into account that in this case 2/3 of MSW is water saturated and the aeration measures are still ongoing, even if with a low-cost system.

3.2.2. Reported biochemical processes during in-situ aeration

While for natural ecosystems the discussion of carbon quality is well established, the discussion of diminishing carbon quality during the in-situ aeration process is missing, with few exceptions (Prantl et al. 2006b; Tesar et al. 2007). This lack of discussion concerning carbon quality derives presumably from the difficulties arising

with the determination of **waste stability**, a phrase omnipresent but hardly directly addressed in waste management (e.g. Kelly et al. 2006).

The majority of in-situ aeration studies were focused on developments related to nitrogen species during in-situ aeration as will be shown in the following paragraphs.

A review of different nitrogen removal options for bioreactor landfills presented different in-situ aeration techniques (Berge et al. 2005), while aerobic treatments were subdivided in three distinctive categories. The three presented categories were strictly *aerobic bioreactor landfills* (“classical” in-situ aeration), *hybrid bioreactor landfills* with a combination of aerobic and anaerobic conditions and *facultative bioreactor landfills* with an external leachate aeration system.

The decrease of $\text{NH}_4\text{-N}$ in the leachate upon aeration start was observed in numerous studies (e.g. Giannis et al. 2008; Hao et al. 2010; Heyer et al. 1999; Heyer et al. 2005; Prantl et al. 2006b; Ritzkowski et al. 2006; Sekman et al. 2011; Shao et al. 2008).

Ammonia reduction was reported to exceeded nitrification rates (Hao et al. 2010; Shao et al. 2008) and the decrease in $\text{NH}_4\text{-N}$ was commonly contributed to occurring nitrification/denitrification processes (Onay and Pohland 1998; Prantl et al. 2006b; Ritzkowski et al. 2006; Sekman et al. 2011; Shao et al. 2008; Sun et al. 2015). However, these processes were rarely quantified (Berge et al. 2007) but usually only mentioned on a qualitative base. The formation of N_2O was also discussed in a few articles (Berge et al. 2006; He et al. 2011; Wang et al. 2014). It could be shown that N_2O formation was increased with a low COD/TN ratio and also the concentration of O_2 influenced its formation (He et al. 2011; Wang et al. 2014).

The influence of O₂ and temperature on denitrification was investigated (Berge et al. 2007), with the conclusion that higher temperatures decrease denitrification efficiency and that leachate NH₄-N is reduced in a broad temperature range upon aeration. This is of high relevance, since aerobic degradation was reported to increase waste temperatures (Ritzkowski et al. 2006). Finally, the understanding of different transformation pathways of nitrogen was identified as a major necessity for successfully applying nitrogen removal technologies (Berge et al. 2005).

While numerous studies target the microbial community for the composting process or the methane oxidation (e.g. Amir et al. 2008; Herrmann and Shann 1997; Klamer and Bååth 1998; Ryckeboer et al. 2003; Scheutz et al. 2009), or the anaerobic landfill/anaerobic digesters (Matejczyk et al. 2011; McDonald et al. 2012; Nayak et al. 2009; Staley et al. 2011a; Staley et al. 2011b), so far only few studies target the alteration of the microbial community during the aeration of landfilled MSW (Mellendorf et al. 2010). It could be shown that upon aeration, total microbial biomass increased (assessed with phospholipid fatty acid (PLFA) analysis) with an increase mainly in gram+ bacteria. The group of methanogenic Archaea was totally diminished in the aerobic case.

Even if an increasing amount of studies on in-situ aeration are getting published, the following question concerning in-situ aeration remains poorly addressed: how will the waste body react upon termination of the aeration in terms of nitrogen and carbon emissions? So far, complete carbon and nitrogen balances including the solid body during in-situ aeration were not presented for various reasons. Such balances of in-situ aeration are presented here for the first time, even if only for a laboratory experiment. The carbon balance could be closed, while for the nitrogen balance the

amount of denitrification was calculated (see 0 and Appendix III). The presented carbon and nitrogen balances will help assessing the future emission potential of aerated landfills and support the decision making process for determining if in-situ aeration is a feasible solution on a certain landfill site.

4. Performed analyses and experiments

4.1. Investigating the solid body of landfills

It is evident, that for predicting future emissions emerging from old landfill sites, their solid waste composition should be known at least to some extent. Solid sampling in landfills is a costly procedure, as excavators are required and a high amount of samples needs to be taken for reliable information due to the heterogeneous nature of landfilled waste (see Fig. 3).

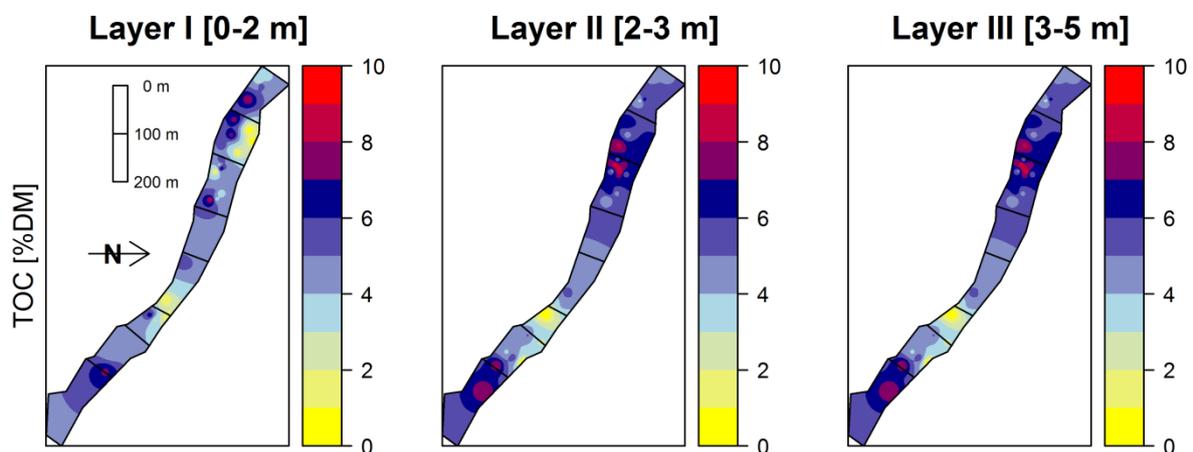


Fig. 3 Visualization of landfill heterogeneity - TOC

Typically, for the risk assessment of old sites numerous variables are measured, with only few of them being meaningful for gaining a representative picture of the overall landfill body. To increase the benefit of solid waste sampling campaigns, a statistical tool was developed (Appendix I).

In brief, twelve (chemical) response variables could be predicted by applying a multilinear regression model based on four predictor variables. The predictor variables were selected in view both of costs and to achieve maximal informative

value from the model application. The selected predictor variables were loss on ignition (Loi), the pH-value, the electrical conductivity (EC) and the chloride content after elution. From the twelve predicted variables, eight were representing solid contents and four were measured after elution.

The model was created (or calibrated) on landfill data measured for this thesis and applied on data from another Austrian landfill. To improve the prediction, a set of fully measured samples (=all the twelve response variables) was necessary, to adjust the model outcome to the new site. The model result was adjusted likewise with linear regression, however only with one predictor and one response variable (predicted vs. measured) for the model adjustment. Depending on the variation of the response variable, a differing amount of fully measured samples (all twelve response variables) was needed. This necessary amount was determined for each response variable via bootstrapping (or rather cross-validating, since here bootstrapping was performed without sample replication).

4.2. Carbon and nitrogen during in-situ aeration – a lab-scale experiment

The essential reasoning behind performing the here presented lab-scale in-situ aeration experiments was to provide a reference value for determining the time point of terminating an ongoing in-situ remediation project of an old landfill near the city of Schwechat in Lower Austria. This was done, since it was highly recommended in the scientific literature to compare the in-situ aeration measures in the field with a laboratory experiment (e.g. Ritzkowski et al. 2006). The main difficulties for the evaluation of in-situ aeration projects arise from assessing the remaining biological activity potential; standardized biological tests for either anaerobic gas production or

aerobic activity end after a short duration of either 21 or 4 days. It becomes evident, that for assessing long-term emissions this is not sufficient, thus laboratory experiments with a longer duration are needed.

The applied experimental setup consisted of six landfill simulation reactors (LSR), with three pairs each kept under differing conditions (treatments). Four reactors were kept aerobic, where for one pair water was added and the other pair was operated without water addition (aerated wet and aerated dry, as seen in Fig. 4).



Fig. 4 Landfill simulation reactors (aerated dry treatment)

As a reference, one pair of reactors was kept under anaerobic conditions (anaerobic). The decision of not adding water was made due to the observed dryness of the sampled landfill material. This was referred to the climatic conditions of the landfill

(e.g., precipitation of 550 mm a⁻¹ and potential evapotranspiration of 650 mm/a). Furthermore, during the ongoing full scale in-situ aeration no water was added either. Roughly 80 kg of waste material were placed in each reactor and the operation temperature was around 36 °C, controlled with a thermostat.

For carbon balancing the amount of initial TOC was used as the starting point. The following carbon species were measured for creating the carbon balance: TOC in solid and leachate, CO₂ and CH₄ in the gas phase. For the nitrogen balance the starting point was the initial total nitrogen (TN) content. The following nitrogen species were measured: TN in the solid, NH₃ and N₂O in the off-gas, and NO₃, NH₄ and TN in the leachate (Table 1). The contribution of denitrification (formation of N₂) was assessed indirectly via mass balancing.

Table 2 Carbon and nitrogen measurements of the laboratory experiment used for balancing

	Carbon	Nitrogen	Microbial Activity
Solids	TOC, Lignin _s , Cellulose	TN, NH ₄ [*] , NO ₃ [*]	RI ₄ , GP ₂₁ , BOD ₅ [*]
Leachate	TOC, BOD ₅	NH ₄ , NO ₃ , TN	BOD ₅
Gas	CO ₂ , CH ₄	NH ₃ , N ₂ O	-

Notes: Microbial activity measurements were provided for discussing substrate quality. The stars indicate measurement after elution. BOD₅ biological oxygen demand after 5 days, GP₂₁ residual gas producing potential after 21 days, Lignin_s acid soluble lignin fraction, TN total nitrogen, TOC total organic carbon, RI₄ respiration index after 4 days.

Further details on the experimental setup can be found in 0 and Appendix III.

4.3. Aerobic degradation of a natural substrate

Investigating rather complex biological landfill processes makes it obvious that the field of solid waste management can benefit from inputs outside of the typical waste management world. Mechanistic studies of degradation processes in landfills are blurred by high substrate diversity and highly heterogeneous conditions in the landfill bioreactor. Studying the substrate change under rather homogenous conditions can increase the understanding for the more complex case. In the present case, a short term biological degradation experiment performed with beech litter (Fig. 5) was conducted to study similar biological processes occurring during landfill in-situ aeration.



Fig. 5 Beech litter decomposition – a microcosm

A microbial degradation experiment of air dried beech (*Fagus sylvatica* L.) litter collected from four different Austrian forests was conducted over eight weeks. Various elemental and water contents, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ after elution, microbial biomass after chloroform-fumigation extraction, CO_2 -production, mass loss and phospholipid fatty acids (PLFA) were analyzed. Most of the analyses were performed weekly upon destructive sampling of the respective microcosms containing roughly 40 g of shredded litter material. The material used in this degradation experiment was comparably homogenous. Additional information on the experimental setup and measurements can be found in 0.

5. Results and Discussion

5.1. The spatial distribution of chemical properties of solid wastes

Solid landfill characterization studies were rarely performed although the significance of knowledge about the spatial distribution of mainly “organics” with respect to future emissions became already common knowledge. With the created multilinear model a prediction of significant variables related to the future emission potential of landfills becomes possible. One of the predicted variables, the TOC content in the solids, also plays a dominant role in the assessment of the ongoing in-situ aeration measure.

It could be shown, that in measuring four relatively cheap predictor variables, the prediction of at least eight response variables led to reasonably good results, after some adaption procedures this applies even for samples from another landfill. The predictor variables were Loi , pH, electrical conductivity and Cl after elution and the response variables were the solid variables water content (WC), TOC, TN, Cr, Cu, Pb, Zn, RI_4 , and the variables NH_4-N , SO_4 , COD and BOD_5 after elution. The model worked rather well for WC, TOC, TN, NH_4-N , COD and BOD_5 (Fig. 6, Appendix I).

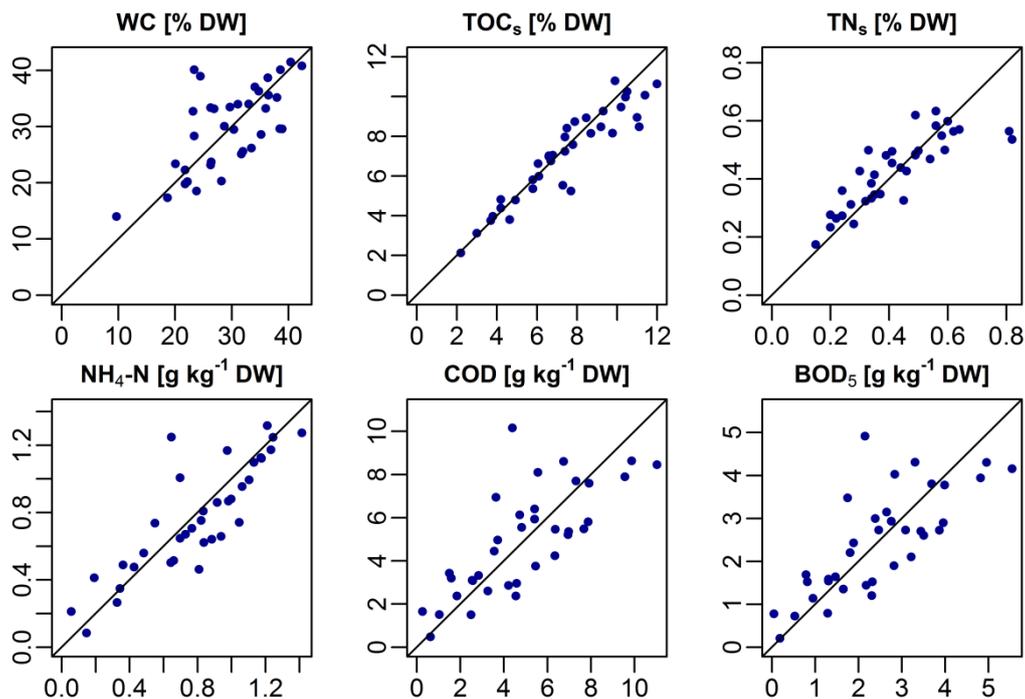


Fig. 6 Selected multilinear model results

Notes: The model was applied on another landfill after model adaption based on 10 random fully measured data points. DW dry weight, BOD₅ biological oxygen demand after 5 days, COD chemical oxygen demand, WC water content

Unfortunately, none of the measured variables was a reliable predictor for the aerobic short-term reactivity of the material (R_{I_4}).

The reliable assessment of the TOC-content on a full scale landfill might improve the assessment of in-situ aeration, however with certain drawbacks. It is quite obvious that certain waste fractions as paper or plastics also show a high TOC-content but are not or only very slowly biodegradable. The relationship of BOD₅ and COD however could give an indication for waste stabilization and both variables could be predicted in a reliable way, even for another MSW landfill. Finally, the created tool allows gaining improved information about the spatial distribution of the quality of solids in a landfill. The assessment of future landfill remediation projects can be

facilitated with its application. The application of this statistical tool could also be highly beneficial for municipal authorities or landfill operators. By decreasing the costs due to less chemically analyzed parameters, the spatial information gained could be increased with an increased amount of samples taken.

5.2. *Lab-scale in-situ aeration*

Even though many lab-scale in-situ aeration experiments have been conducted, no complete (closed) carbon balance was published so far. It could be shown, that during the degradation of old MSW in the presented laboratory setup, carbon losses via leachate were only of minor significance, making up less than 0.5 % of the initial TOC. One of the main outcomes of this study was that the gaseous C-losses were of similar quantity for all aerated treatments, regardless of water addition. This observation could be related to a differing macroscopic structure of the material from the different treatments and to microbial water production occurring during aerobic degradation, which sustained almost constant water content throughout the experimental period of 2 years even for the dry treatment. The observed respiration activity was higher in the beginning for the dry aerated reactors with a more pronounced decrease later on (see Fig. 7).

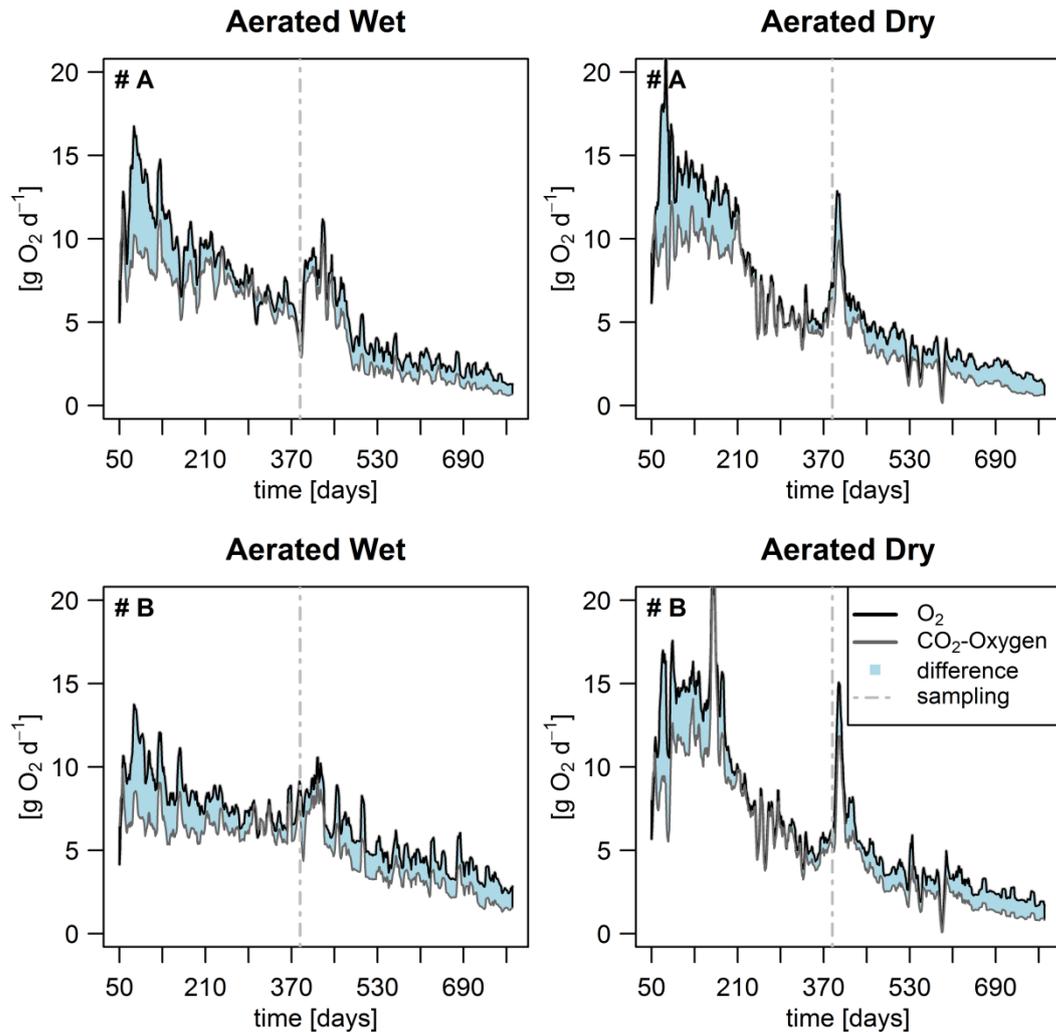


Fig. 7 CO₂ Respiration and O₂ consumption (both given in g O₂ per day)

The overall C-discharge was roughly twice as high for the aerated treatments in comparison to the anaerobic treatment. Concerning the carbon quality, all treatments showed a profound exhaustion of cellulose during the experiment. For the aerated treatments another observation could be made: an increase in acid soluble lignin indicated an increased stabilization of the organic fraction during the aeration experiment, which did not occur for the anaerobic LSR.

In combination with the short-term activity tests the presented results indicate an exhaustion of the anaerobically degradable C-pool during aerobic degradation, but

not vice versa. This would to some extent confirm the applicability of the MBT process prior to landfilling: the methane producing potential should be largely reduced after intensified aerobic degradation.

Unlike for the presented carbon investigations, it could be shown that water addition and leachate recirculation had a profound influence on the nitrogen balance during in-situ aeration. Gaseous nitrogen discharge was strongly increased for the aerated wet treatment (~17 % initial TN) in comparison to the dry aerated treatment (6-12 % initial TN). Thus denitrification was enhanced in the aerated wet treatment leading to improved nitrogen removal. Denitrification was spatially assigned mainly to the leachate reservoir, as for a long time span of the experiment NO_3 was not detectable in the leachate, especially when its biological oxygen demand was relatively high (Fig. 8).

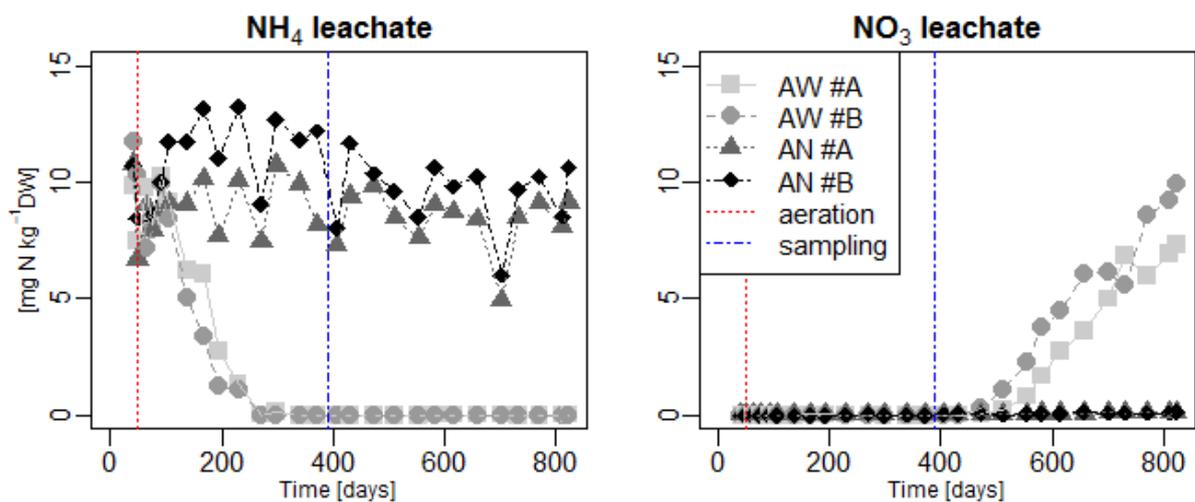


Fig. 8 Ammonium and nitrate concentrations in the leachate

This could mean that the readily accessible carbon sources were used for denitrification and are thus responsible for low NO_3 -concentrations. Denitrification also was enhanced by the experimental setup; there was a certain time span

between a recirculation and a sampling event (at least 16 h) to provide consistent sampling conditions and especially sample amounts, as the water percolation after recirculation would have taken an unknown timespan. Via recirculation the leachate might have collected degradable carbon utilizable for denitrification. In the presented leachate development there was a gap, where $\text{NO}_3\text{-N}$ as well as biological oxygen demand was near zero (see Appendix III). In this phase denitrification activity might still have exceeded nitrification, up until later stages, when the readily accessible carbon sources were vastly depleted.

For all treatments, the nitrogen largely remained in the waste solid body, ranging from 78 over 86 to 90 % initial TN for the aerated wet, anaerobic and aerated dry treatments respectively. The anaerobic treatment exceeded the aerated dry treatment in nitrogen removal via leachate which generally was highest for the anaerobic treatment. Laughing gas emissions were highest for the aerated dry treatments, while their overall contribution to the nitrogen balance was rather insignificant (below 0.1 % TN initial for all treatments).

To summarize, the carbon transformation was less affected by the water addition than the nitrogen transformation. However, both total organic carbon and total nitrogen mostly remained in the solid body of the incubated material. The crucial question yet to be answered will be, how this reduced remaining C and N pool will react after the termination of in-situ aeration?

Concerning the carbon degradation there are hints that methanogenesis is greatly reduced after in-situ aeration, as biological short-term tests did not reveal remaining activity (0). Nonetheless, it could be clearly shown that the degraded C-pool under aerobic conditions greatly exceeded the C-pool accessible under anaerobic

conditions. This makes the direct comparison between aerobic and anaerobic C-discharge rather meaningless.

The remaining nitrogen (TN) seemed to be largely incorporated chemically in the remaining organic matter after the aerobic treatment. This could be proven with the application of leaching tests: standard leaching tests with distilled water showed that $\text{NH}_4\text{-N}$ decreased strongly after in-situ aeration. Another series of leaching tests applying a strong osmotic solution (3 M KCl) applied on material taken at the end of the experiment showed that roughly twice the amount of leachable ammonium by aqueous elution is still ionically bound with the substrate. Thus the amount of nitrogen associated via cation exchange must have become comparably small.

The combination of these results points into the direction that long-term stability after in-situ aeration might be achieved, but it should be noted that so far a long-term assessment based on observations is lacking. The chemical quality of the remaining organics is still largely unknown and the presented results were obtained via a laboratory experiment. Thus the comparison of these findings with field-scale measures remains a challenge. For comparing field and laboratory results, it is essential to get hold of a common denominator. For the presented case only the specific C-discharge remains as an option, as leachate emissions were not measured in the field. The stress lies on the term **specific**, since establishing reliable solid landfill inventories requires much more effort than the measurement of process parameters like gaseous O_2 - or CO_2 -concentrations.

Especially landfills lacking proper management or old landfill sites commonly show a lack of information about their waste distribution. Knowing the spatial distribution and quality of MSW, especially of the organic fraction, is important for assessing the

benefits of remediation methods as in-situ aeration, and also for predicting future landfill emissions. This is principally precarious if the landfill not only consisted of MSW but other waste types as well.

5.3. Aerobic degradation in natural ecosystems in relation to in-situ aeration

Leaf litter decomposition is considered to be mainly controlled by climatic factors, which govern temperature and litter moisture content, and by litter chemistry (Prescott 2010). The ratio of “lignin”:nitrogen was identified as the most consistent predictor for future decay rates, and increased nitrogen may lead rather to humification than to degradation of the underlying organic substrate. Slower degrading fractions of litter were reported to accumulate with higher nitrogen supply, and the faster-paced short-term degradation of more labile carbon pools was reported to be increased leading to a decrease of the readily degradable fractions (Hobbie et al. 2012). The aerobic litter degradation process strongly changes its behavior with time; in earlier stages rather easily accessible carbon sources are degraded, while at later stages degradation slows drastically down, due to enrichment of more recalcitrant fractions (Berg 2000). It is important to bear these differences in mind when assessing the in-situ aeration process: so far only “short-term” degradation studies are available.

For the short-term aerobic degradation experiment of beech litter it was shown that microbial biomass N incorporation was significantly negatively related to the NH_4 -concentration (0), indicating quick microbial incorporation of free NH_4 , which was already hypothesized elsewhere (Fellner and Laner 2011). The applied beech litter material was air dried before the experimental start. Before the aeration start the

landfill material used in the LSR experiment was incubated under anaerobic conditions. Both systems thus underwent drastic changes before initializing the aerobic degradation process. For the short-term degradation of beech litter, the soluble carbon and nitrogen fractions exerted high influence on the degradation process. This is the case in a similar manner for in-situ aeration, since due to the exponential nature of the degradation process (Barlaz et. al. 1990; Prantl 2007, p. 81) the initial microbial activity is typically the highest, either under anaerobic or aerobic conditions. The presumably highly varying microbial activity in the beginning could however not be highlighted for the LSR, as the solid sampling frequency was much lower. Nonetheless, the estimated decay rates (also decomposition constants, k-rates) were of a comparable magnitude as well (**Table 3**), even if the duration (730 days of aeration vs. 56 days of aerobic decay), the experimental setting (e.g. 36 °C vs. room temperature) and the underlying organic matrix (MSW vs. beech litter) substantially differed.

Table 3: Decomposition constants for waste and litter decomposition

LSR		Litter Degradation	
Reactor	k-rate [a ⁻¹]	Site	k-rate [a ⁻¹]
AW #A	0.91	AK	1.09
AW #B	0.61	KL	1.35
AD #A	1.15	OR	1.01
AD #B	1.12	PE	1.06
Mean	0.95	Mean	1.13
AN # A	10.7		
AN # B	14.7		

Notes: AD aerated dry, AK Achenkirch, AN anaerobic, AW aerated wet, KL Klausen-Leopoldsdorf, OR Orth, PE Perg.

Concerning nitrogen, the NH₄ concentrations dropped upon experimental start, which was also reported for in-situ aeration (e.g. Heyer et al. 2005; Prantl et al. 2006b;

Ritzkowski 2005) and could be confirmed with the presented data from the in-situ aeration experiment (see **Fig. 8** and **Fig. 9**).

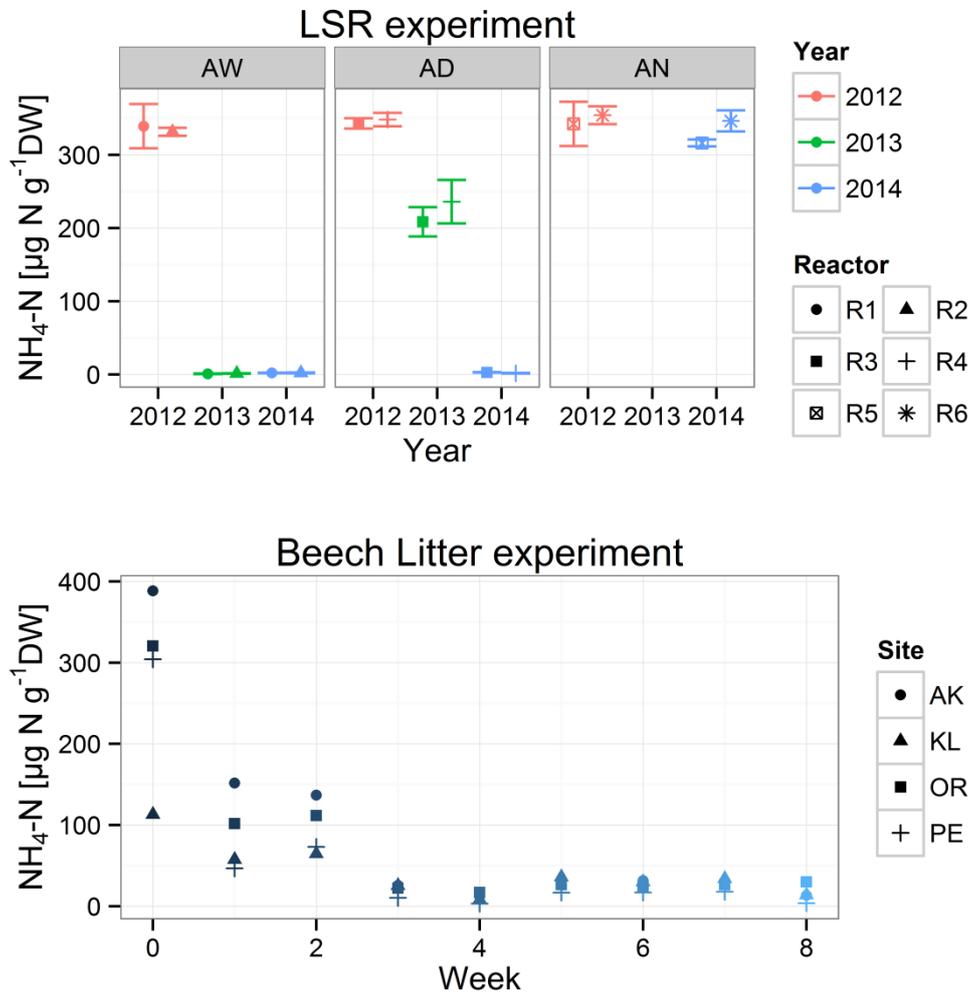


Fig. 9 Natural system vs. landfill: NH₄-N after elution

Notes: The elution was performed with aqua dest. in the LSR experiment and with 1 M KCl for the beech litter experiment.

The microbial community development during in-situ aeration requires further scientific attention. In the presented beech litter experiment the observation of a drastic change in the microbial community, with an increase in fungi and gram+ bacteria and a decrease of gram- bacteria, was already made after 8 weeks,

assessed by PLFA analysis. The application of this technique was rarely reported so far for in-situ aeration (Mellendorf et al. 2010). Nonetheless they made a comparable observation of an increase of fungi and gram+ bacteria and also detected a slight decrease in gram- bacteria in the solids after 15 weeks of aeration. It would be advisable to consider the here observed highest changes in the microbial community during the very beginning of the experiment for sampling campaigns of future LSR-experiments targeting the microbial community.

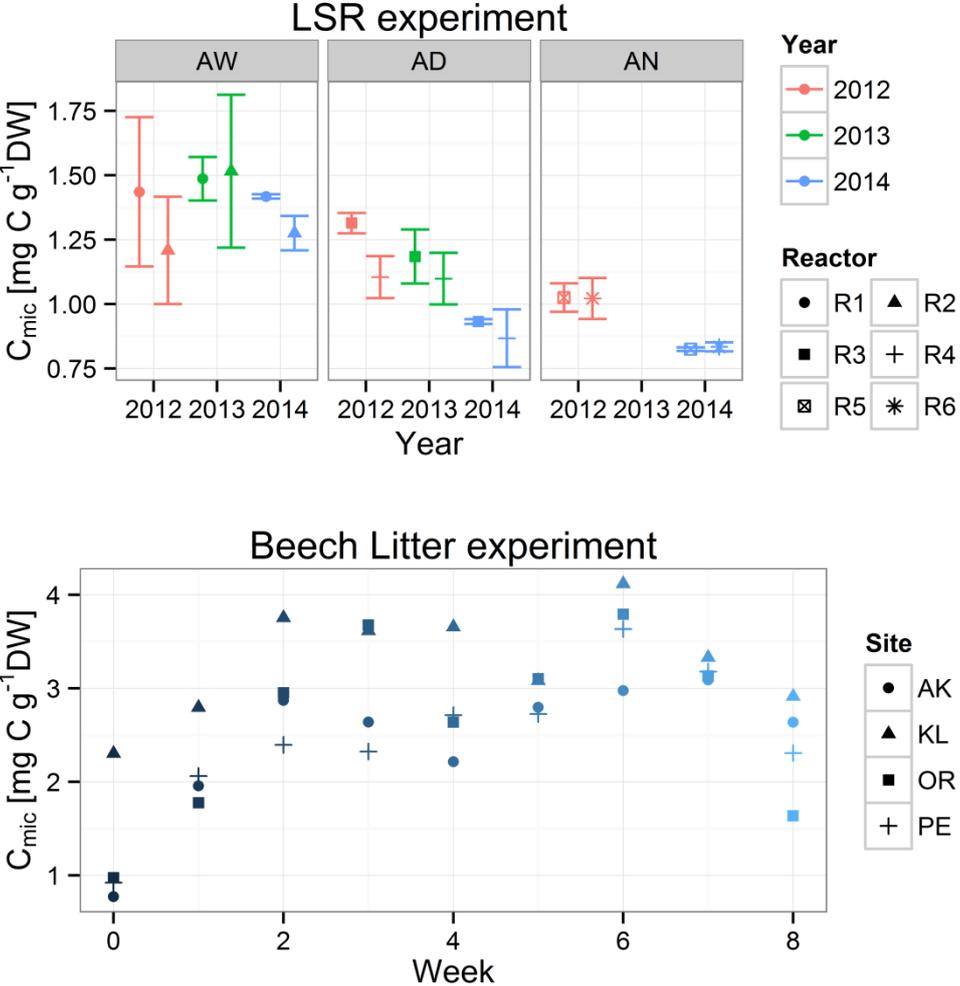


Fig. 10 Natural system vs. landfill: microbial biomass C

To summarize, the highest activity in aerobic batch degradation experiments generally occurs in the earlier stages, where soluble carbon is still comparably abundant. Aerobic degradation induces strong microbial community changes, independent of the previous history of the organic material; be it anaerobic or air dried. The degradation course is to some extent comparable for organic material of different origin. Other researchers already used peat bog as natural analogy for anaerobic landfills (Bozkurt et al. 2001; Döberl 2004), showing that microbial processes occurring in landfills can be studied from the viewpoint of natural biological systems.

In contrary to old landfilled waste, the studied matrix (beech litter) only consisted of organics, but also in landfills biological processes are related to the organic fraction. Putrescible waste mainly stems from plant material (e.g. biological waste in the form of food remains, green wastes and even paper) and the inorganic parts of landfills, e.g. construction and demolition waste, mainly account for physical properties or might negatively influence anaerobic degradation, due to high heavy metal or sulfuric (e.g. gypsum) contents (Chen et al. 2008). Inorganic parts are also abundant in litter-soil ecosystems, stones as the so-called “soil skeleton”, which are not accessible to microbial decay as well.

Microbial degradation of organics in landfills during in-situ aeration and leaf litter decomposition proved to show numerous analogies. The degradation velocities were similar in the presented laboratory experiments and an immediate decrease in $\text{NH}_4\text{-N}$ during aerobic decay was found to be consistent on a general level of aerobic decay of solid organic matter.

6. Conclusions and Outlook

On a global scale landfilling of MSW will further increase and thus the need for in depth understanding and assessing landfill metabolism prevails as well. The main requirement for predicting landfill reactions is (spatial) knowledge of the landfill body composition. The here presented statistical model will help in acquiring this knowledge and it can also serve as a tool for evaluating the success of remediation measures like in-situ aeration. It would be highly advisable to agree on a standardized sampling protocol and to pool the available data in a common landfill characterization database. The goal would be the prediction of future gaseous and leachate landfill emission potentials based on the underlying solid body composition data.

During the aerobic degradation of old MSW waste, the addition of water did not result in an increased carbon discharge which was partly explained by microbial water production during aerobic degradation and by differing morphology of the material. Concerning nitrogen, the process of denitrification was highly favored under aerobic wet conditions, also partly because of the applied sampling design. Nitrous oxide emissions on the contrary were highest for the aerated dry reactors. Total organic carbon and total nitrogen largely remained in the solid fraction. Transferred to full-scale, this could mean that water addition would increase nitrogen removal, but not carbon removal. This would imply a higher degree of freedom for this aerobic remediation technique in dependence of the remediation goal.

Aerobic laboratory batch degradation experiments of organic matter show a remarkable resemblance, independent of the substrate origin. In early degradation stages, easily degradable substances get mineralized, while with ongoing experiment

duration more and more rather recalcitrant organic matter is decomposed. This is also accompanied by fast changes in the microbial community.

The here presented work will help to increase the understanding of the anaerobic and aerobic microbial waste degradation process and provides an increased information base for performing future in-situ aeration projects. From a mechanistic view, questions concerning the substrate quality change during aerobic and anaerobic degradation should be intensely addressed: how do these anaerobic and aerobic degradable pools interact and how stable is the remaining organic substance? The utmost goal for improving the assessment of in-situ aeration should be the monitoring of implemented and completed measures after termination of in-situ aeration. Only then the sustainability of this remediation method can be assessed in a satisfactory way. Nevertheless the present work provides valuable information with respect to the design and operation of future landfill aeration projects and also for monitoring the success of these projects.

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Appendix

Appendix I. Using multivariate regression modeling for sampling and predicting chemical characteristics of mixed waste in old landfills



Using multivariate regression modeling for sampling and predicting chemical characteristics of mixed waste in old landfills



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ABSTRACT

Municipal solid waste landfills pose a threat on environment and human health, especially old landfills which lack facilities for collection and treatment of landfill gas and leachate. Consequently, missing information about emission flows prevent site-specific environmental risk assessments. To overcome this gap, the combination of waste sampling and analysis with statistical modeling is one option for estimating present and future emission potentials. Optimizing the tradeoff between investigation costs and reliable results requires knowledge about both: the number of samples to be taken and variables to be analyzed.

This article aims to identify the optimized number of waste samples and variables in order to predict a larger set of variables. Therefore, we introduce a multivariate linear regression model and tested the applicability by usage of two case studies. Landfill A was used to set up and calibrate the model based on 50 waste samples and twelve variables. The calibrated model was applied to Landfill B including 36 waste samples and twelve variables with four predictor variables.

The case study results are twofold: first, the reliable and accurate prediction of the twelve variables can be achieved with the knowledge of four predictor variables (Loi, EC, pH and Cl). For the second Landfill B, only ten full measurements would be needed for a reliable prediction of most response variables. The four predictor variables would exhibit comparably low analytical costs in comparison to the full set of measurements. This cost reduction could be used to increase the number of samples yielding an improved understanding of the spatial waste heterogeneity in landfills.

Concluding, the future application of the developed model potentially improves the reliability of predicted emission potentials. The model could become a standard screening tool for old landfills if its applicability and reliability would be tested in additional case studies.

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1. Introduction

Municipal solid waste (MSW) landfills pose a long-term threat to human health and environment via leachate and gaseous emissions. The source of these emissions, the solid body of landfills is typically not very well examined. This is especially the case for older MSW-landfills, where no documentation about the deposited

material is available. For assessing the long-term emission potential, the highly heterogeneous solid body composition is of major interest. The emissions eventually derive from the solid body, which particularly applies for gas production (Barlaz et al., 1990).

The lack of information concerning the landfilled waste is related to high sampling and chemical analytical costs. Furthermore, the extracted information of such solid waste sampling campaigns is limited, since the heterogeneity of the landfill body typically overshadows the results (e.g. Östman et al., 2006). In comparison to solid waste sampling, leachate sampling campaigns are more common, mainly because leachate is easier to access and also directly related to groundwater pollution (Eggen et al., 2010). However, leachate also strongly varies in its composition within a landfill spatiotemporally (Kjeldsen et al., 2002) and at most older landfill sites leachate cannot be collected as they are not equipped with a base lining system.

Abbreviations: BOD₅, biological oxygen demand after 5 days; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; ICP-AES, inductively coupled plasma atomic emission spectroscopy; Loi, loss on ignition; MSW, municipal solid waste; RI₄, respiration index after 4 days; RMdSPE, root median square percentage error; SD, standard deviation; sqrt, square root; TN, total nitrogen; TOC, total organic carbon; WC, water content.

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Typical sampling campaigns of MSW-landfills, as rarely as they are conducted, lead to 20–40 valid samples (Mor et al., 2006; Sormunen et al., 2008), where a wide range of analytical procedures in view of emission potential is applied. According to the Austrian standard ON S 2087, a guideline for the investigation of contaminated sites such as old landfills, in standard situations eight solid variables should be analyzed for as well as twelve variables after elution. Measuring twenty variables would lead to high analytical costs per sample. According to this guideline, it is recommended to take samples every 20×20 m. In view of landfill heterogeneity, we propose to take a larger number of samples and measuring less variables. This would ideally lead to an improved understanding of the emission source and enable site administrators to better identify for example hot spots of organic matter.

The aim of this article hence is to identify the optimized number of waste samples and chemical variables in order to predict a larger set of chemical variables. To achieve this goal, we applied a linear multivariate model based on four selected predictor variables with low analytical costs (Loi (loss on ignition), pH, EC (electrical conductivity) and Cl (Chloride)). By that we obtained predictions about twelve response variables for two fairly differing landfills.

2. Material and methods

In this work, we present a multivariate linear model. The model was formulated in the view of low analytical costs and with data from Landfill A. To show that the model can be applied to other MSW-landfills as well, the resulting model coefficients were applied on data from a second Landfill B. Afterwards, the model outcome was adjusted as will be explained below. For the sake of clarity we provide a short glossary with the most crucial statistical terms in the context of this article:

Variable: Method of measurement (e.g. Loi, TOC, WC); column in a typical dataset.

Observation: The measured values for every variable of one sample; row in a typical dataset.

Predictor variable: Variables used for prediction (here: Loi, pH, EC and Cl).

Response variable: The predicted variable (here by applying multilinear modeling).

Model adjustment criterion: Maximum 10% RMdSPE deviation from adjustment based on all measured variables.

Model evaluation criterion: Maximum 35% RMdSPE deviation predicted vs. measured.

2.1. Site characteristics and sampling

2.1.1. Landfill A

Landfill A contains approximately 220,000 m³ (fresh matter) of waste with an average deposition height of 3.7 m. According to test pitting conducted the landfilled waste mainly consists of MSW (66% moist mass), excavated soil (18% moist mass) and construction and demolition waste (16% moist mass). Landfilling took place at the site from 1965 to 1974 and resulted in a total landfill volume of approximately 240,000 m³ including top soil (Brandstätter et al., 2013).

2.1.2. Landfill B

At Landfill B about 210,000 m³ (fresh matter) of untreated municipal and commercial solid waste have been deposited between 1976 and 1995 (Prantl, 2007; Prantl et al., 2006a,b). The site is characterized by an average waste depth of 7.7 m and is divided into two sections differing in reactivity and age. The waste samples analyzed for this article originate from both sections.

2.1.3. Sampling

Sampling and chemical analyses of the deposited waste at Landfill A were conducted by the authors of the present study, while information about Landfill B was obtained from the literature (Prantl, 2007; Prantl et al., 2006a,b). At both landfills the excavated material was sieved with a mesh width of 20 mm. For the sampling campaign in Landfill A an excavator and for Landfill B a grab-excavator with 600 mm diameter was used. The average sample size in both cases was ~20 kg. At Landfill A in total 56 samples from 17 pits were taken and at Landfill B 54 samples from 20 excavated holes. For the sampling campaign in Landfill A, a priori information about the distribution of organic matter in the landfill was available (unpublished study), performed after the evaluation of a risk assessment study from the Austrian environmental agency (Environmental Agency Austria, 2005). Based on this information, the herein described sampling campaign at Landfill A focused on zones rather rich in organics.

2.2. Chemical analyses

This section provides additional information to Table 1 which contains the applied analytical devices and/or the standardized methods.

2.2.1. Solids

For chemical extraction of Cr_s, Cu_s, Pb_s and Zn_s in Landfill A, a microwave oven (Start 1500, MLS GmbH, Leutkirch Germany) was used (200 °C). The applied solvent was aqua regia (HCl and HNO₃ in the volumetric ratio of 3:1). The analysis of the elemental content was performed with inductively coupled plasma atomic emission spectroscopy (ICP-AES Ultima 2, Horiba Jobin Yvon, Munich, Germany). The RL₄ (respiration index after 4 days) of solid waste samples taken from Landfill A was analyzed by Agrolab Austria GmbH and for samples of Landfill B it was determined according to Binner and Zach (1999).

2.2.2. Eluate

For eluting the fresh waste material a water/solid ratio of 10 l/kg was applied for both landfills. The material was eluted in an orbital shaker at 250 rpm for 24 h at room temperature. For Landfill A, the EC and pH were measured with a pH meter (Seven Excellence S470 kit, Mettler Toledo, Ohio, USA) and the variables Cl and SO₄ were analyzed using ionic chromatography (IC Dionex ICS 900, Thermofisher Scientific Inc., Massachusetts, USA).

2.3. Statistical analyses

2.3.1. Data selection with plausibility tests

All statistical analyses were performed with the program R (ver. 3.0.1, R Core Team, 2013). For selecting plausible data from the full datasets we applied two reproducible criteria on data of each of the landfills: the first criterion was that the ratio of Loi and TOC_s (total organic carbon; total carbon – total inorganic carbon) should be lower than 2.4. The second criterion was that the ratio of TOC_s and TN should be higher than 8.

The reasoning behind the first criterion was that when investigating the ratio of Loi and TOC_s for organic substances present in landfills (such as glucose, cellulose, lignin, fats, protein or different plastic polymers), this ratio can theoretically vary between 2.5 for glucose (cellulose, hemicellulose and lignin show a ratio of 2.25, 2.31 and 1.5, respectively) and 1.08 for polystyrol, while polyethylene and polypropylene are characterized by a ratio of 1.17 (Kost, 2001)). A table indicating TOC:TN values of different polymers is given in supplementary material (Appendix 1). Taking possible measurement errors into account as well as the fact that there will be always a mixture of different organic substances in landfills

Table 1
Chemical analyses.

Landfill Parameter	A		B		Source
	Method	Device	Method	Device	
<i>Preparation</i>					
Milling	Ball mill		Centrifugal mill		a
Sieving	0.5 mm Mesh width		0.63 mm Mesh width		a
<i>Solids</i>					
WC	105 °C, 24 h	Drying chamber	105 °C, 24 h	Drying chamber	a
Loi	550 °C	Muffle furnace	545 °C	–	a
TOC _s	TC-TIC	Macro CHNS	TC-TIC	Variomax CNS analyser	a
TN _s	–	Macro CHNS	–	Variomax CNS analyser	a
Cr _s	Aqua regia extraction	ICP-AES	ON EN ISO 11885	–	b
Cu _s	Aqua regia extraction	ICP-AES	ON EN ISO 11885	–	b
Pb _s	Aqua regia extraction	ICP-AES	ON EN ISO 11885	–	b
Zn _s	Aqua regia extraction	ICP-AES	ON EN ISO 11885	–	b
RL ₄	ON S 2027-1	–	–	Voith Sulzer sapromat	a
<i>Eluted</i>					
EC	–	Seven excellence S470	ON M 27888	–	c
pH	–	Seven excellence S470	ON EN 6244	–	c
NH ₄ -N	DIN EN ISO 11732	–	DIN EN ISO 11732	–	a
Cl	–	Dionex ICS 900	ON EN ISO 15682	–	b
SO ₄	–	Dionex ICS 900	ON EN ISO 10304-1	–	b
COD	DIN 38409-43	–	ON M 6265	–	a
BOD ₅	DIN EN 1899-1	–	ON M 6277	–	c

Notes: Sources: a: Prantl et al., 2006a,b; b: Prantl et al., 2006a,b (Project Interland); c: Prantl, 2007. The subscripted suffix s stands for solid. The italic parameters were used as independent variables for the linear models. BOD₅, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; TN, total nitrogen; RL₄, respiration index after 4 days; TOC, total organic carbon.

present, we applied a maximum ratio of 2.4. Potential errors could derive from either the measurements of Loi or TOC. The Loi could be overestimated, if the sample is not absolutely dry and the TOC being calculated based on two measurements is subject to two potential analytical error sources. The measurement values of the excluded samples are listed in summarized in [supplementary material \(Appendix 2\)](#).

The reasoning behind the second criterion was that the ratio of TOC:TN in landfilled MSW would be never go below the TOC:TN ratio found in microbial biomass, assuming that proteins (about 3:1) and nylon (about 5.1:1) are not the dominant organic compounds in MSW. During the sampling campaign at Landfill A we found some nylon tissue, but this was not the main plastic source. In addition nylon was to a large extent removed during sieving. For old waste material it is unlikely, that available proteins have not been incorporated to microbial biomass or mineralized.

According to [Cleveland and Liptzin \(2007\)](#) the average (geometric mean) molar C:N ratio in microbial biomass of soil microbes was 8.6 based on 48 published sources. Soil as a habitat shows many commonalities to landfills, like e.g. an organic matrix (humic substances) and alternating CO₂ and O₂ soil gas concentrations. Transferred to mass ratios this molar C:N ratio in microbes would result in a TOC:TON ratio of 7.4. Including potential measurement errors and taking into account potential flexibility of soil microorganisms we defined this criterion rather tolerant with 8:1 (TOC:TN) or higher.

In total, analytical results of six samples out of 56 from the dataset of Landfill A failed on the first criterion, and 18 samples out of 54 from Landfill B. Applying the second criterion did not result in the removal of any samples.

2.3.2. Statistical testing

As a test for normality, Shapiro–Wilk-Test (S–W-test) was chosen, since it is considered to be the most powerful in comparison to other typically applied normality tests ([Razali and Wah, 2011](#)). If the *p*-value was higher than 0.05, the distribution was not considered to be significantly different from a normal distribution in accordance with other standard test procedures of normality ([Lizik et al., 2013](#)). For testing of significant differences between

two groups, either the parametric *t*-test (for normally distributed data, mean) or otherwise the non-parametric Mann–Whitney-*U*-test (median) was applied. Even though we are aware of the fact, that linear regression is sensitive to outliers, we did not transform the data prior to performing linear regression. Firstly, transformation procedures did not improve the outcome drastically (data not shown), secondly the interpretation of the results would have been more complicated, and thirdly the practical application of the presented model would be more difficult. Instead we applied the above mentioned criteria for data selection to remove potential implausible data.

2.3.3. Statistical modeling

2.3.3.1. Model formation. We selected four predictor variables for describing the remaining response variables with multiple linear regression analysis. We selected these four variables in view of gaining the maximum information about the chemical composition with minimum measurement effort. The four predictor variables were: Loi, pH, EC and Cl. The mathematical formulation of the model is as follows ([Weisberg, 2014](#), pp. 50):

$$y_p = D + a * Loi + b * pH + c * EC + d * Cl \quad (1)$$

with y_p as the respective response variable, D as the intercept and a , b , c and d as coefficients. The units of the predictor variables are given in [Table 3](#). We calculated the model with data from Landfill A and applied the model to Landfill B. After model application we adjusted the model to improve the prediction as will be explained in [2.3.3.1 Step 3](#).

2.3.3.2. Model cycle. An overview of the model cycle and its five modeling steps is given in [Fig. 1](#). The individual steps of the model cycle will be explained below.

Step 1 – Model building

The formulated model was calculated with data from Landfill A. As already described, we used the four predictor variables Loi, pH, EC and Cl for modeling of the respective response variables.

Table 2
Regression coefficients from the calibration model of Landfill A.

Parameter	r^2	Intercept Coefficient		Loi a		EC b		pH c		Cl d	
<i>Solids</i>											
WC	0.56	14.6	ns	1.17	***	-2.05	*	-0.44	ns	0.001	ns
TOC _s	0.97	-3.41	-	0.60	***	0.12	ns	0.33	ns	0.000	ns
TN _s	0.78	0.25	ns	0.02	****	0.02	*	-0.03	ns	0.000	ns
Cr _s	0.13	-270	ns	5.24	-	-15.4	ns	42.5	ns	0.003	ns
Cu _s	0.12	-1712	ns	30.0	-	5.04	ns	231	ns	-0.008	ns
Pb _s	0.34	-1112	ns	57.3	***	19.7	ns	131	ns	-0.353	-
Zn _s	0.32	-3284	ns	76.8	**	74.8	ns	437	ns	0.127	ns
RI ₄	0.16	14.6	*	-0.11	-	0.15	ns	-1.40	-	0.001	ns
<i>Eluted</i>											
NH ₄ -N	0.71	-227	ns	4.21	ns	-11.0	ns	31.9	ns	0.65	***
SO ₄	0.66	-16,418	*	158	-	3946	***	1816	-	-3.68	*
COD	0.76	44,775	***	-435	**	3758	***	-6014	***	11.8	***
BOD ₅	0.73	27,684	**	-290	**	2936	***	-3828	**	8.08	***

Notes: The corresponding units are presented in Table 3. The subscripted suffix *s* stands for solid. Significance levels: (ns $p > 0.1$; $p < 0.1$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$). BOD₅, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; TN, total nitrogen; RI₄, respiration index after 4 days; TOC, total organic carbon.

Table 3
Results of the model application.

Units	r^2	Non-adjusted RMdSPE (% measured)	Adjusted ($n = 10$) RMdSPE (% measured)
<i>Solids</i>			
WC (% DW)	0.45	13.5	11.2
TOC _s (% DW)	0.87	19.0	6.3
TN _s (% DW)	0.69	26.4	13.2
Cr _s (mg kg ⁻¹ DW)	0.36	387	25.4
Cu _s (mg kg ⁻¹ DW)	0.10	219	26.1
Pb _s (mg kg ⁻¹ DW)	0.08	264	31
Zn _s (mg kg ⁻¹ DW)	0.19	183	61.7
RI ₄ (mg O ₂ g ⁻¹ DW)	0.00	40.7	31.8
<i>Eluted</i>			
NH ₄ -N (mg kg ⁻¹ DW)	0.73	16.2	11.8
SO ₄ (mg kg ⁻¹ DW)	0.04	162	251.1
COD (mg O ₂ kg ⁻¹ DW)	0.57	78.3	26.9
BOD ₅ (mg O ₂ kg ⁻¹ DW)	0.57	127	25.6

Notes: The values are based on the measurements of Landfill B. All numbers have been rounded to three significant figures. The subscripted suffix *s* stands for solid. BOD₅, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; LF, landfill; TN, total nitrogen; RI₄, respiration index after 4 days; RMdSPE, root-median square percentage error; TOC, total organic carbon; WC, water content.

Step 2 – Application of the model

The calculated model was applied on data from Landfill B. This is shown in Fig. 1 Step 2, application – red¹ triangles.

Step 3 – Model calibration

Model adjustment

Since the considered landfills differ in many aspects (see Fig. 2), it was necessary to adjust the model results. For adjustment a simple (univariate) linear regression was performed. We used the predicted values from the multilinear model as predictor variable and the measured values as response variable. This means, that here the regression had to be reversed. The resulting coefficients from this second regression analysis (intercept and slope) would then be applied on the unadjusted model values.

For estimating the amount of observations needed for a reasonably good model adjustment we used bootstrapping for

cross-validating. Typically a bootstrap sample is obtained by randomly sampling n times, with replacement, from the original data points (Efron and Tibshirani, 1994). Replacement would mean that e.g. the same variable could be drawn twice. This bootstrapping was performed for an increasing amount of observations for each predicted variable. One prerequisite for this procedure would be a goodness of fit criterion of the model result to assess the output quality.

Goodness of fit criterion

The model adjusting would not affect the typically applied coefficient of determination (r^2) because all the predicted values from each variable are adjusted with the same coefficients. Therefore we applied a different criterion for evaluating the final model result. For comparing the model output prior to and after adjustment we used the root median square percentage error (RMdSPE, Hyndman and Koehler, 2006). This criterion was chosen for maximum comparability between different variables, since it is based on percentage errors and the RMdSPE is considered to be less sensitive to outliers than others based on the arithmetic mean. The criterion describes the deviation between the measured and the predicted values.

The following equations were adapted in agreement with Hyndman and Koehler (2006). The percentage error (PE) is given as:

$$PE_i = \frac{100 * (yp_i - ym_i)}{ym_i} \quad (2)$$

with i as index for each point and yp_i as the predicted values and ym_i as the measured values.

And the RMdSPE as:

$$RMdSPE = \sqrt{\text{median}(PE_i^2)} \quad (3)$$

Bootstrapping

After defining the quality criterion RMdSPE we investigated the necessary amount of measured response variables of Landfill B to obtain a reasonably good adjustment of the applied model to fit the measured data accurately.

Here we applied a bootstrapping procedure to estimate, how many observations would be needed to gain a reasonably good adjustment function and consequently model output. For every

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

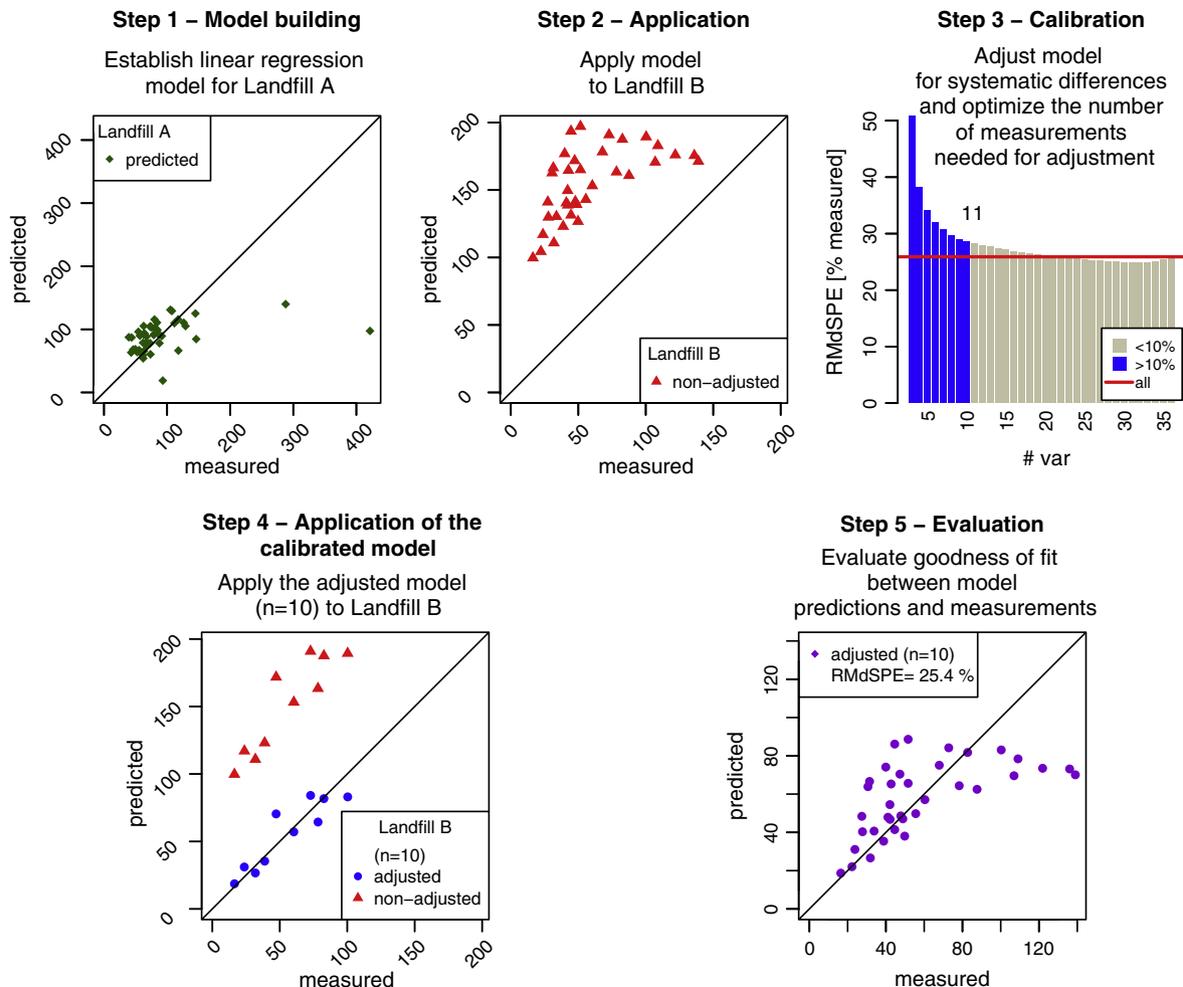


Fig. 1. Graphical overview of the model cycle. Notes: RMdSPE, root-median square percentage error.

bootstrap subsample we first predicted the response variable of Landfill B with the model from Landfill A (Step 2). Next we applied the model adjustment for every subsample, with the corresponding subsample of the non-adjusted prediction. This resulted in adjusted model values for each subset, of which we then calculated the RMdSPE.

In total we created 5000 bootstrap-subsamples from each response variable, for an increasing amount of observations with ($n = \{3 \dots 36\}$) instead for the full dataset as is typically performed in bootstrapping. We started from three values, since the application of linear regression based on two data points was not considered as reliable. We then calculated the arithmetic mean from each bootstrapping with 5000 subsamples resulting in 34 values ($3 \dots 36$) per response variable.

The arithmetic mean of all RMdSPE results for each amount of drawn variables ($=5000$ (bootstrap replicates) $\times 3 \dots 36$ (variables selected) $\times 12$ (response variables)) was compared to the prediction based on the model adjustment using all observations of the response variables. We arbitrarily considered a difference between the errors from the bootstrap subsamples and from the errors of the whole dataset below 10% as sufficiently accurate for determining the amount of observations needed for adjusting the model (Model adjustment criterion).

Because of our study design, we applied bootstrapping without replacement. Performing linear regression with two exactly same values would not be reasonable. So, even if between-sample correlation would be higher without replacement than with replacement (Stephenson et al., 2010), we chose to apply bootstrapping

without replacement to investigate how many measured values would be needed.

Step 4 – Application of calibrated model

Anticipating the results, for the majority of response variables the selection of ten observations would suffice to fulfill our predefined model adjustment criterion. So we performed the adjustment using ten randomly selected observations of Landfill B.

Step 5 – Model evaluation

The result of the unadjusted model ($n = 36$) was finally adjusted with univariate linear regression based on the previously selected ten observations ($n = 10$) in analogy to Step 3 model adjustment. The quality of the model result was assessed with the RMdSPE. For the goodness of fit criterion of the multilinear model we defined that everything below 35% of RMdSPE deviation from the measured observations would be considered as accurate (model evaluation criterion).

3. Results

3.1. Solid body analysis

The analytical results of the solid waste sampling are summarized in Fig. 2.

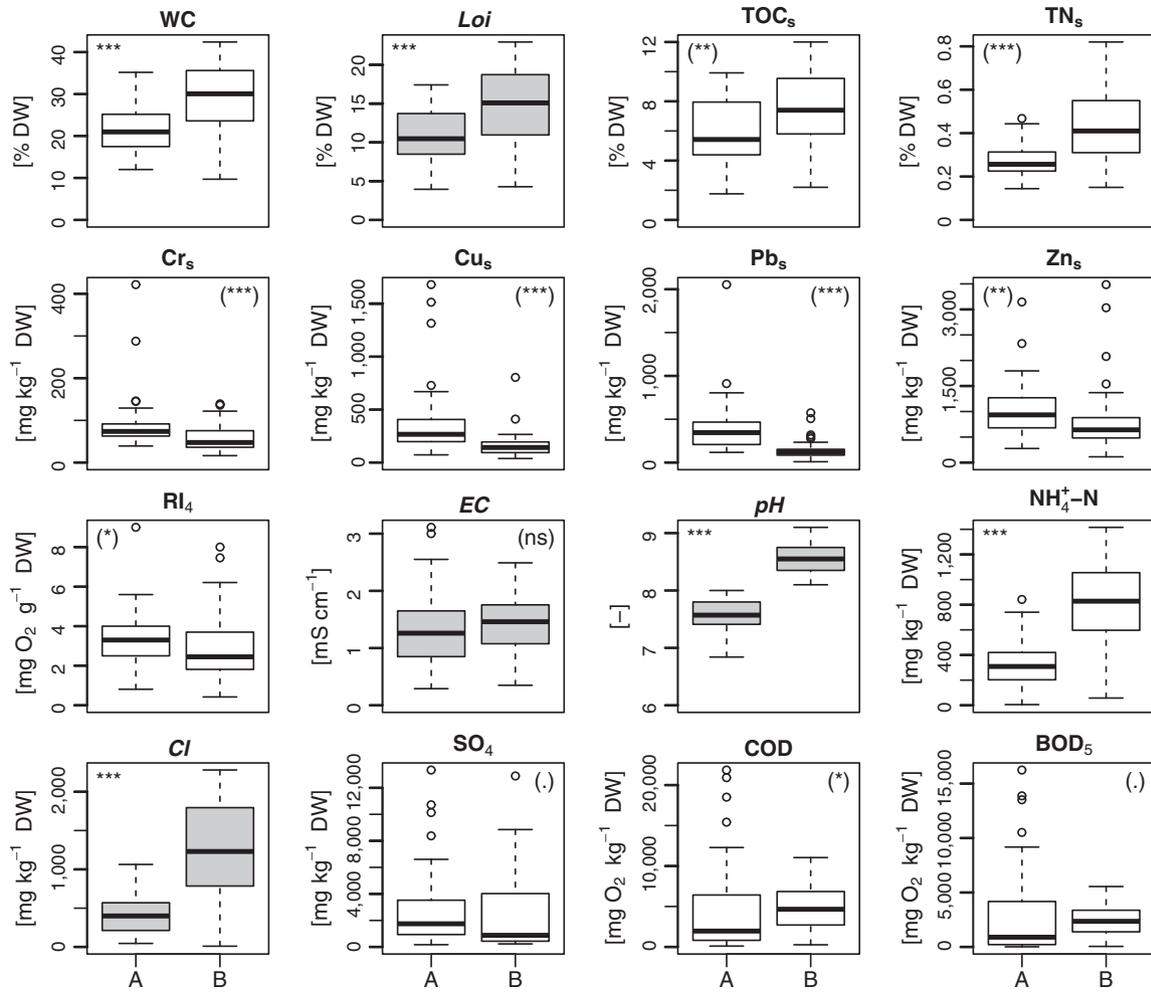


Fig. 2. Overall comparison between Landfill A and B. *Notes:* Boundaries of the box plots with the bold line representing the median indicate the 25th and 75th percentiles; whiskers have a maximum length of 1.5-fold interquartile range. Circles are outlying points. The gray scaled variables were used as predictor variables for the linear models. If one of the groups was considered as not normally distributed (significant Shapiro–Wilks test), Mann–Whitney *U*-test was applied for testing between the landfills (indicated by brackets), else a Student *t*-test. Significance levels: (ns $p > 0.1$; $p < 0.1$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$). The subscripted suffix *s* stands for solid. BOD₅, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; TN, total nitrogen; RI₄, respiration index after 4 days; SD, standard deviation; TOC, total organic carbon.

The two different landfills showed significant differences in nearly all variables, except for EC, SO₄ and BOD₅. The variables Loi, TOC_s, TN, NH₄-N, Cl and COD, typically considered as correlated with organic matter (except for Cl) were significantly higher in Landfill B. The pH however was significantly higher in Landfill B than in Landfill A and the BOD₅ did not differ significantly. Generally Landfill B had a higher MSW-content, but the sampling campaign of Landfill A targeted at sections high in organics. This sampling approach resulted in four high outlying values in COD and BOD₅.

The statistical distribution of the variables varied drastically as it is typical for landfill samples. In Landfill B four variables showed a more equal distribution than in Landfill A (*S*-*W*-test, TOC_s, TN, COD and BOD₅).

3.2. Linear regression model for Landfill A

We applied the multivariate linear model (Loi, EC, pH and Cl) on Landfill A for twelve response variables. As can be estimated by the coefficients from Table 2 the solid variables were mainly influenced by Loi whereas the eluted variables by EC, pH and Cl, but also by Loi. The metal contents and the RI₄ could be

explained the least ($r^2 < 0.4$), while all the other variables showed a rather good fit ($r^2 > 0.65$), except for WC which was mediocre ($r^2 = 0.56$).

In Fig. 3, the model results are shown graphically by comparing measured and predicted values. In the *xy*-plots for the modeling results (Figs. 3 and 5), we applied the same range for the *x*- and *y*-axes. The model results from the metal contents as well as from the RI₄ are influenced by a few high outlying values.

3.3. Prediction of dependent variables for Landfill B

The results of the non-adjusted predicted model are shown in Table 3 (left result column) and Fig. 4. Similar to the calibration model, r^2 was low for the metal contents as well as for RI₄. The best predictions were achieved for TOC_s, NH₄ and TN_s, followed by BOD₅ and COD. We could not produce a reasonable fit for SO₄ and the WC was mediocre as before ($r^2 = 0.45$). For the non-adjusted model results of WC, TOC_s, TN_s and NH₄-N the accuracy criterion RMdSPE was below 30%, while for the metals it was above 180%. The eluted variables except for NH₄-N also showed a high RMdSPE (78.3% for COD, 127% for BOD₅ and 162% for SO₄).

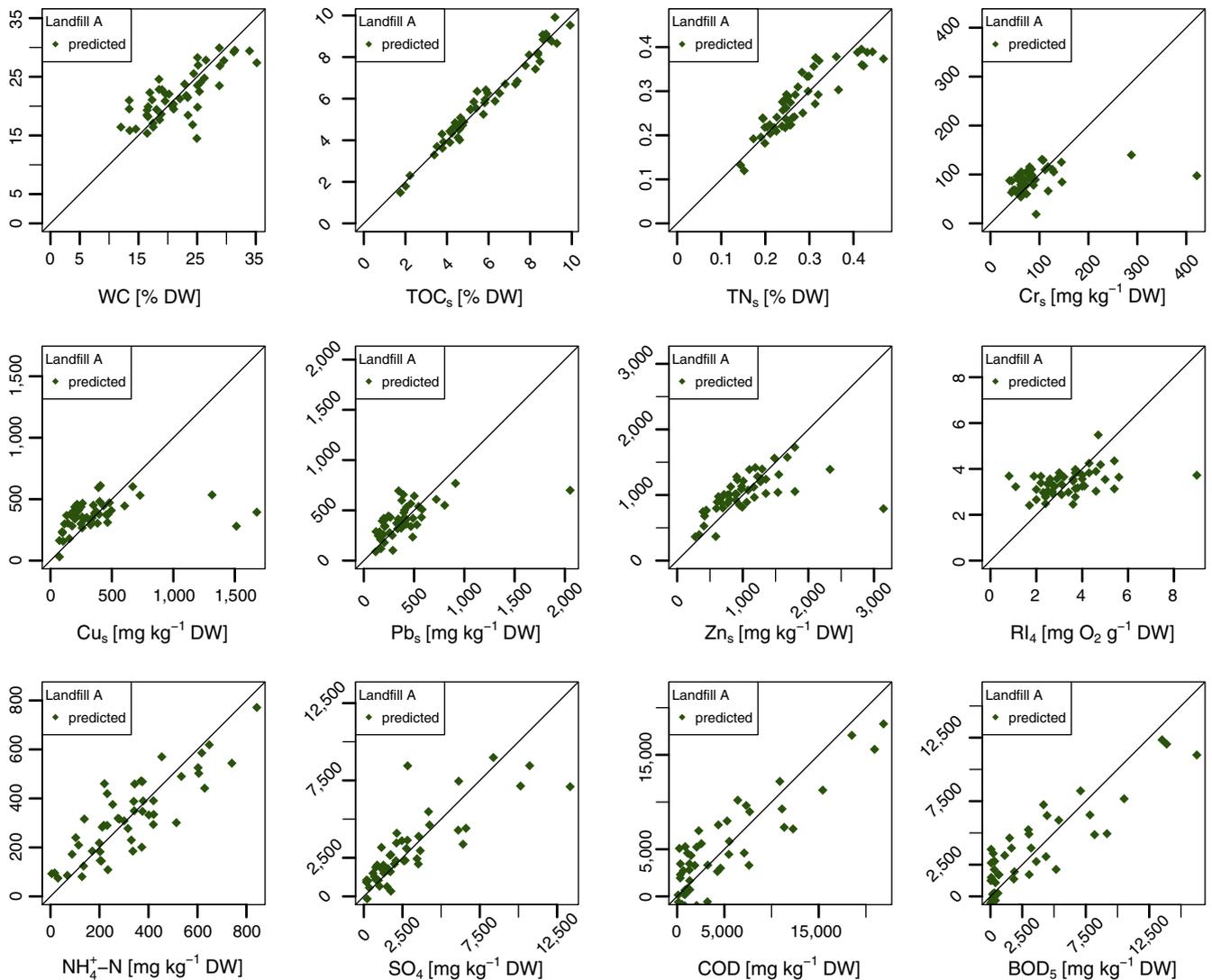


Fig. 3. Model creation for Landfill A (comparison between predicted and measured values of 12 variables). *Notes:* The x-axes can be considered as the measured values and the respective y-axes as predicted. The subscripted suffix s stands for solid. BOD₅, biological oxygen demand after 5 days; COD, chemical oxygen demand; DW, dry weight; TOC, total organic carbon; WC, water content.

3.4. Bootstrapping

The results of the RMdSPE bootstrapping were summarized in Fig. 4. The applied model adjustment criterion (less than 10% deviation from the adjustment with all data) was reached for WC, TOC_s, Pb_s and Zn_s as well as the eluate variables by using only few full measurements. This means, that \leq ten variables for which the response variables are known as well, are needed for adjustment.

Fulfilling the criterion for Cr_s needed 11 observations (including the response variable) and TN_s, Cu_s and RI₄ needed more than 20 values (representing the whole plausible data set of Landfill B).

3.5. Application of the calibrated model ($n = 10$)

The results when adjusting the response variables with linear regression of ten observations (representing ten waste samples for which all response variables are known) and ten predicted values (subsequently named testing model) are shown in Fig. 5 and Table 3 (adjusted). Even though the bootstrapping test indicated that in many cases more than ten response variables would be needed to gain a reasonably good fit, the testing model was more accurate for most variables in comparison to the non-adjusted

model. Only for SO₄ it was less accurate. This result is based on one random sample of ten response variables distributed over the whole dataset. For the bootstrapping procedure all observations were potentially considered, including extreme values. Most variables were predicted quite accurately with the RMdSPE below 30%, except for Pb_s, Zn_s, RI₄ and SO₄.

4. Discussion

4.1. Overall model quality

From the twelve predicted response variables, ten showed an RMdSPE below 35% (Model evaluation criterion), only for two (SO₄ and Zn_s) the accuracy was low (see Table 3 and Fig. 5). It has to be noted, that this criterion is based on the median, which is more robust to outlying values. The adjusting was performed by usage of ten observations out of 36, or 28% of all samples. If this number of required observations is specific for the present case (for Landfill A and Landfill B) or generally sufficient should be subject to further testing.

The variable SO₄ showed high variation for both landfills (Fig. 2), while in Landfill A this variable was probably stronger

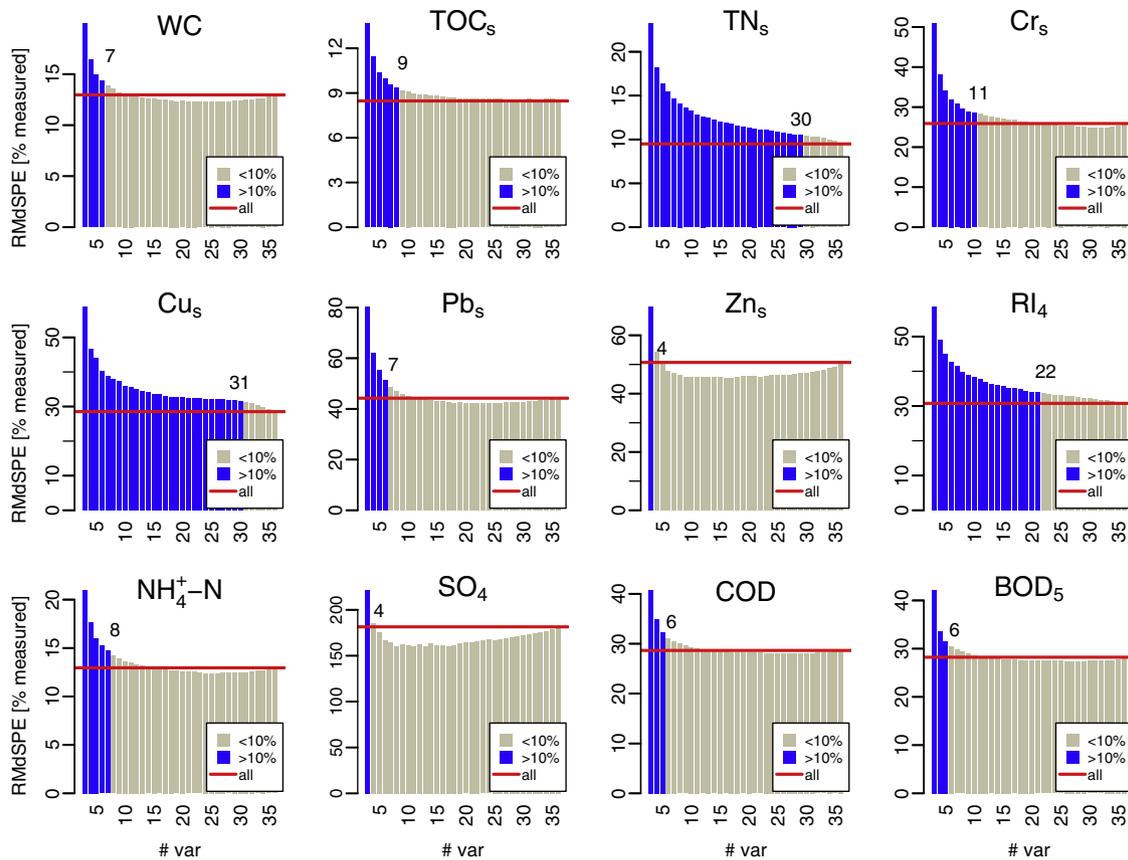


Fig. 4. Bootstrapping of the model results with a reduced amount of samples (RMdSPE). *Notes:* The red line represents the mean RMdSPE (root median square percentage error) of the model adjusted with all ($n = 36$) response variables. The figures above the bars indicate the amount of measurements to fulfill the 10% model adjustment criterion. The subscripted suffix s stands for solid. BOD₅, biological oxygen demand after 5 days; COD, chemical oxygen demand; RI₄, respiration index after 4 days; TOC, total organic carbon; WC, water content. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

influenced by construction and demolition waste, presumably containing gypsum, than in Landfill B. This could explain why the prediction for SO₄ was not as accurate as for other variables. Although the model did not predict some extremely high values correctly for the metal content and RI₄, the adjusted results for most of the variables were reasonably accurate. For assessing the spatial distribution of different variables inside landfills, it would be of higher significance to possess viable approximate values than fewer correct values. As an example, if we could assess the distribution of Cu_s showing a range from (38 to 804 mg kg⁻¹ DW) in Landfill B with 26.1% (RMdSPE) accuracy after adjustment with higher sampling resolution, the information increase of the relative distribution would more than outweigh the inaccuracy of the model prediction.

The model should be applied for MSW-landfills only, since the calibration was performed for this landfill type. To increase the model accuracy especially for the underestimated higher values, the application of e.g. quadratic regression should be considered. Within the present article we introduced a linear model as a first step for the sake of applicability. Instead of our approach of adjusting the available model of Landfill A, it would also be possible to directly calculate the multivariate model for Landfill B by using as well ten measured values for calibration. But, as can be seen from Table 4, on average the result would be better with the presented model (lower RMdSPE). Moreover the variation of the outcome would be also lower (SD) for the majority of variables, proving that our presented approach would lead to more robust results. These results were as well derived with bootstrapping ($n = 5000$) without replacement for both models. We assume that

by including the information of another dataset the variation of variables might be reduced. If the variation of a variable is high, showing e.g. many extreme values, the chance of sampling extreme values would rise as well. Directly calculating multilinear models based on these extreme values would possibly raise the variation in comparison to applying the model created on the basis of a whole additional dataset.

Another possibility would have been to calibrate the model for Landfill B and use the calibrated model to predict waste composition at Landfill A. This was accomplished (data not shown), however the model results were better in the presented way. Possible reasons for that might be that at Landfill A more samples were available for statistical modeling (50:36), the different landfill age (Landfill A is older and hence less affected by too pronounced relations), or also the sampling campaign focus might influence the model calibration.

4.2. Leachate loadings

Elution experiments target to simulate the potential leaching behavior of waste. With our model we addressed NH₄-N, SO₄, COD and BOD₅ as eluted response variables (unknown and hence to be predicted), while EC, pH and Cl were considered as eluted predictor variables (known). For the model of Landfill A, all four response variables (NH₄-N, SO₄, COD and BOD₅) could be predicted quite well. The lowest agreement between measured and predicted values has been observed for SO₄ with an r^2 of 0.66 (Table 4). The prediction of Landfill B was less successful, especially for SO₄, as already described under general model quality (see 4.1). The

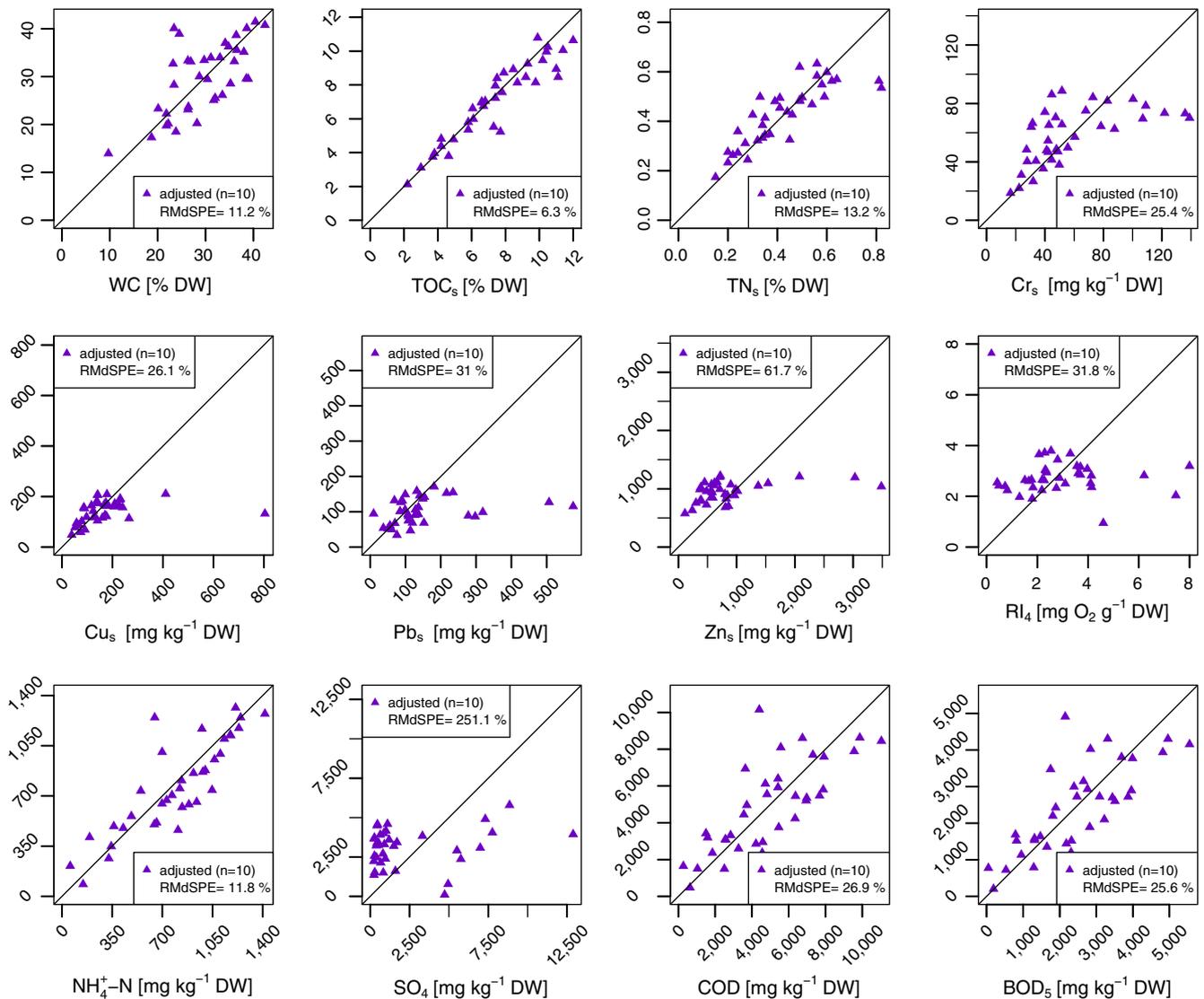


Fig. 5. Model testing via adjustment function derived from 10 random samples. *Notes:* The x-axes show the same range as the respective y-axes. The subscripted suffix *s* stands for solid. BOD₅, biological oxygen demand after 5 days; COD, chemical oxygen demand; DW, dry weight; RI₄, respiration index after 4 days; RMdSPE, root-median square percentage error; RMSPE, root-mean square percentage error; TOC, total organic carbon; WC, water content.

remaining elution response variables showed good (NH₄-N) to mediocre (COD, BOD₅) agreement (Table 3). After adjusting the results, the RMdSPE was below 30% for all the three variables. It has to be noted, that for COD and BOD₅ six predicted non-adjusted values were below zero and for SO₄ one, which became positive after the adjustment. For very low values of COD, BOD₅ and SO₄ the application of the model would possibly result in negative values, if the dataset has not been adjusted.

As discussed before, the tradeoff between measuring accuracy and frequency must be considered; applying our model to an increased amount of solid waste samples for which only four variables would have to be analyzed (higher measuring frequency with lower analytical extent) would result in an increased knowledge about the spatial distribution, while decreasing the measurement accuracy. This would certainly pose a disadvantage for values in the range of legal threshold values, but on the other hand improve the precision of the spatial distribution inside the landfill, which would be of higher importance for applying target-orientated mitigation measures, especially in large landfills. Finally, for assessing leachate migration preferential pathways inside the landfill (Laner et al., 2011) and the flow direction of the leachate plume still

would need to be assessed. Without knowledge of the groundwater flow and the subsurface geology as it is often the case, solid waste sampling at landfills prevails the only method for assessing future emission potentials. With spatial knowledge about the potential leachate loadings, at least the emission source could be better characterized. The presented tool might help identifying these sources and thus facilitating such sampling campaigns.

4.3. Substance inventory

The prediction of the solid contents for Landfill A was mostly based on Loi and partly also on EC (WC and TN_s, Table 2). There was no significant explanation for Cr_s and Cu_s to be found at a 95% confidence interval. Still the RMdSPE of the adjusted model of Landfill B was below 35% for all solid variables except for Zn_s (RMdSPE 61.7%). As can be seen from Fig. 2, selected measured values of Cu_s, Pb_s and Zn_s in Landfill B were extraordinarily high in comparison to the remaining values, which was also the case in Landfill A. These few values were estimated far too low (Fig. 5). Generally, the applicability of the model was better for lower values, than for very high values. The upper limits for metal

Table 4
Comparison between the adjusted model and a directly applied multivariate model.

Bootstrap $n = 5000$	Presented model with scaling RMdSPE (% measured)		Direct application on Landfill B RMdSPE (% measured)	
	Mean	SD	Mean	SD
<i>Solids</i>				
WC	13.0	2.37	13.9	3.49
TOC _s	9.11	2.20	10.8	3.05
TN _s	13.2	2.67	16.3	4.59
Cr _s	28.5	4.11	36.5	10.1
Cu _s	36.0	14.6	48.9	32.0
Pb _s	45.0	15.1	50.7	19.9
Zn _s	45.8	12.3	56.3	22.2
RI ₄	38.2	9.7	30.4	12.2
<i>Eluted</i>				
NH ₄ -N	13.6	3.4	14.2	3.17
SO ₄	162	83.6	162	72.9
COD	29.3	3.1	25.8	8.15
BOD ₅	28.6	3.0	26.2	8.12

Notes: Both methods were performed based on 10 measured variables (5000 times). All numbers have been rounded to three significant figures. The subscripted suffix *s* stands for solid. BOD₅, biological oxygen demand; COD, chemical oxygen demand; DW, dry weight; EC, electrical conductivity; Loi, loss on ignition; LF, landfill; TN, total nitrogen; RI₄, respiration index after 4 days; RMdSPE, root-median square percentage error; TOC, total organic carbon.

concentrations according to the Austrian landfill ordinance are summarized in [supplementary material \(Appendix 3\)](#).

Besides the metallic contents, the TOC_s, the TN_s as well as the WC could be predicted quite accurately (RMdSPE < 15%). We could not predict the Fe_s-content for Landfill B as it was not measured there, but for Fe_s the r^2 of Landfill A would have been 0.64 (data not shown).

4.4. Summary of the model application

For an improved applicability of the model, a short application guideline is presented:

- Step A – Solid waste sampling campaign performed.
- Step B – Analysis of Loi, pH, EC and Cl for all samples taken.
- Step C – Analysis of the response variables (that are to be predicted) at selected points (28%, or 10 out of 36 observations).
- Step D – Application of model with measured variables (Step B) from [Table 2](#) with units from [Table 3](#) for each variable of interest.
- Step E – Calculation of linear regression with the measured response variables (Step C) as predictor and the predictor variables from the same selection (28%, Step D) as response variables.
- Step F – Adjustment of model output (Step D) with coefficients (distance + slope) from Step E.

The applied and adjusted model allowed for a reliable prediction for most of the examined response variables. It could be clearly shown, that for a good prediction it would not be necessary to measure every value during a sampling campaign. Especially for larger sites the presented tool could be useful for gaining an improved picture about the distribution of different substances in a landfill body with less analytical effort. There are two ways of future development of this tool: first it should be tested with solid waste data from other landfills in order to evaluate the number of variables required to perform reliable predictions of chemical waste characteristics. A second way would be to establish different multivariate linear regression coefficients for different

types of landfills, to generally improve the prediction. For this second way, we strongly encourage establishing a database for landfill solid sampling data for improved statistical analysis and thus more accurate model prediction.

4.5. Landfill gas production

Present models predicting gas emissions are generally based on the content of degradable organic carbon ([Kamalan et al., 2011](#)). The TOC_s in Landfill A could be easily replaced by Loi ($r^2 = 0.97$, [Table 3](#)), which is simpler and cheaper to analyze, especially as also the prediction of TOC_s for Landfill B using Loi was of high accuracy (6.3% RMdSPE after adjustment). It has already been discussed by e.g. [Prantl \(2007\)](#) that in older MSW samples the correlation between TOC_s and the potential for landfill gas production diminishes. With the developed model, the RI₄ could only be predicted with low accuracy, since none of the underlying predictor variables significantly influenced the model result for the variable RI₄ ([Table 2](#)).

5. Conclusions

The application of the presented model would facilitate landfill sampling campaigns by reducing analytical efforts. In the prevailing case, a model adjustment on base of ten measured values (28%) led to quite accurate prediction values (<35% RMdSPE) for the majority of the observed variables.

In combination with higher sampling resolution, better spatial information concerning future emission potentials could be generated with the drawback of accuracy loss. Especially for bigger landfills without available waste inventories and a lack of information concerning groundwater flow and subsurface geology this screening tool could lead to an increased source understanding at reduced analytical costs.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.wasman.2014.08.009>.

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Appendix II. Carbon pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes



Carbon pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes



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ABSTRACT

Landfill aeration has been proven to accelerate the degradation of organic matter in landfills in comparison to anaerobic decomposition. The present study aims to evaluate pools of organic matter decomposing under aerobic and anaerobic conditions using landfill simulation reactors (LSR) filled with 40 year old waste from a former MSW landfill. The LSR were operated for 27 months, whereby the waste in one pair was kept under anaerobic conditions and the four other LSRs were aerated. Two of the aerated LSR were run with leachate recirculation and water addition and two without. The organic carbon in the solid waste was characterized at the beginning and at the end of the experiments and major carbon flows (e.g. TOC in leachate, gaseous CO₂ and CH₄) were monitored during operation. After the termination of the experiments, the waste from the anaerobic LSRs exhibited a long-term gas production potential of more than 20 NL kg⁻¹ dry waste, which corresponded to the mineralization of around 12% of the initial TOC (67 g kg⁻¹ dry waste). Compared to that, aeration led to threefold decrease in TOC (32–36% of the initial TOC were mineralized), without apparent differences in carbon discharge between the aerobic set ups with and without water addition. Based on the investigation of the carbon pools it could be demonstrated that a bit more than 10% of the initially present organic carbon was transformed into more recalcitrant forms, presumably due to the formation of humic substances. The source of anaerobic degradation could be identified mainly as cellulose which played a minor role during aerobic degradation in the experiment.

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1. Introduction

Landfilling still represents the dominant method for the disposal of municipal solid waste (MSW) on a global scale (Organisation for Economic Co-operation and Development, OECD, 2004). While the share of direct MSW landfilling is decreasing in many OECD countries, in particular in Europe due to the European Landfill Directive (Council of the European Union, 1999), there is a shift in non-OECD countries from open dumping or burning to waste disposal in controlled landfills (UNEP, 2010). Due to continuous

emissions of landfill gas and leachate from the deposited waste, MSW landfills still pose a threat to human health and the environment decades to centuries after landfill closure (Laner et al., 2012b). Therefore, old MSW landfills need to be managed also in countries such as Austria, Germany or the Netherlands, where the disposal of untreated MSW has been banned for several years already.

In order to shorten the potentially long periods of aftercare for MSW landfills (Laner et al., 2012a) and to reduce negative impacts associated with the release of landfill gas and leachate, in-situ aeration has been put forward as a measure to enhance waste degradation in landfills and thereby decrease the remaining emission potential (Ritzkowski and Stegmann, 2010). Low-pressure landfill in-situ aeration was used worldwide mainly for biological stabilization to reduce gaseous (CH₄, odors) as well as leachate emissions (mainly NH₄) and to decrease landfill volumes (Ritzkowski and Stegmann, 2012).

During landfill in-situ aeration the degradation of organic matter is accelerated by oxidative respiration. Aerating organic fractions of MSW shows various effects during the enhanced degradation caused by immediate oxygen availability. During in-situ aeration the formation of CH₄ was reported to be suppressed

Abbreviations: Bd, biodegradable fraction; BOD₅, biological oxygen demand after 5 days; C, carbon; CI, confidence interval; COD, chemical oxygen demand; DW, dry weight; GP₂₁, residual gas producing potential; LSR, landfill simulation reactor(s); MSW, municipal solid waste; NL liter, at standard temperature and pressure (0 °C and 1013 mbar); Nm³ m³, at standard temperature and pressure (0 °C and 1013 mbar); RID, refractive index detector; RI₄, respiration index after 4 days; RMSE, root mean square error; SD, standard deviation; TOC, total organic carbon; TOC_{init}, initial total organic carbon; TW, total weight; WC, water content.

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(Ritzkowski and Stegmann, 2010), with an increased amount of carbon being released as CO₂ (Ritzkowski et al., 2006). In the leachate, NH₄ (He et al., 2011; Heyer et al., 1999) and also chemical as well as biological oxygen demand (Prantl et al., 2006; Ritzkowski et al., 2006) were reported to be reduced during in-situ aeration. Still, the main fraction of total nitrogen during aeration of MSW is considered to remain in the waste material (Fellner and Laner, 2011), even if the NH₄-concentration in the leachate decreases during aeration.

Aeration measures are generally classified as successful if the waste material is considered biologically stabilized. This biological stabilization is measured in terms of aerobic (respiration index after 4 days, RI₄ – ON S 2027-1 (2002)) or anaerobic (residual gas potential after 21 days, GP₂₁ – ON S 2027-3 (2004)) biological reactivity. The reduction of these biological parameters was in addition to the differences in gaseous discharges used as a proof of concept for aeration measures, if possible (Hrad et al., 2013; Prantl et al., 2006; Ritzkowski et al., 2006). However, these biological tests only allow for assessing the readily degradable (short-term, 4 respective 21 days) biological available carbon pool of the waste material. These difficulties with the determination of the biodegradable fraction led to the development of a stabilization criterion for in-situ aeration measures: if in full scale more than 90% of the biodegradable fraction determined during lab-scale experiments was degraded, the landfill is considered stabilized (Ritzkowski et al., 2006).

For numerically assessing the performance of the applied aeration measures with respect to gaseous emissions, the aerobic and anaerobic cases are usually directly compared in terms of C-discharge. The mathematical difference between the carbon released during the aerobic and the anaerobic experiments is subsequently used to describe an acceleration effect of in-situ aeration measures in comparison to the non-aerated cases (Hrad et al., 2013; Prantl et al., 2006; Ritzkowski et al., 2006; Ritzkowski and Stegmann, 2010). This direct comparison of the anaerobic and the aerobic case would require that the degraded C-pools for both cases corresponded to each other, which has not been investigated so far.

Moreover, despite the fact that numerous lab scale aeration experiments have been conducted so far, no entire balance of all carbon flows and pools has yet been accomplished. Hence, the goal of this study is to investigate the extent of carbon mobilization during in-situ aeration of landfilled MSW in comparison to anaerobic landfill conditions. Thereto all flows (gaseous and leachate emissions) and pools of carbon are recorded for altogether six landfill simulation reactors, which are operated differently: two under anaerobic conditions, two under aerobic conditions without water addition and two under aerobic conditions with water addition. For all reactors cross referenced carbon balances are presented, including a discussion about carbon quality change for the respective settings as well as providing insight into the influence of water addition on aerobic degradation.

The latter was investigated for two reasons: firstly, the excavated waste from the landfill was very dry due to the conditions at the site (climate, low-permeability soil cover) and therefore it was of interest, whether the low water content (WC) could have an inhibitory effect on aerobic waste degradation during the full-scale project. And secondly, higher moisture content is generally considered to accelerate aerobic degradation of MSW (Pommier et al., 2008) and thereby might have an effect on carbon mobilization.

2. Material and methods

During the experiment, waste material from an old landfill was placed into six LSR and then incubated under different conditions: aerobic wet, aerobic dry, and anaerobic. Organic carbon flows and

pools were monitored by means of solid waste analysis, gas and leachate flow as well as concentration measurements. Mass balances were established considering the initial and final TOC (total organic carbon) content of the waste as well as for the carbon losses via leachate and gas. Gaseous C-discharge was modeled using a first order degradation model for the anaerobic and aerobic treatments. Changes of the carbon pool were observed via biological testing and lignin and cellulose analysis.

2.1. Experimental setup

2.1.1. Waste material origin

The waste material was gathered from a landfill containing approximately 220,000 m³ (fresh matter) of waste with an average deposition height of 3.7 m. The landfilled waste mainly consisted of MSW (66% moist mass), excavated soil (18% moist mass) and construction and demolition waste (16% moist mass, Brandstätter et al., 2014a). Landfilling took place at the site from 1965 to 1974. The excavated material was sieved with a mesh width of 20 mm. Before placing the material into the respective LSR, the total amount of waste material (~430 kg) was pooled and thoroughly mixed with shovels. The material was selected from landfill areas comparatively rich in organics, since one aim of the experiment was to determine the maximum degradation potential (Landfill A, Brandstätter et al., 2014b). Upon LSR installation, the material showed a WC of 23.2% and a dry bulk density of 846 (kg m⁻³).

2.1.2. Landfill simulation reactor experiments

The experimental vessels consisted of stainless steel and they have already been used in a similar manner (Ritzkowski et al., 2006). The total volume of each vessel was 121 L. Analogous to Ritzkowski et al. (2006) the LSR were operated in duplicates, meaning that two LSR (A and B) were operated under the same conditions.

Three distinct experimental conditions (from here on named treatments) were applied: under the first treatment the waste material was aerated, water was added and leachate was recirculated (aerated wet). In the second treatment, only aeration took place, without leachate recirculation and no water addition (aerated dry). And in the third treatment, leachate was recirculated, but the material was kept anaerobic (anaerobic). The decision to not add water during the second treatment was made to investigate the impact of water addition and leachate recirculation on the acceleration of aerobic waste degradation.

The common design elements of all six LSR were as follows: To prevent water accumulation at the bottom of the waste columns, 8 cm from the LSR bottom a fine meshed grid was emplaced. This measure insured that excess water could drain out by gravity. The discharged leachate was captured in a closed container just before sampling. The temperature inside the waste columns was controlled by coating the LSR with insulation wool (2 cm thickness) and placing a temperature sensor in the center of the waste material. This sensor was connected to a thermostat, controlling a heating wire, which had been placed between the LSR wall and the insulation wool (see Fig. 1). After placing the waste material in the LSR it was slightly compacted with a closed steel pipe (Ø ~10 cm).

For the aeration treatments, air was introduced into the respective LSR via gas flasks (synthetic air, LINDE, Germany). One flask provided air for each treatment duplicate. From the gas flask the air flowed through a rotameter for pressure reduction, then through a splitter followed by non-return valves for each LSR and consequently by additional pressure reducing valves. All the tubes consisted of polyvinyl chloride (PVC). Afterward the air was streamed through digital mass flow meters (EM1NH, Sensirion

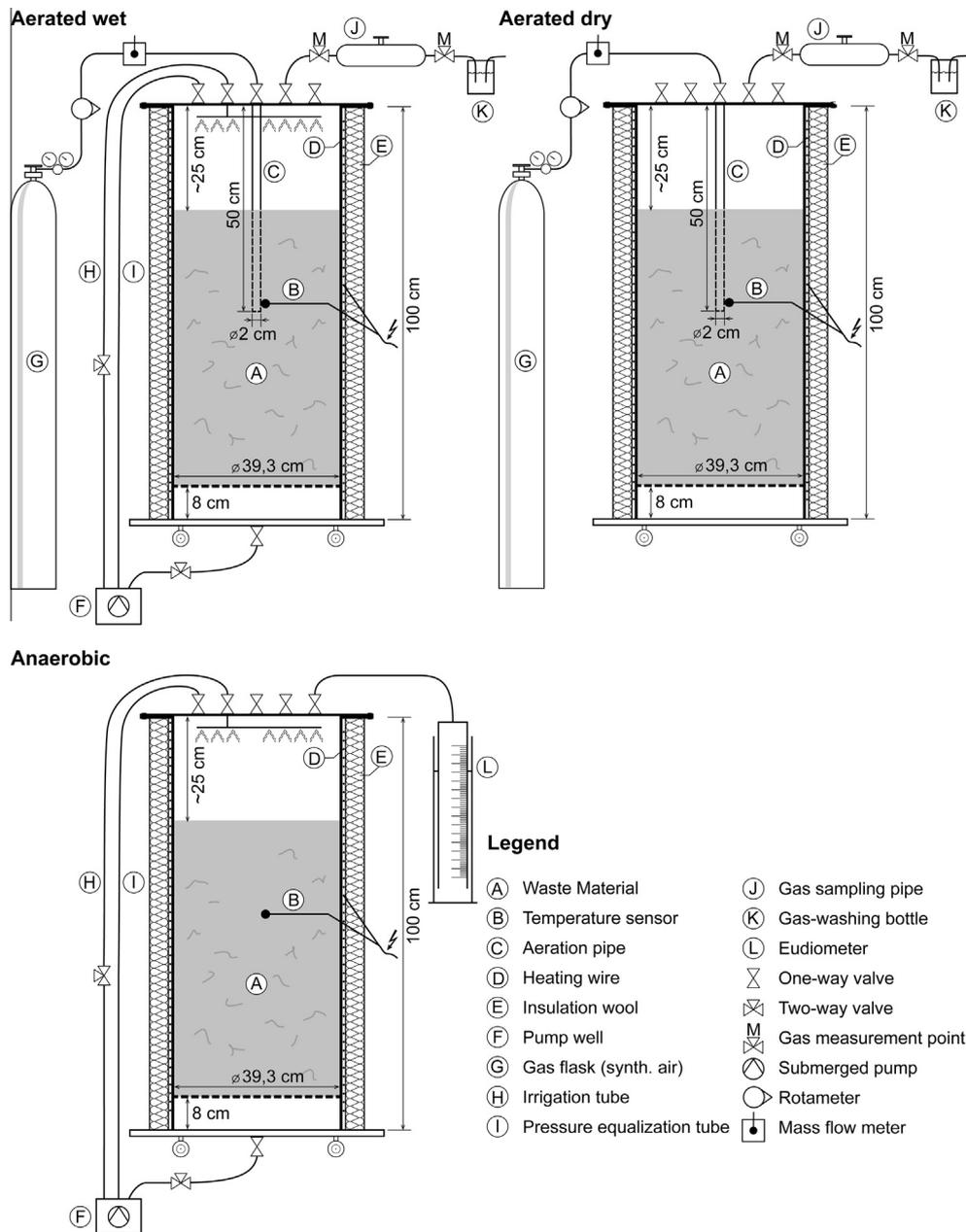


Fig. 1. Schematic cross sections of the Landfill Simulation Reactors (LSR) used for the waste degradation experiments.

AG, Switzerland), with a measurement range from 0 to 0.05 NL min^{-1} . The principle of measurement was based on temperature changes inside the measuring unit caused by the gas stream (CMOSens[®] sensor, Sensirion AG, Switzerland). The control program was written with the software processing (ver. 1.5.1, Processing Foundation, 2012) and the flow meters were connected to a desktop PC via RS-232 interface. The aeration was initiated by opening the according valves after 92 days of anaerobic operation. The flow rate was adjusted manually to an initial airflow of approx. 40 mL h^{-1} and roughly kept constant during the whole experiment.

After passing the mass flow meters, the gas was introduced to the LSR over a simple aeration lance made of a drilled plastic tube (drilling every $\sim 4 \text{ cm}$ from four sides). The applied lance did not reach to the bottom of the waste material in order to avoid the oxidation of the leachate accumulating at the bottom of LSR. This set up was chosen in accordance to Ritzkowski et al. (2006). The rather

loose packing of the waste, and its low oxygen consumption, especially in later stages allowed a rather complete aeration of the material.

The offgas was discharged from the LSR via gas sampling pipes and was finally conducted over a gas washing flask containing H_2SO_4 at pH 2. The aeration setup was complemented by various valves for gas sampling (Fig. 1).

For the irrigated treatments, in the first operation week roughly 2 L of deionized water was added daily until the waste reached field capacity. Except for this beginning period, fresh deionized water was added only after removing a similar amount of recirculated water thereby trying to maintain almost constant WC. The amount of water per recirculation was estimated as 1.8 L, since some leachate constantly remained in the reservoir due to the usage of a submerged pump (max. capacity: 10 L min^{-1}). The water from the reservoir was recirculated every working day over PVC-tubes. The respective valves for the leachate were per default

closed and only opened during recirculation or addition of new water. On the top lid a water distribution system was installed, consisting of perforated steel pipes ($\varnothing \sim 30$ mm) arranged in cross-shaped order.

The amount of landfill gas produced in the anaerobic phase/treatment was determined with eudiometers (Fig. 1, Anaerobic). A modified measuring cylinder was placed upside down in a closed plastic cylinder containing HCl (pH 1). The acid should prevent CO₂ from dissolving into the liquid. Beforehand the pedestal of the measuring cylinder was removed and in the center a tapped bore was drilled for attaching a PVC tube on a screwed adapter coated with Teflon band. The amount of gas produced could be read from the scale of the measuring cylinder.

A summary of the operational data is given in Table 1. The height of the waste for determining the waste volume and dry bulk density was measured at four sides from the top.

2.2. Analytical methods and sampling

The presented data material originated from a laboratory experiment, lasting 823 days from February 2012 to July 2014. The displayed time course data represent daily average values.

2.2.1. Gas measurements

The concentrations of CH₄, CO₂ and O₂ were determined at 350 measurement points, (starting from daily measurements and then increasing the interval between measurements to roughly twice a week with increasing duration of the experiment) with a mobile device holding an internal measuring pump (GFM 400, Gas Data Limited, Coventry, UK).

The concentrations of CO₂ and CH₄ were determined via infrared absorption and those of O₂ electrochemically (Clark electrode). The respective accuracies were below 6% for CO₂, below 3% for CH₄ and 0.5% for O₂ [relative%]. The average duration of each gas analysis was 40 s, which corresponds to a gas volume analyzed of around 200 mL. The gas measurements have been terminated after the observed concentrations have become almost constant.

The gas was collected and analyzed at the gas sampling pipes at the outlet for the aerated treatments. The valves (M, Fig. 1) were

arranged in a manner, that the measured gas was reintroduced in the gas sampling pipes during each measurement (circulation).

The anaerobic gas production drastically decreased over time, thus in later stages of the experiment (second year), the sampling rate for the anaerobic LSR has been decreased. This is also reflected by the reduced amount of recirculated water for the anaerobic treatment (Table 1), since the leachate was recirculated at every gas measurement event. The reason for this practice was that the water reservoirs were not entirely connected to the LSR, but a valve had to be opened during each recirculation event. In order to avoid unaccounted gas losses via the leachate reservoir, waste recirculation was limited to the times of gas measurements only.

2.2.2. Solids

Solid waste samples have been taken and analyzed at three time points:

- During the initial placement of the material, three samples were taken from each LSR (6 * 3 samples).
- The second sampling campaign was conducted only for the aerated treatments at 389 days after starting the experiment, leading to 12 (4 * 3) samples.
- The final solid sampling campaign was conducted at the end of the experiment (6 * 3 samples).

Before taking the samples at the latter two sampling campaigns, the material from each LSR was rigorously mixed. The GP₂₁ was, due to relatively high analytical costs, only measured for one mixed sample per LSR at each sampling time point. For determining biological activity the RI₄ and the GP₂₁ were analyzed by Agrolab Austria GmbH according to ON S 2027-1 (2002) and ON S 2027-3 (2004), respectively. Described in brief, the RI₄ of a water saturated sample (at least 30 g) is determined using a sapromat or respiromat. Either the CO₂ production or O₂-consumption is continuously measured (96 h after an initial lag-phase). For determining the GP₂₁, 50 g of the sieved or shredded sample is incubated with digested sludge (50 mL) and 300 mL of water is added. This mixture is transferred to a laboratory flask with a ground glass joint. This flask is purged with gaseous N₂ and then connected to a eudiometer (containing acidic sealing liquid) for measuring the produced gas. The gas amount produced at an incubation temperature of 35 °C is at least recorded in daily intervals (working day). After a lag-phase at the beginning, the incubation lasts for 21 days.

The TOC was analyzed using a MACRO CHNS analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

The fraction of acid soluble lignin (denoted as “lignin_s”) was measured following Tappi UM 250 (1999). The cellulose content was determined as the amount of free glucose in the hydrolysate from the lignin determination following Sluiter et al. (2008). Since the determination of lignin in waste samples is somewhat problematic (see discussion), double quotes are used for “lignin_s” in the present study. For sugar determination an Agilent 1200 series HPLC equipped with a refractive index detector (RID) and a Shodex sugar SP0810 column were used. For determining the WC, roughly 2.5 kg of the sampled waste material was placed in a drying oven for at least 24 h, or until constant weight.

2.2.3. Leachate

In total 27 leachate samples (~2 L) were taken and replaced by deionized water for each irrigated LSR. The sampling frequency was reduced over time from weekly to six weeks after one year of experiment, since the highest variation was expected in the beginning of the experiment. The leachate TOC concentration was determined according to DIN EN 1484 (1997).

Table 1

Landfill simulation reactors: operational data.

Treatment	Unit	Aerated wet		Aerated dry		Anaerobic	
		A	B	A	B	A	B
Operational volume	(L)	121	121	121	121	121	121
Initial waste mass	(kg TW)	90	90.8	94.6	90.9	85.9	86.3
Initial waste volume	(L)	82.2	82.2	83.1	83.7	79.2	78.8
Initial water content	(% TW)	23.6	23.1	23.2	23.4	22.7	22.9
Initial dry bulk density	(kg m ⁻³)	837	850	874	832	838	844
Average core temperature	(°C)	36.1	36.2	36.2	36.2	35.6	35.0
Anaerobic period	(d)	92	92	92	92	823	823
Aerobic period	(d)	731	731	731	731	0	0
Total air-Inflow	(Nm ³)	39.7	40.1	38.6	39.1	0	0
Specific aeration	(Nm ³ kg ⁻¹ DW)	0.76	0.75	0.69	0.73		
Total fresh water addition	(L)	54.3	54.2	0	0	52.5	53.1
Total water recirculated	(L)	776	776	0	0	616	616

Notes: DW dry weight, TW total weight.

2.3. Calculations

2.3.1. C-Discharge via gas

For calculating the aerobic C-Discharge based on CO₂ and CH₄ production, the general gas equation (Eq. (1)) was applied:

$$n = \frac{RT}{pV} \quad (1)$$

with n as the amount of CO₂ + CH₄ ((mol); 1 mol C = 12 g for each Mol CO₂ or CH₄), R as the universal gas constant 8.314 (J mol⁻¹ K⁻¹), T as the LSR core temperature (K), p as the atmospheric pressure 101,325 (Pa) and V (m³) as the volumetric fraction ($=c[\text{CO}_2] * \dot{V}$, or $=c[\text{CH}_4] * \dot{V}$) for a certain time point.

For the aerobic treatments the flow rate of aeration was measured at the inlet and the concentrations in the off-gas at the outlet of the LSR. This was necessary, since the mass flow meters were calibrated for dry synthetic air. If the measured volume flow would not have been corrected for humidity, the C-discharge from the aerobic LSR would have been underestimated. The mass flow meters returned NL, so no temperature correction was necessary. By passing through the relatively humid LSR at rather low velocity, the dry gas was humidified to some extent. We assumed maximum water saturation at 36 °C for the discharged air of all aerobic treatments, since even the waste of the dry LSR showed free water upon sampling. In total the contribution of water vapor increased the outlet gas flow by roughly 5% in comparison to the injected amount of air. Since for the anaerobic treatment the measured gas production was directly measured at the outlet, this adjustment was not necessary.

For calculating the C-loss under anaerobic conditions the produced gas was a mixture containing only CO₂ and CH₄; therefore, 1 NL of landfill gas produced was assumed to contain 0.536 g carbon. The reason for this approach was that we noticed that especially at later stages the anaerobic LSR were not 100% airtight. Thus the measured gas concentrations would have been diluted by intruded air, mainly nitrogen. In addition, the vessels were purged with N₂ prior to the experiment, meaning that also in the beginning of the anaerobic degradation observed landfill gas composition was strongly affected by dilution with N₂ initially present inside the vessels.

2.3.2. Degradation model

In accordance with the IPCC guidelines for national Greenhouse Gas Inventories (IPCC, 2006) a common first order decay model was applied without further converting the discharge to produced gas volume (Eq. (2)):

$$\text{C-discharge}_{[t]} = (\text{TOC}_{\text{init}} * bd) * e^{-kt} \quad (2)$$

with TOC_{init} as the initial TOC-pool (g), bd as the biodegradable fraction (-), k the decay constant (a⁻¹) and t as time (a). The initial TOC-pool of the aerobic treatment was corrected for the gaseous C-discharge during the first anaerobic phase.

For model fitting, the parameters bd and the decay constant k were numerically optimized. The global quadratic distance between the measured data and the model was minimized with a minimization algorithm (Nelder and Mead, 1965). The model was applied using the function `optim()` of the statistical software R (ver. 3.1.0, R Core Team, 2014). The model fit was calculated for the actual gaseous C-discharge (Fig. 2) as scale dependent root mean square error RMSE (Hyndman and Koehler, 2006). The CI (confidence interval) for the model was calculated using a random Student's t-distribution with the statistical properties of the model output and at a confidence level of 95% using the function `CI()` from the `Rmisc` package in R (Hope, 2013).

2.3.3. Mass balancing

The mass balance for the solid content of organic carbon was calculated as difference between start and end of the experiment (denoted as ΔTOC_s). For the aerobic treatments the removal of organic matter (TOC, lignin and cellulose) due to the sampling of solid waste (after 389 days) has been accounted for in the presented balances.

Since the gas flow rates were measured continuously while the concentrations and temperature were determined in total 350 times, the concentration and temperature values were linearly interpolated to produce continuous curves. The C-discharge via gas was calculated as the sum of CH₄- and CO₂-discharge ($C_{\text{gas}}^{\text{(ae+an)}}$). The TOC-discharge via leachate was calculated as the total amount of withdrawn water * TOC concentration (TOC_l).

The total TOC-balance for each LSR was calculated as (g C):

$$\text{Error}_{\text{TOC}} = \Delta\text{TOC}_s - \text{TOC}_{\text{sampling}} - C_{\text{gas}}^{\text{(ae+an)}} - \text{TOC}_l \quad (3)$$

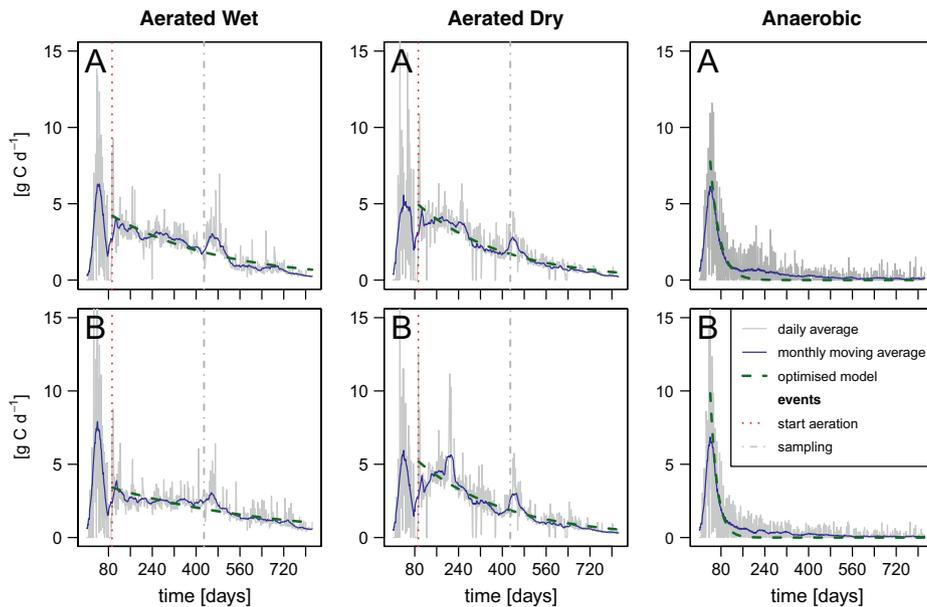


Fig. 2. Gaseous C-discharge during the experiment for the replicates (A and B) of each treatment.

with $Error_{TOC}$ representing the total TOC balance difference between solid, gas and liquid, ΔTOC_s the loss of solid TOC (initial – final), $TOC_{sampling}$ removal of organic carbon due to the sampling of waste for the aerobic treatments, $C_{gas (ae+an)}$ the aerobic and anaerobic gaseous C-discharge and TOC_l the TOC-discharge via leachate. All units are g C.

2.3.4. Error analysis

In general, uncertainties due to measurement errors were considered in the mass balances. All measurement errors are assumed to be independent and normally distributed with zero mean and given by the standard deviations. Gaussian error propagation was used to determine the uncertainty of the carbon flows and pools determined for the experiment. For the solids measurements, errors were determined by calculating the experimentally estimated standard deviations of the mean values for TOC_s and respective amounts of dry matter for each LSR and time point.

For the aerobic gaseous C-discharge, the errors of the mass flow meter measurements and the measurements using the mobile device were given by the manufacturer's error curves. In addition, standard deviation of the gas volume measurement using eudiometers was assumed to be 5% (relative to the gas production). For the anaerobic treatment, only the volume measurement was considered for calculating the standard deviation. For the leachate measurements, a relative standard deviation of 5% was assumed for the water amount removed as well as for its TOC concentrations, since no replicates were available.

2.3.5. Statistical testing

For testing of significant differences between two groups, either the parametric t-test (normally distributed, mean) or the non-parametric Mann-Whitney-U-test (median) was applied (Mann and Whitney, 1947). For the GP_{21} , no statistical tests were applied, due to only one sample being available for each LSR.

3. Results

3.1. Gaseous C-Discharge

Over the time course of the experiment the daily C-Discharge decreased for all treatments (Fig. 2). The anaerobic LSR showed high activity in the beginning, with a rapid decrease, while for the aerobic treatments the activity decrease was slower. The presented data in this paragraph were derived from average values from two independent LSR per treatment. The calculated CH_4 -contribution to the total C-discharge was on average 4.4% for the aerobic wet treatment, 3.3% for the aerobic dry treatment (without the initial anaerobic phase for both) and around 57% during the anaerobic treatment (according to measured data, not used for balancing). On average the gaseous C-discharge was highest for the aerated dry treatment (35.1% initial TOC) followed by

the aerated wet treatment (33.7%) and anaerobic treatment (11.8%), whereby for the latter some leakage of the reactors might have resulted in an underestimation of the total gaseous C discharge. This hypothesis is supported by the fact that the observed TOC loss of the solid phase (17.4% of the initial TOC – see Fig. 5) is significantly higher than the gaseous C discharge measured.

3.2. Degradation model

The degradation model provided a reasonable fit over the whole time course for the actual C-discharge (Fig. 2, Table 2). The TOC removal during the second sampling of the aerobic treatments was considered in the model as well as for the measured data in Fig. 3.

For the aerated treatments the degradable fraction of the TOC-pool was of similar size, between 31% and 46% of the TOC-pool initially present in the waste (Table 3). The decomposition constant was higher in the aerated dry treatment in comparison to the aerated wet treatment ($1.1\text{--}0.8\text{ a}^{-1}$). For the anaerobic treatment, the calibrated degradable TOC-pool was comparatively small (5–6% of the initial TOC pool) and the degradation constant was the highest of all treatments (12.7 a^{-1}).

3.3. Biological activity and evolution of the carbon pool

For all treatments, biological activity, measured as the amount of gas produced per time (Fig. 2), decreased over time, as it is common for biological degradation experiments (e.g. Brandstätter et al., 2013). The decrease might partially have been influenced by leaching through water recirculation, but leachate recirculation did not have a drastic influence on the degradation process, since the wet aerated treatment showed a roughly comparable reduction in biological activity as the dry aerated.

Cellulose was essentially exhausted for every treatment during the experiment (Tables 3 and 4, Figs. 4 and 5). At the final sampling, cellulose could be detected, but not quantified for some LSR. For these cases, a final concentration of 0.015% DW was assumed (limit of detection). The acid-soluble lignin-pool ("lignin_s") increased for the aerobic treatments during the experiment (Tables 3 and 4, Figs. 4 and 5). For the anaerobic treatment the C-discharge was mainly influenced by cellulose degradation (on average 28% of gaseous C-discharge), while for the aerobic treatment cellulose-degradation constituted a much smaller fraction of the total C-discharge (on average 14% of gaseous C-discharge, Figs. 4 and 5). The C-content of cellulose was 44.4 (% DW) according to its elemental composition.

Biological tests generally revealed a significant decrease in activity over time for all treatments (Table 3). The GP_{21} also decreased substantially, but statistical significance was not tested due to the low number of observations ($n = 2/\text{treatment}$). The decrease in both, RI_4 and BOD_5 was higher for the aerated

Table 2
Initial TOC-pool and fitted parameters of the degradation model for each LSR.

Treatment	Replicate	TOC _{init}		Optimized model			Model fit	
		Mean	SD	TOC _{init} * bd	k-rate	CI	RMSE	
Unit		(g)	(g)	(% TOC _{init})	(g)	(a ⁻¹)	(g C d ⁻¹)	
Aerated wet	A	5620	312	31.7	1780	0.91	0.07	0.76
	B	4840	113	45.6	2210	0.61	0.05	0.73
Aerated dry	A	5300	98.6	31.2	1650	1.15	0.09	0.77
	B	4740	155	37.9	1800	1.12	0.09	1.01
Anaerobic	A	4280	93.2	6.27	268	10.7	0.08	0.90
	B	4590	85.4	5.42	249	14.7	0.09	0.93

Notes: All numbers were rounded accordingly. The mean and SD of the TOC-measurements are based on three replicates/LSR ($n = 3$). bd biodegradable fraction, CI confidence interval, SD standard deviation, TOC_{init} initial total organic carbon.

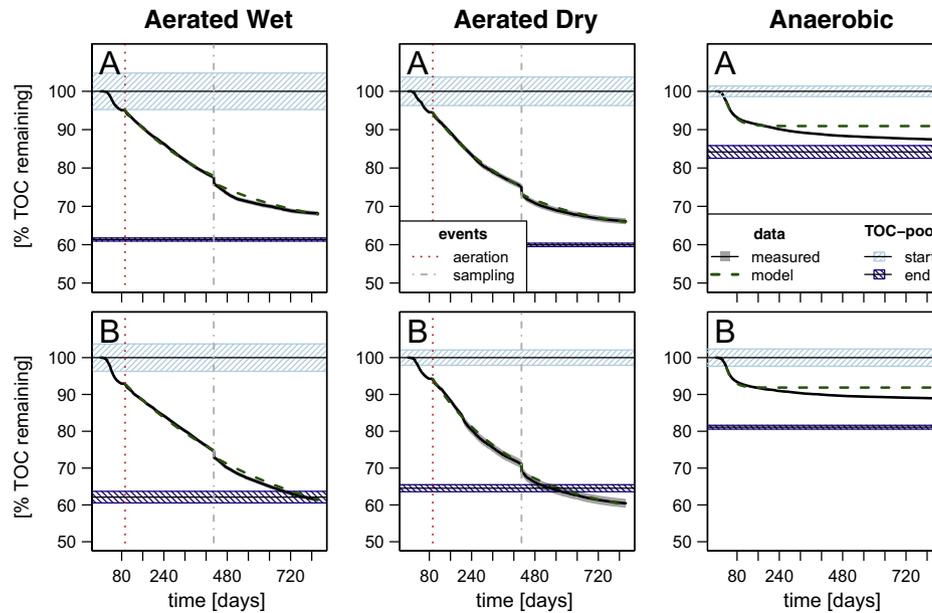


Fig. 3. Remaining TOC and TOC discharge. Notes: The letters A and B denote the respective replicates and the filled areas and grey shades denote the SD.

Table 3
Initial and final contents of the incubated waste material.

Unit	Aerated wet			Aerated dry			Anaerobic				
	2012	2014	Stat. test	2012	2014	Stat. test	2012	2014	Stat. test		
<i>Solid content</i>											
WC	(% TW)	Mean	23.3	28.7	***	23.3	21.2	***	22.8	26.9	***
	(n = 6)	SD	0.68	0.42		0.71	0.19		0.57	0.80	
TOC	(% DW)	Mean	7.55	5.15	**	7.05	4.81	***	6.67	5.55	***
	(n = 6)	SD	1.15	0.45		0.66	0.16		0.44	0.26	
Cellulose	(% DW)	Mean	0.93	0.00	(**)	0.68	0.01	(**)	0.51	0.02	(**)
	(n = 6)	SD	0.36	0.00		0.19	0.02		0.06	0.03	
"Lignin _s "	(% DW)	Mean	0.98	2.36	***	0.99	2.53	***	1.01	1.11	ns
	(n = 6)	SD	0.16	0.08		0.06	0.12		0.04	0.15	
<i>Biological testing</i>											
RL ₄	(mg O ₂ g ⁻¹ DW)	Mean	1.75	0.08	(**)	2.88	0.11	***	3.20	2.22	*
	(n = 6)	SD	0.50	0.06		0.66	0.04		0.73	0.39	
GP ₂₁	(NL kg ⁻¹ DW)	Mean	2.66	0.20	-	2.60	0.50	-	3.27	0.71	-
	(n = 2)	SD	0.93	0.11		0.52	0.21		1.15	0.00	
<i>After elution</i>											
COD	(mg L ⁻¹)	Mean	342	14.4	***	384	58.6	***	399	112	***
	(n = 6)	SD	15.2	2.26		26.3	2.88		33.4	9.44	
BOD ₅	(mg L ⁻¹)	Mean	195	1.24	***	225	2.42	***	229	37.5	***
	(n = 6)	SD	5.75	0.18		17.3	0.48		14.1	3.32	

Notes: All numbers were rounded accordingly. For improved display, mean values were indicated in bold format. The level of significant differences according to t-test (or u-test in brackets) is shown for each treatment. Significance levels: (ns $p \geq 0.05$;

* $p < 0.05$;

** $p < 0.01$;

*** $p < 0.001$). AD aerobic dry treatment, AW aerobic wet treatment, AN anaerobic treatment, BOD₅ biological oxygen demand after 5 days, COD chemical oxygen demand, DW dry weight, GP₂₁ residual gas producing potential, RL₄ respiration index after 4 days, SD standard deviation, TW total weight, WC water content.

Table 4
Cellulose and "Lignin_s" balance given in g carbon.

Replicate	(g C)	Aerated wet		Aerated dry		Anaerobic	
		Mean	SD	Mean	SD	Mean	SD
Cellulose	A	312	2.42	224	0.94	139	0.17
	B	246	0.38	181	0.10	153	0.07
"Lignin _s "	A	-529	1.52	-635	1.16	-22.3	0.58
	B	-477	0.54	-538	1.32	-54.9	1.09

Notes: All numbers were rounded accordingly. Negative values indicate an increase of substances. Loss via solid sampling for the aerated treatments was excluded. The number of measurements was 6 per treatment ($n = 6$). SD standard deviation.

treatments. The values of COD remained relatively high for the aerated dry treatment but still lower than in the anaerobic LSR (Table 3). For the anaerobic treatment the reduction of GP₂₁ was higher than the reduction of RL₄, indicating that these reactivity tests may characterize different pools of organic matter.

3.4. Mass balancing

Mass balances were established for every LSR, since the amounts of material built in and their composition slightly differed for each set-up (Fig. 4). As expected, the majority of TOC was lost via gas and only a minor amount via leachate for the irrigated

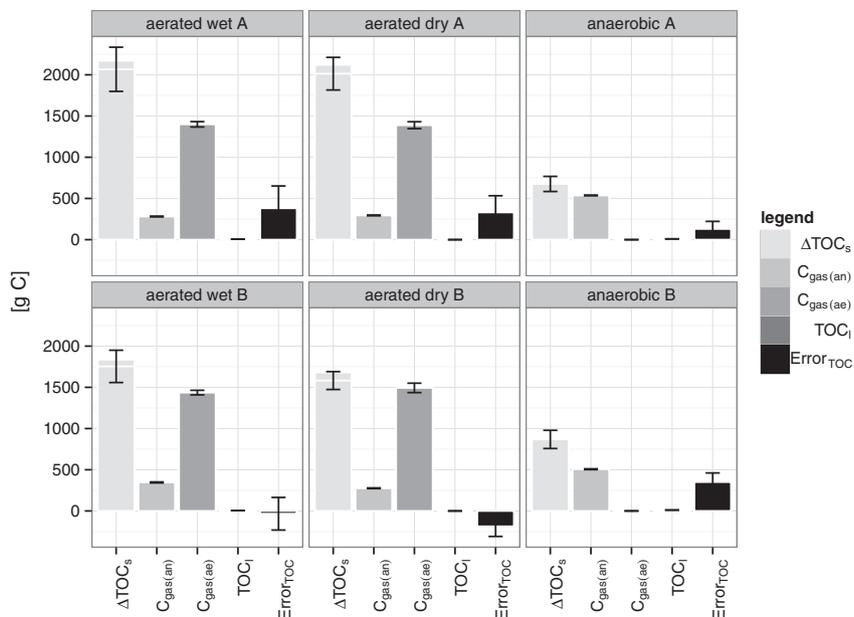


Fig. 4. Changes in the observed TOC pools and flows.

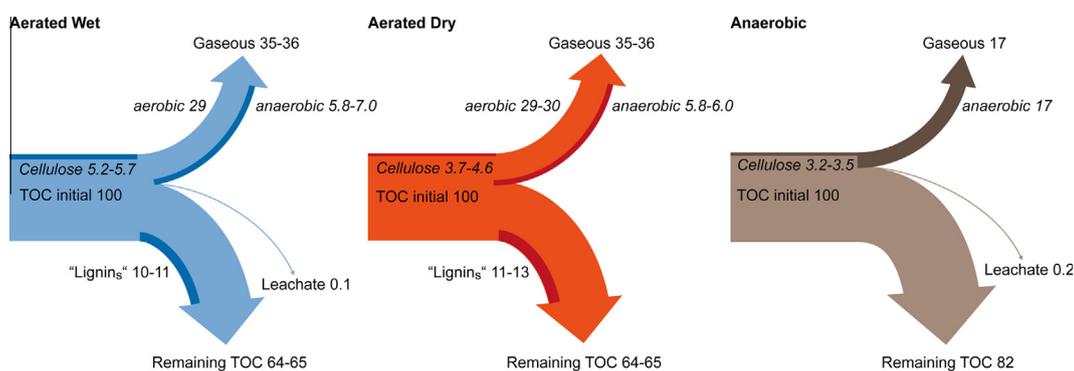


Fig. 5. Transfer coefficients for TOC into the various outputs of the treatments.

treatments with 0.3% TOC_i of ΔTOC_s for the aerated wet and 1.7% for the anaerobic treatment. The degradation for the aerobic treatments was roughly 2-fold higher than for the anaerobic treatment (relative loss TOC_{init} , Fig. 3).

Comparing solid and gaseous TOC-loss revealed that for the aerobic wet treatment the deviation between solid and gaseous losses was on average 9.4% ($\% Error_{TOC}$, Figs. 3 and 5), calculated with Eq. (4):

$$\%Error_{TOC} = \left| \frac{Error_{TOC}}{\Delta TOC_s} \right| * 100 \quad (4)$$

For the aerobic dry treatment the $\% Error_{TOC}$ was on average 4% and for the anaerobic reactors 32%. The rather high deviation of the anaerobic reactors may be attributed to some leakage of the vessels, which led also to the intrusion of N_2 into the reactors.

Notes: The tips above the ΔTOC_s represent the removal during the second sampling campaign. The figure was drawn using the R-package ggplot2 (Wickham, 2009). Negative values of the $Error_{TOC}$ indicate an overestimation of the measured flows in comparison to the solid TOC-loss. Suffixes: ae aerobic an anaerobic, g gaseous, l liquid, s solid.

Notes: Units are in% initial TOC. For the aerated treatments, the withdrawn solid samples were subtracted from the initial TOC pool. The ranges are given by the respective values from each

reactor for each treatment. The balance errors between gaseous and solid C-discharge were added to the gaseous C-discharge for the anaerobic treatment. For the aerobic treatments, they were equally (50/50) split between the gaseous losses and the remaining TOC. The dark lines indicate the respective subfractions (e.g. the share of cellulose of the initial TOC) for each flow.

4. Discussion

4.1. Data plausibility

The total TOC balance ($Error_{TOC}$) was relatively accurate for the aerobic wet treatment (with an average balance error of 207 g referred to a total loss in organic carbon of solids of about 1800 g, calculated as absolute mean), showing a high correspondence between mainly gaseous (TOC_g) and solid TOC-loss (ΔTOC_s , Fig. 4). For the aerobic dry treatment, the accuracy was slightly lower (260 g referred to a total loss in organic carbon of solids of about 1910 g, Fig. 4). For the anaerobic LSR the gap in the total TOC-balance was on average 241 g (observed loss in organic carbon of solids 770 g), with the gaseous losses most probably being underestimated due to some gas leakage from the reactors (especially #B). Given the long time period of the experiment, in particular with low gas production, some air might have

intruded and produced gas might have been lost. Especially the entrance point of the temperature sensor was extremely difficult to sustain airtight. Nonetheless, the anaerobic character of the waste material was perceivable, especially in comparison to the aerobic treatments (Fig. 6). For improving future LSR experiments it should be noted, that in particular at the very beginning of the experiment gas production was the highest. We recommend properly testing for air tightness prior to a real experiment (e.g. monitoring gas pressure inside the LSR for some time after causing a defined pressure overload).

The TOC_s showed losses from 33.4% to 38% TOC_{init} for the aerobic treatments and 15.8% to 18.9% for the anaerobic treatment. This was not in total agreement with the measured gas data, especially for the anaerobic case (as discussed above) as well as with the biodegradable fraction of the presented model. Only one compound of waste with one degradation constant was modeled, potentially leading to an underestimation of the slower degradable fraction of TOC. The here presented relatively high k-rates for the anaerobic model (Table 2) were considered as a result of the suddenly available carbon sources for microorganisms after mixing and heating the material.

Caution needs to be taken concerning the lignin data (“lignin_s”, Table 4), since the measurement of lignin poses numerous analytical problems, depending on the analyzed material and the measurement method (Hatfield and Fukushima, 2005). The herein discussed fraction of lignin was the acid soluble fraction during Klason-lignin determination, relying on UV absorption. The underlying protocol Tappi UM 250 was developed for wood chemistry. The highly heterogeneous MSW could contain organic molecules of various origins (e.g. paper, plastics ...) some of them potentially influencing the measurement. We are aware of the fact that in total lignin could not have increased during the degradation experiment. The acid soluble lignin pool is to be seen as a fraction of the total available lignin. The average C-content of lignin was considered as 62.7 (% DW) based on Kost (2001).

4.2. Anaerobic vs. aerobic degradation

For the aerobic treatments, roughly 24–25 g C kg⁻¹ DW was in total discharged via gas after 731 days according to our measurements. Literature values for similar experiments range from 12 to 19 g C kg⁻¹ DW for a duration of 342–513 days (Prantl et al., 2006), for slightly younger waste material and around 20 g C kg⁻¹ DW for an aeration period of 553 days (Ritzkowski et al., 2006).

Total anaerobic gaseous C-discharge based on measured data ranged from 7.6 to 8.1 g C kg⁻¹ DW after 823 days. Likewise, literature values from comparable experiments ranged from roughly 2.5 to 4 g C kg⁻¹ DW (Prantl et al., 2006) and about 15 g C kg⁻¹ DW for anaerobic treatments (Ritzkowski et al., 2006).

For improved comparison of aerobic and anaerobic degradation the degraded non-cellulosic TOC-pools would need a more detailed investigation. In our case, this degraded non-cellulosic C-pool contributed 86% of the total gaseous C-discharge or 1488 g C for the aerobic case and 72% of the total gaseous C-discharge or 376 g C for the anaerobic case. More sophisticated models for biodegradation under aerobic (e.g. Zhang et al., 2012) or anaerobic (e.g. Reichel et al., 2007) regimes apply different factors of biodegradability for different waste fractions. The organic waste in these models is mainly divided into lignin, hemicelluloses and cellulose. Even though the here applied model showed a reasonably good fit (Table 2), for a direct comparison of this non-cellulosic degraded fraction improved chemical knowledge about the organic compounds in the waste matrix would be necessary, in particular with respect to the determination of lignin.

The finding that the anaerobically and aerobically degradable C-pools differ in terms of quantity, quality and rate of degradation was supported by mathematical modeling (Table 2 and Figs. 2 and 3) and mass balancing (Figs. 4 and 5). In addition it could be shown, that after anaerobic incubation, the relative reduction in RL_4 was significantly smaller in comparison to the observed decrease in GP_{21} (Table 3). This was not the case the other way round: for the aerobic treatments, both RL_4 and GP_{21} were reduced. Thus, it can be deduced, that generally the anaerobic C-pool was degraded during the aerobic treatments, but not vice versa.

The acid soluble lignin fraction “lignin_s” increased for the aerobic treatments (Tables 3 and 4, Figs. 4 and 5). In addition to the previously discussed differences in carbon pool accessibility, this could indicate a transformation of organic matter to harder degradable organic compounds, and thus to some kind of stabilization of the material during in-situ aeration as was already discussed (Ritzkowski et al., 2006). Possibly the acid soluble “lignin” fraction, measured at 220 nm corresponded to some extent to the fraction of humic substances (Prantl et al., 2006), measured at 400 nm. From a visual characterization (Fig. 6), a detectable amount of browning reactions occurred in the aerobic LSR, also indicating further stabilization.

4.3. Aerated wet vs. aerated dry

Even though laboratory experiments in LSR were supposed to show an improved water distribution in comparison to the field scale experiments (Fellner et al., 2009), and the negative impact of water accumulation during field scale in-situ aeration was already discussed (Hrad et al., 2013), the slightly higher C-discharge of the dry reactors was not expected. A priori we were expecting lower degradation activity for the aerobic dry treatment compared to the aerobic wet treatment due to dry-out effects caused by continuous aeration of the LSR with dry air, since a

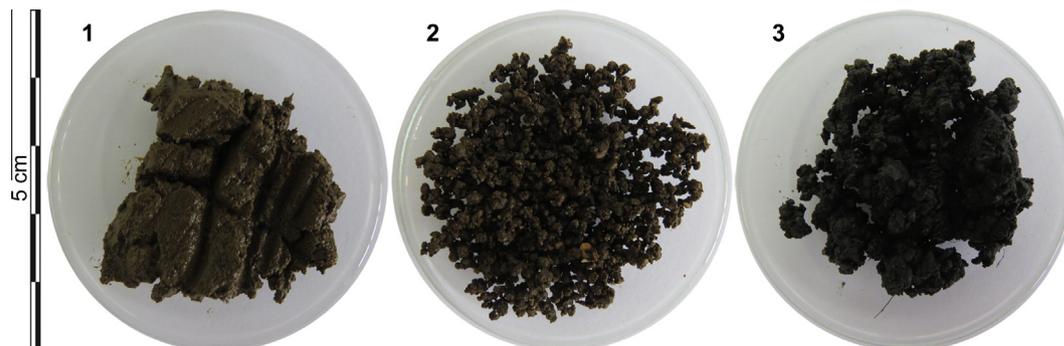


Fig. 6. Photograph of the fine fraction (<2 mm) of the material for each treatment. Notes: 1 aerated wet, 2 aerated dry, 3 anaerobic.

higher water amount is supposed to accelerate degradation (Pommier et al., 2008).

One possible explanation could be the production of H₂O under aerobic degradation. The summarized chemical reaction of aerobic cellulose degradation is as follows:



even if cellulose (and thus glucose) degradation comprised only a minor part of the total C-degradation. Transferred to mass ratios, aerobic degradation (based on cellulose) would lead to the production of roughly 56% (of cellulose mass) H₂O. For correcting the volumetric air flow of the off-gas stream in the aerated reactors we applied maximum saturation or 47.29 g H₂O m⁻³ air. That would roughly have led to an average gaseous water loss of 1860 g during the aeration. On the other hand, the production of H₂O during aerobic microbial degradation was estimated at 1741 g for the dry treatment and 1690 g for the wet treatment. Thus the H₂O production through degradation lessened the water loss for the dry treatment, sustaining a sufficiently moist atmosphere. At the final sampling campaign, the dry reactors even exhibited water-saturated layers with small water ponds being present in the waste.

Visually, the material obtained after each treatment showed different characteristics. Microbiological soil analytics require the sieving of fresh material below 2 mm, since this fraction is considered as the most active for its high surface/volume ratio. Even though the sieving turned out to be difficult for waste samples, Fig. 6 gives another potential explanation for the rather insignificant differences between the dry and wet treatment. The structure of the fine fraction of both irrigated treatments was rather smeary, especially for the aerated treatment, while the material of the aerated dry treatment showed a rather porous structure.

This observation has been confirmed by calculating the gas filled porosity of the waste at the end of the experiments. Thereto data about the bulk density of the waste, its water content,

as well as assumptions regarding the particle density of the waste (1640 kg m⁻³ according to Stoltz et al., 2010) have been used. The results of the calculations indicate that for the dry reactors the average air filled pore space amounted to 0.21 m³ m⁻³, whereas for the wet (aerobic and anaerobic) reactors a significantly lower value of 0.15 m³ m⁻³ was determined. This higher gas filled porosity of the dry waste might have led to an increased air intrusion in comparison to the aerated wet treatment and could potentially explain the comparatively improved C-discharge.

Beside microbial water production and structural differences between the aerobic treatments, the aerobic dry treatment is characterized by higher O₂ consumption rates (see Fig. 7) and thus also higher CO₂ releases in the beginning of the experiment (first 200 days after aeration start). This can again be attributed to the larger pore space accessible for gas exchange. Afterward a fast decrease of O₂ consumption in the dry reactors has been observed (200–400 days). The solid sampling campaign induced again a higher reactivity peak in the dry LSR, either implicating that the substrate in the dry reactors was less mixed and accessible for microorganisms or that dried out areas in the LSR suddenly came into contact with water.

Notes: The letters A and B denote the respective replicates. The O₂ consumption rates were calculated based on the measured O₂ concentrations as well as volumetric flows (rolling weekly average) in reference to the inlet concentration (20.5 vol.%). The units (g d⁻¹) are given either in g C for the CO₂ discharge or in g O for the O₂ consumption.

4.4. Full scale implications of the experiment

As was shown, the anaerobic and aerobic degradation differed in the degradable C-pool. At some point in the distant future, old landfills (without waste pretreatment) are considered to show a

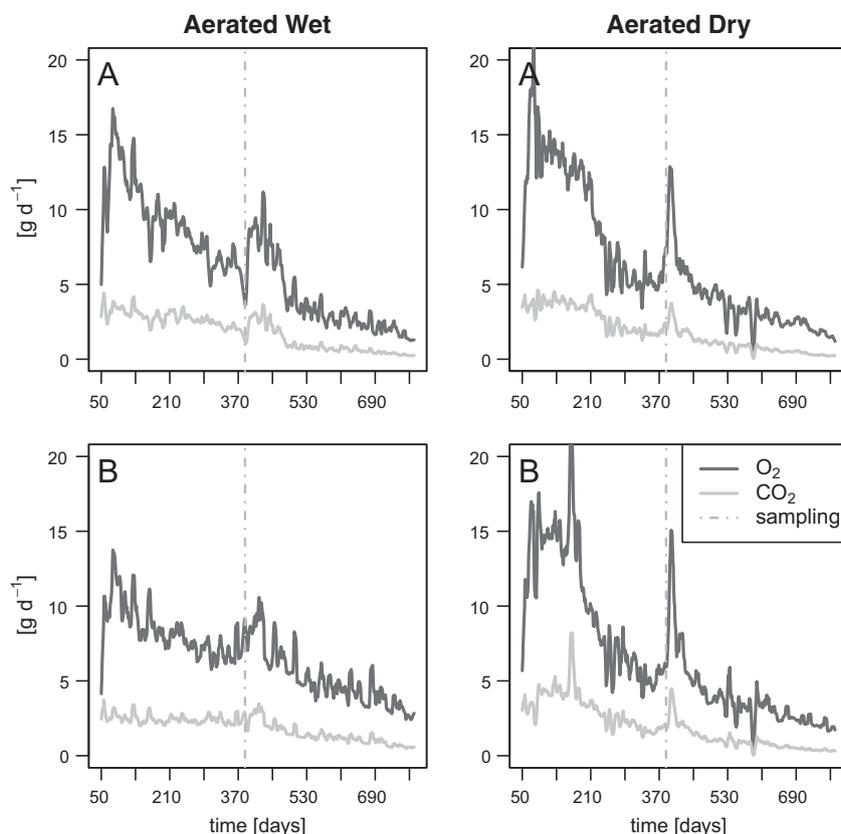


Fig. 7. O₂ consumption rates for the aerated LSR.

stage of air intrusion (Christensen et al., 1996). In accordance with our results at this stage an increased fraction of the TOC-pool would possibly become accessible for microbial degradation and thus transforming a relatively big fraction of bound carbon (sink) to gaseous CO₂ (source). Since over long time periods conditions within MSW landfill may become aerobic due to air intrusion, these CO₂ emissions would probably occur in any case. Moreover, as this CO₂ originates from biogenic matter it can be regarded as climate neutral (Ritzkowski and Stegmann, 2010). Nevertheless, a translation of the total C release during aeration into prevented LFG emissions (50% CO₂ and 50% CH₄) during anaerobic waste degradation would significantly overestimate the reduction of greenhouse emissions induced by landfill aeration.

The direct comparison of the anaerobic and aerobic gaseous C-discharge however is not fully correct, since the degraded TOC-pools for the respective cases do not entirely correspond to each other. Instead in-situ aeration projects should be evaluated in a target oriented way, depending on the desired remediation goal. This can only be achieved by customized monitoring programs during and after remediation.

Another consequence for the full scale application of in-situ aeration based on the presented results would be that the aerobic microbial activity remained high, or actually exceeded the wet treatment even under relatively dry conditions. For the field scale application, the benefits of water addition were mainly discussed for temperature control. This effect was not investigated here, since the temperature was kept at a constant level. A negative side of water accumulation in the respective landfill would be the occupation of pore space, hindering air intrusion or even blocking the gas pipes for aeration (Hrad et al., 2013; Ritzkowski and Stegmann, 2012). However, if the aeration rates exceed the microbial water production, dry out effects cannot be excluded and water intrusion might also increase the microbial accessibility of degradable substrate through mixing effects (Fellner et al., 2009).

5. Conclusions

The degradation of old waste material in LSR showed a complete exhaustion of cellulose under aerobic as well as under anaerobic conditions. The share of cellulose-C in total C discharge was higher for the anaerobic degradation. The degraded C-pools differed mainly between the aerobic and anaerobic treatment, questioning their direct comparability. This finding also might affect future carbon emissions of old landfills after air intrusion and thus be relevant for determining the fraction of organic carbon sequestered (on the long term) in landfills.

Improved characterization of the TOC-pool before and during the degradation of MSW would be necessary for improved assessment of long term benefits or drawbacks of aeration with respect to C release and sequestration. According to the here discussed results, some parts of the anaerobically degraded TOC are also degraded aerobically, but apparently not vice versa. Under the aerobic treatment further transformation of the organic carbon pool was observed in terms of “lignin_s” increase and browning reactions. The addition of water to the aerobic treatment did not increase the gaseous C-discharge under the operational conditions and the rather old waste material of the presented study.

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Appendix III. Nitrogen pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes (submitted)

Nitrogen pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes

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Abstract

Nitrogen emissions from municipal solid waste (MSW) landfills occur primarily via leachate, where they pose a long-term pollution problem in the form of ammonium. In-situ aeration was proposed as a remediation measure to mitigate nitrogenous landfill emissions, turning the anaerobic environment to anoxic and subsequently aerobic. As in-depth studies of the nitrogen cycle during landfill aeration had been largely missing, it was the aim of this work to establish a detailed nitrogen balance for aerobic and anaerobic degradation of landfilled MSW based on lab-scale experiments, and also investigating the effect of different water regimes on nitrogen transformation during aeration. Six landfill simulation reactors were operated in duplicate under different conditions: aerated wet (with water addition and recirculation), aerated dry (without water addition) and anaerobic (wet). The results showed that more than 78% of the initial total nitrogen (TN_{init}) remained in the solids in all set ups, with the highest nitrogen losses achieved with water addition during aeration. In this case, gaseous nitrogen losses (as N_2 due to denitrification) amounted up to 18% of TN_{init} and around 4% of TN_{init} was discharged via leachate. The aerated dry set-up showed lower denitrification rates (6-12% of TN_{init} was released as N_2), but was associated with the highest N_2O emissions. For the anaerobic treatment the main pathway of nitrogen discharge was the leachate, where NH_4 accounted for around 8% of TN_{init} . These findings provide the basis for improved management strategies to enhance nitrogen removal during in-situ aeration of old landfills.

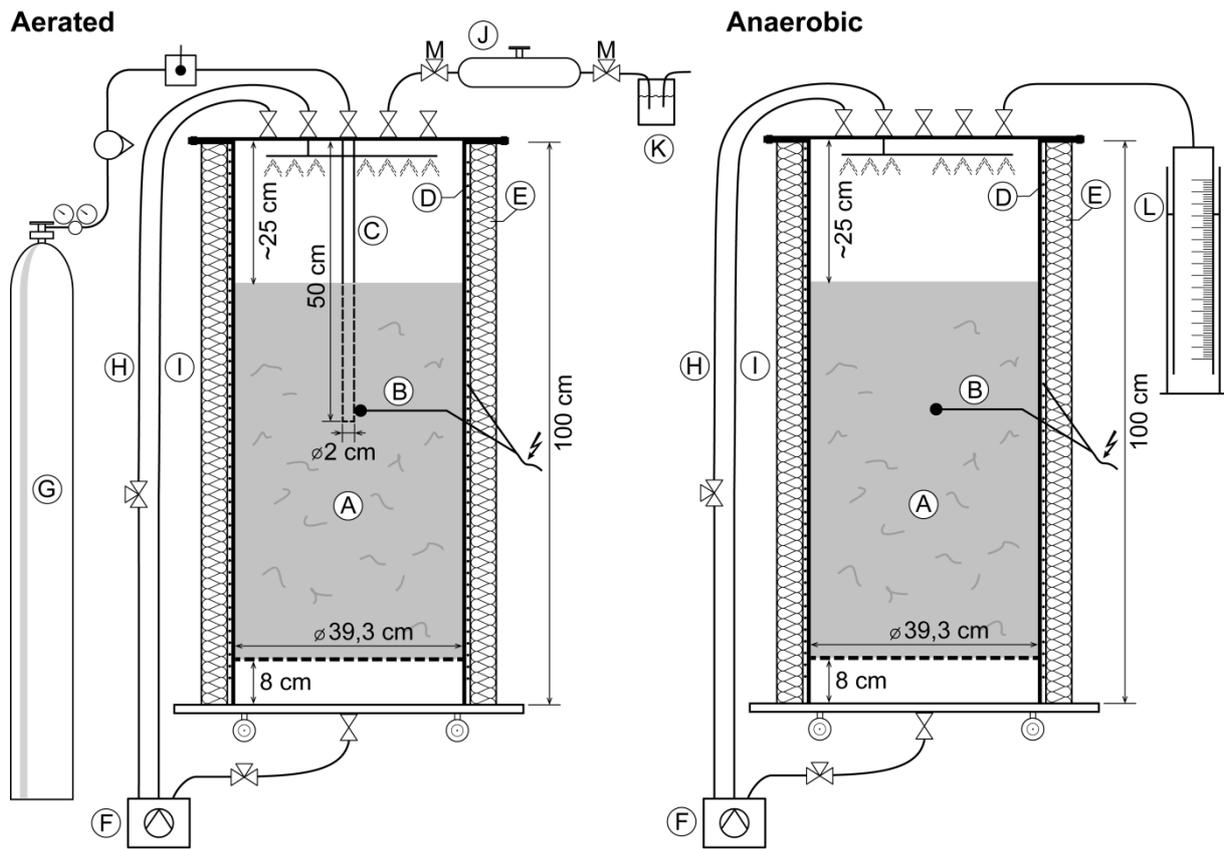
Keywords: Denitrification, In-situ aeration, Landfill, Municipal solid waste, Nitrogen, Nitrous oxide

1. Introduction

Old municipal solid waste (MSW) landfills pose a significant threat to human health and environment, mainly in the form of gaseous and leachate emissions. Gaseous emissions of landfills are mainly discussed for their carbon release (CH_4 and CO_2) but also N_2O has come increasingly into focus due to its high greenhouse gas potential (Rinne et al. 2005). Also for the leachate emissions nitrogen plays a dominating role, as released NH_4 is known to cause toxic effects and increase the eutrophication potential of water systems (Thomsen et al. 2012). In anaerobic landfills NH_4 is accumulating and discharged mainly via landfill leachate. While MSW landfills remain largely anaerobic as long as degradable organic matter is present, some aerobic micro-environments may exist due to air intrusion (Jung et al. 2011) and on the very long term (thousands of years) oxygen diffusion has been speculated to turn the landfill environment aerobic (Bozkurt et al. 2000) Christensen et al. 1996). Apart from natural processes, the forced aeration of landfills has been put forward as method measure for in-situ stabilization of older landfills containing organic wastes (e.g. Heyer et al. 1999; Prantl et al. 2006; Ritzkowski et al. 2006; Ritzkowski and Stegmann 2012). During in-situ aeration, the oxidation of a formerly anaerobic landfill body affects the degradation of organic matter and thereby also nitrogen transformation processes (Fig. 1) towards increased nitrification (Prantl et al. 2006), nitrous oxide formation (Rinne et al. 2005), and, hypothetically, increased microbial uptake (Fellner and Laner 2011). A simplified overview of the nitrogen cycle with respect to landfills is given in Fig. 1, where different line types indicate different nitrogen pathways. Unlike in natural ecosystems, organic input is terminated after landfill closure, thus the waste material is the primary nitrogen input, with an unclear contribution of nitrogen fixation (Bodelier and Steenbergh 2014). In the strict anaerobic case NH_4 would accumulate in the landfill if not discharged via leachate while upon oxygen availability (aerobic or anoxic), the nitrification pathway becomes possible.

Mobile water plays a crucial role for the degradation of organic matter in MSW landfills (Bookter and Ham 1982). With respect to in-situ aeration, positive and negative effects of water phases on waste stabilization were observed: whereas high moisture content is supposed to accelerate aerobic degradation in general (Pommier et al. 2008), too much water hinders the introduced air to occupy a substantial part of the deposited waste's pore space (Ritzkowski and Stegmann 2012). Whereas nitrogen cycles have been investigated for different environments (e.g. in river systems N_2O formation is favored under regimes of moderate oxidation (Shcherbak et al. 2014)), hardly any studies put a focus on the role of the water regime for nitrogen transformation processes during landfill in-situ aeration (Lubberding et al. 2010; Prantl et al. 2006; Valencia et al. 2009). So far, investigations addressing the fate of nitrogen mainly focused on in-situ aeration as a strategy to lower the concentration of NH_4 in landfill leachate, with numerous reports of significant NH_4 reduction in landfill leachate during and after in-situ aeration (e.g. Hao et al. 2010; Hrad et al. 2013; Prantl et al. 2006; Ritzkowski et al. 2006). The observed reduced nitrogen concentrations were explained by nitrification and denitrification processes within the waste body (Berge et al. 2006; He et al. 2006; Onay and Pohland 1998; Price et al. 2003; Vigneron et al. 2007). Therefore, nitrogen balances distinguishing major pools and flows during in-situ aeration of landfills, have not been accomplished or on an aggregate level only (Lubberding et al. 2010; Valencia et al. 2009) due to various reasons impeding detailed nitrogen balances (Berge et al. 2006; Fellner and Laner 2011; Ritzkowski 2005).

It is the goal of this study to provide a detailed nitrogen balance for aerobic and anaerobic degradation of landfilled MSW based on lab-scale experiments. Apart from mapping the flows and pools of various nitrogen species, we also investigate the effect of different water regimes on nitrogen transformation during in-situ aeration. Thereto, six landfill simulation reactors (LSR) were set up and operated pair-wise (replicates) under different conditions: two were operated aerobically with leachate



Legend

- | | | |
|------------------------|--------------------------------|-------------------------|
| (A) Waste Material | (G) Gas flask (synth. air) | ⊗ One-way valve |
| (B) Temperature sensor | (H) Irrigation tube | ⊕ Two-way valve |
| (C) Aeration pipe | (I) Pressure equalization tube | M Gas measurement point |
| (D) Heating wire | (J) Gas sampling pipe | ⊙ Submerged pump |
| (E) Insulation wool | (K) Gas-washing bottle | ⊖ Rotameter |
| (F) Pump well | (L) Eudiometer | □ Mass flow meter |

Fig.2 Schematic cross sections of the landfill simulation reactors (LSR). The LSR of the aerated treatments were identical, except that the aerated dry treatment did not contain the elements F, H and I.

2.1. Origin of the waste material

The waste material was gathered from an old landfill containing approximately 220,000 m³ (fresh matter) of waste with an average deposition height of 3.7 m. The landfilled waste mainly consisted of MSW (66% moist mass), but also excavated soil and construction and demolition waste as described in Brandstätter et al. (2015). Landfilling took place at the site from 1965 to 1974. The excavated material was sieved with a mesh width of 20 mm. Before placing the material into the respective LSR, the total amount of waste material (~430 kg) was pooled and thoroughly mixed with shovels. The material was selected from landfill areas comparatively rich in organics, since one aim of the experiment was to determine the degradation potential of the waste (Landfill A, Brandstätter et al. 2014).

2.2. Landfill simulation reactor experiments

The experimental vessels consisted of stainless steel with an internal volume of 121 L. Three experimental conditions (treatments, each with two replicates) were applied: the waste material was either aerated with leachate recirculation (aerated wet), or aerated without leachate recirculation (aerated dry) or kept anaerobic with leachate recirculation (anaerobic, see Table 1). The material was aerated from top for the aerated treatments and leachate was allowed to accumulate in the LSR bottom (landfill simulation reactor(s)). Only for recirculation and sampling the bottom valve to the leachate reservoir was opened. To prevent water accumulation in the waste material itself, the waste material was placed on top of a permeable fine meshed grid (mesh width ~ 2 mm) located 8 cm from the bottom of the vessels.

The temperature was controlled with a thermostat having the sensor placed in the center of the waste material and the LSR were coated with insulation wool of 2 cm thickness (Fig. 2). The experimental design was explained in greater detail elsewhere (Brandstätter et al. 2015). For the aeration treatments synthetic air was introduced via gas flasks (compressed air, UN 1002; Messer, Austria). The flow rates were measured with digital mass flow meters (0-0.05 NL min⁻¹, EM1NH, Sensirion AG, Switzerland) and controlled via various pressure reducing valves. The aeration rate was roughly controlled according to off-gas CO₂ and O₂ concentrations. Since the respiratory activity decreased over time, the aeration rate was reduced from about 40 to 30 ml h⁻¹ after 306 days of operation.

The control program for the mass flow meters was written with the software Processing (ver. 1.5.1, Processing Foundation, 2012). The off-gas was discharged through gas washing flasks containing H₂SO₄ at pH 2 for stripping of NH₃. For irrigation, deionized water was added in the first week of operation until field capacity was reached, and afterwards to replace the sample leachate and to maintain constant water content over time. The amounts of added water and synthetic air are presented in Table 2.

2.3. Analytical methods

2.3.1. Gas measurements

Nitrous oxide (N₂O) samples were taken in the off-gas of the aerated reactors with a glass syringe in a gas sampling pipe using a septum. For the anaerobic case, samples were directly taken from eudiometers (devices to measure the amount of gas produced), or if no gas production occurred between two sampling times directly from the reactors. The samples were put into evacuated glass vials with aluminum caps and rubber stoppers (20 ml) under slight over pressure and after sealing with silicone stored at 4°C upon measurement. In total 52 N₂O samples were taken per reactor with five missing for the anaerobic treatment (between 200 and 270 days).

The concentrations of N₂O were determined in two laboratories. In the first laboratory, a GC-system (HP 5890 Series II, USA) with a ⁶³Ni-electron-capture detector (ECD) was used (Kitzler et al. 2006), connected to an automatic sample-injection system (DANI Instruments HSS 86.50, Italy). The oven temperature was 330°C and N₂ was applied as carrier gas. For cross evaluation of the results from the first laboratory at selected time points, in the second laboratory a GC-MS system was used (Thermo Scientific DSQ II Series Single Quadrupole GC/MS, USA). This validation was only applied for selected time points of the aerated LSR.

The amount of off-gas was determined for the aerated treatments continuously at the inlet site and for the anaerobic treatment at discrete time events (in total 350 times) at the outlet. Since the gas concentrations were measured at the outlet and the volumetric flow at the inlet for the aerated treatments, the volumetric flow of the off-gas had to be corrected for water uptake leading to an increase of roughly 5 %. For calculating the loading of N₂O, the N₂O measurements were linearly

interpolated between the single measurements and multiplied by the gas flow measurements of the respective LSR. For determining gaseous NH₃ losses for the aerated treatments the acidic liquid in the gas washing flasks was replaced ten times during the whole experiment and analyzed for NH₄-content according to the German Standard DIN EN ISO 11732 (CFA Section 4, 2005). For the anaerobic treatment the off-gas NH₃ concentration was monthly analyzed with Dräger tubes (Type: Ammoniac 2/a, measuring range from 2 to 30 ppm NH₃).

2.3.2. Leachate measurements

For the wet treatments, the leachate was recirculated after measuring the gas concentrations in the off-gas with a mobile device (mainly related to the C-cycle: see Brandstätter et. al. 2015). The leachate was typically allowed to percolate at least 16 h before sampling, thus ensuring comparable conditions and quantities for each leachate sample over the duration of the whole experiment. The leachate then could accumulate at the bottom of the LSR, until the respective valve at the LSR bottom was opened for leachate withdrawal. After the leachate accumulated in the pump well (see Fig. 1), it was either recirculated without sampling (in total 350 times) or removed (27 times) during a sampling event with the leachate pump and subsequently replaced with deionized water.

Leachate concentrations were analyzed for NH₄, NO₃ (or, more precisely NH₄⁺ and NO₃⁻) and TN concentrations according to the German standards DIN EN ISO 11732 (CFA Section 4, 2005), DIN EN ISO 13395 (1996) and TN DIN EN ISO 11905-1 (1998) respectively, using a continuous flow analyzer (Skalar Analytical, B.V., Netherlands). The concentration of biological oxygen demand after 5 days (BOD₅) was determined according to DIN 1899-1 (1998).

2.3.3. Solid measurements

Solid samples (n=3/LSR) were taken and analyzed at three time points: initially, after 389 days and at the end of the experiment. They were analyzed for TN by combustion (MACRO CHNS Analysator, Elementar Analysensysteme, Germany). Beforehand, the samples were dried at 105 ° C for 24 hours for determining the water content (WC) and consequently ball milled and sieved (0.5 mm mesh width). Elution tests were performed in accordance with the Austrian Standard ÖNORM S 2115 (24 h contact time, mass ratio of waste dry mass (DM) to water 1:10) and for determining the nitrogen species NH₄, NO₃ and TN the same methods as for the leachate were applied.

Additionally, a KCl elution experiment was performed with solid material from the final sampling campaign. The rationale was to assess the amount of NH₄ bound via ionic bonds to the waste material and thus the actual contribution of NH₄ to the whole TN. Thus the elution was performed in a comparable manner to the aqueous elution, but with 3 M KCl as an elution agent instead.

2.4. Calculations

2.4.1. N₂O-discharge via gas

For calculating the N₂O-discharge, the general gas equation (eq. 1) was applied for each discretized time unit:

$$n = \frac{RT}{pV} \quad (1)$$

with n as the amount of N₂O-N ([mol]; 1 mol N₂ = 28 g for each mole N₂O), R as the universal gas constant 8.314 [J mol⁻¹ K⁻¹], T as the LSR core temperature [°K], p as the atmospheric pressure 101,325 [Pa] and V [m³] as the volumetric fraction (concentration * volumetric flow/time; c[N₂O] * \dot{V})

for a certain time unit. For the anaerobic case, the volumetric fraction was the product of the amount of landfill gas generated and the respective N₂O concentration.

2.4.2. Mass Balancing

The mass balance for the solid content of TN was calculated as difference between start and end of the experiment (denoted as ΔTN_s). For the aerated treatments the TN removal due to the sampling of solid waste (after 389 days) has been accounted for in the presented balances. Similar to the calculation of the discharged N₂O, the TN discharge via leachate was calculated as the total amount of withdrawn water * TN concentration (TN_l).

The total TN-balance for each LSR was calculated according to equation 2:

$$BD_{TN} = \Delta TN_s - TN_{\text{sampling}} - TN_l - N_2O - NH_3 \quad (2)$$

with BD_{TN} (balance deviation TN) representing the total TN balance difference between the measured solid, gaseous and liquid phases, ΔTN_s the loss of solid TN (initial - final), TN_{sampling} removal of TN due to the sampling of waste for the aerated treatments, TN_l the TN-discharge via leachate, and N₂O and NH₃ for measured gaseous losses with all units being [g N]. The TN measured in the leachate TN_l , consisted of inorganic (TIN = NH₄+NO₃) and organic nitrogen (TON), thus potential losses as amino acids or proteins were accounted for. Nitrogen from particulate organic matter (POM) was not detected, but was of little importance in the presented experimental setup. Only in the beginning of the experiment small amounts of POM could be detected in the leachate. Therefore, and due to the fine mesh where the material was placed upon, the total loss of POM over the whole experiment was estimated to be less than 10 g per LSR.

For assessing the contribution of inorganic nitrogen (NH₄+NO₃) to the TN_s at the start and at the end of the experiment, NH₄ and NO₃ measurements from the aqueous elution tests were considered. By relating the absolute N balance (Fig. 7) to the initial TN_s content, a direct comparison for individual flows was presented (Fig. 8). The unaccounted nitrogen loss (= BD_{TN} in equation 2) is assumed to be N₂. Given the knowledge about the other N-fluxes and pools, N₂ release due to denitrification can be indirectly determined using mass balancing (Groffman et al. 2006). This is the case in the presented highly controlled laboratory setup. Gaseous NO was not measured because it is considered to be insignificant, generated as an intermediate product of either N₂O or N₂ production (Fig. 1) with generated amounts being 1/10th to 1/20th of N₂O production (Chapin III et al. 2002, p. 211).

2.4.3. Error calculation

In general, uncertainties due to measurement errors were considered in the mass balances. All measurement errors are assumed to be independent and normally distributed with zero mean and given by the standard deviations. Gaussian error propagation was used to determine the uncertainty of the nitrogen flows and pools concerning data for the liquid and solid phases.

For the solids measurements, errors were determined by calculating the experimentally estimated standard deviations of the mean values for TNs and respective amounts of dry matter for each LSR and time point. For the leachate measurements, a relative standard deviation of 5% was assumed for the water amount removed as well as for the concentrations of each nitrogen species, since no replicates were available. For the gaseous nitrogen losses (N₂O and NH₃) an overall error of 5 % (rel.) was applied. More precise estimates would not be warranted in view of their minor importance for the total N mass balance.

2.4.4. Statistical testing and visualization

All statistical tests (Student's t-tests and Mann-Whitney-U-tests) were calculated with the statistical software R (ver. 3.1.0, R Core Team 2014) which was also used for visualization (Figs. 3-7 and 9). For Fig. 7, the package ggplot2 was used (Wickham 2009).

Table 1 Landfill simulation reactors: treatments and sampling

Treatment Replicate	Aerated wet		Aerated dry		Anaerobic	
	#A	#B	#A	#B	#A	#B
Aeration	yes	yes	yes	yes	no	no
Leachate addition and recirculation	yes	yes	no	no	yes	yes
In between solid sampling	yes	yes	yes	yes	no	no
Solid and eluted samples taken per sampling campaign	3	3	3	3	3	3
Total solid and eluted samples taken	9	9	9	9	6	6
N ₂ O samples taken	52	52	52	52	52	52
Leachate samples taken	27	27	0	0	27	27

Table 2 Landfill simulation reactors: operational data

Treatment Replicate	Unit	Aerated wet		Aerated dry		Anaerobic	
		#A	#B	#A	#B	#A	#B
Operational volume	[dm ³]	121	121	121	121	121	121
Initial waste mass	[kg FW]	68.8	69.8	72.6	69.6	66.4	66.6
Initial waste volume	[dm ³]	82.2	82.2	83.1	83.7	79.2	78.8
Initial amount of TN	[g]	251	220	236	239	216	215
Average core temperature	[°C]	36.1	36.2	36.2	36.2	35.6	35.0
Anaerobic period	[d]	92	92	92	92	823	823
Aerobic period	[d]	731	731	731	731	0	0
Total air-Inflow	[Nm ³]	39.7	40.1	38.6	39.1	0	0
Total fresh water addition	[dm ³]	54.3	54.2	0	0	52.5	53.1
Total water recirculated	[dm ³]	776	776	0	0	616	616

Notes: FW fresh weight, TN total nitrogen.

3. Results

3.1. Leachate development

Leachate concentration data exist for two aerated and two anaerobic LSR (see Fig. 3). The NH_4 concentrations decreased rapidly after aeration start for the aerated wet treatment and slightly decreased over time for the anaerobic treatment. The NO_3 concentrations remained low for the longest time for the aerated wet treatment, with a strong increase after 400 days, reaching a maximum value of $\sim 10 \text{ mg N kg}^{-1} \text{ DW}$ at the end of the experiment. For the anaerobic LSR the maximum NO_3 concentration was reached at the end of the experiment as well with $0.1 \text{ mg N kg}^{-1} \text{ DW}$. The leachate TN mainly consisted of the inorganic nitrogen compounds for all treatments, with NH_4 dominating in the anaerobic and in the beginning of the aerated treatment. For the aerated wet treatment the concentrations of NO_3 were prevailing at the end. The BOD_5 decreased fast for the wet treatments (see aerated wet, Fig. 4). It could be observed, that when BOD_5 was high no NO_3 was available and vice versa (Fig. 4).

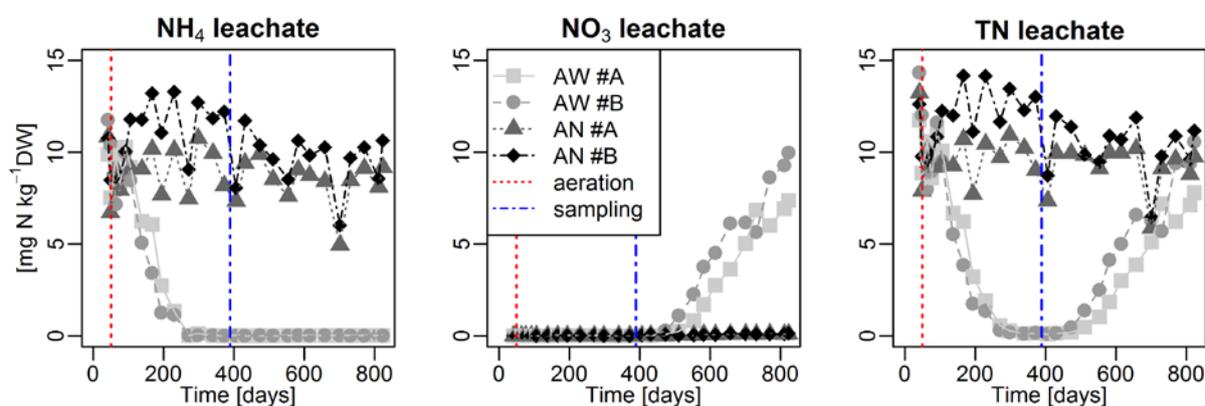


Fig. 3 Specific discharge of nitrogen species via leachate during the experiment

Notes: AN anaerobic, AW aerated wet, DW dry weight, TN total nitrogen

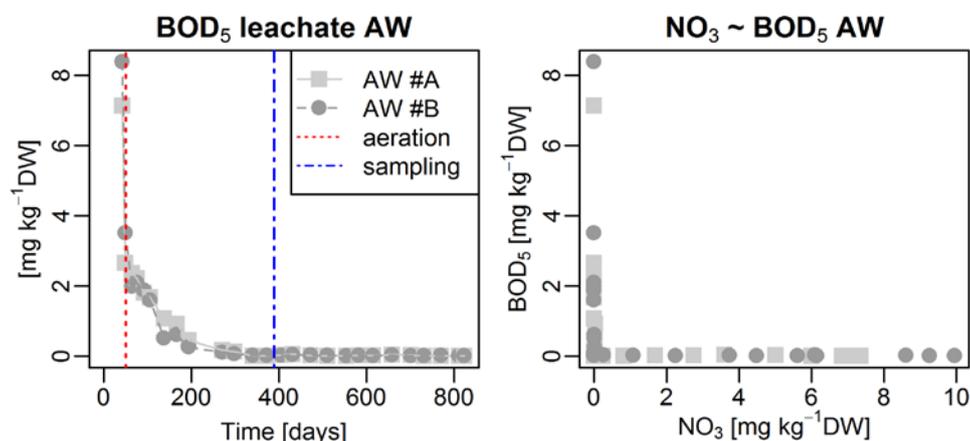


Fig. 4 Biological oxygen demand after 5 days (BOD_5) discharge plotted (left) over time and (right) over NO_3 discharge for the aerated wet treatment

Notes: AW aerated wet, DW dry weight

3.2. Nitrous oxide

Nitrous oxide concentrations in the off-gas were highest for the aerated dry treatment, and in general lower for the anaerobic treatment (Fig. 5). For the dry aerated LSR the N_2O concentrations were highest for the first measurement after the solid sampling campaign (meaning 17 days after 389 days after the experiment start), with 2,480 ppm (maximum averaged for both replicates) in comparison to

the aerated wet treatment (235 ppm) with maximum levels rather in the beginning (# A) or with a delay after the solid sampling (# B). The N₂O measurements from both laboratories corresponded reasonably well to each other. For the anaerobic LSR, the highest peaks occurred after 445-500 days (averaged maximum for both replicates with 98 ppm). While the aerated dry treatment showed a strong decrease, especially after the solid sampling campaign, the N₂O formation remained at a comparably stable level for the aerated wet treatment. Since the measurements of the N₂O concentrations were interpolated with the continuous gas flow measurements, the discrete GC-sampling might have not given the full picture of the development of the N₂O emissions and certain peaks might have eluded detection. For achieving higher measurement accuracy, a continuous N₂O-measurement system would be recommended.

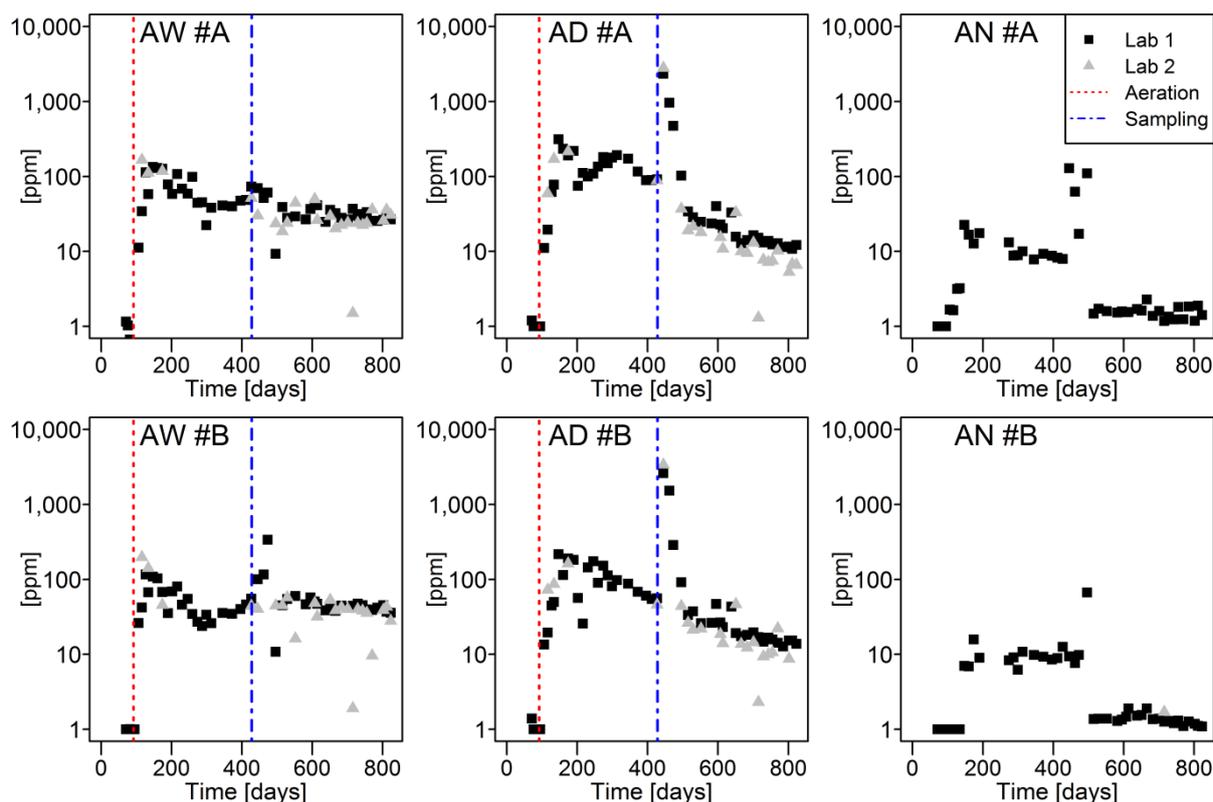


Fig. 5 Gaseous N₂O emissions

Notes: The numbers #A and #B denote respective replicates. AD aerated dry, AN anaerobic, AW aerated wet

3.3. Aqueous elution experiment

The concentrations of eluted NO₃ and TN increased significantly for the aerated dry treatment from start to end point (Fig. 6). For the aerated wet treatment, NH₄ decreased, NO₃ increased and TN decreased significantly. The anaerobic treatment showed a slight decrease in TN, but no significant changes for NH₄ and NO₃. The observations from the eluted nitrogen species corresponded well on a qualitative base to the leachate behavior of the wet treatments (Fig. 3). The measured leachate concentrations however were generally much lower than the concentrations from the elution experiments.

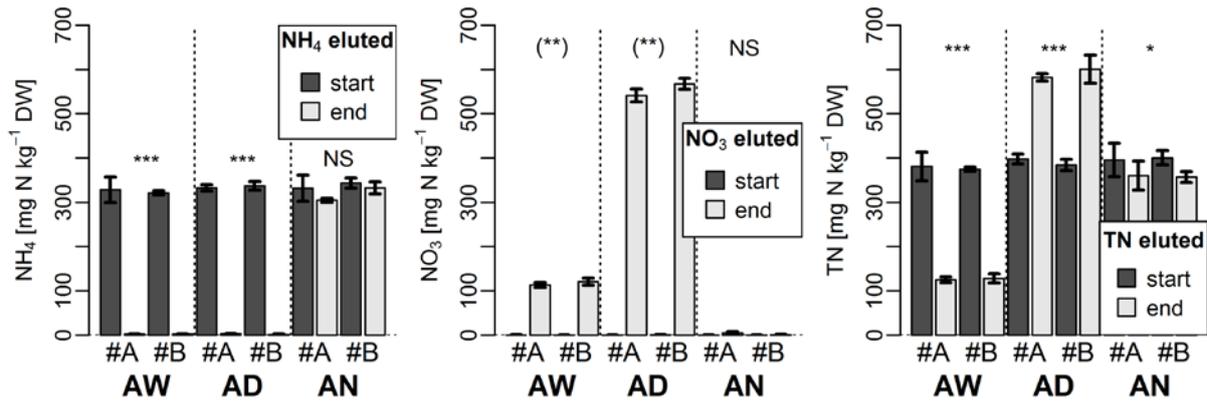


Fig. 6 Eluate concentrations for different N-species after aqueous elution

Notes: Statistical testing (Student's t-test, or Mann-Whitney-U-test in brackets) indicated differences between start and end time for each treatment (n=6). Significance levels: (ns $p \geq 0.05$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$). The numbers #A and #B denote respective replicates. AD aerated dry treatment, AN anaerobic treatment, AW aerated wet treatment

3.4. Nitrogen Balance and transfer coefficients

The overall nitrogen losses in the solid phase (ΔTN_s , Fig. 7) were highest for the aerated wet treatment. From the measured flows, the nitrogen loss via leachate (TN_l) played a minor role for the aerated wet treatment while being the dominating discharge pathway for the anaerobic treatment. In the aerated LSR the concentrations of TN_l were lower for a long time period (Fig. 3), as was consequently the nitrogen discharge via leachate. The N loss as N_2O and NH_3 via gas phase was found to be minimal for all treatments (Fig. 7), with highest losses of NH_3 for the aerated dry treatments.

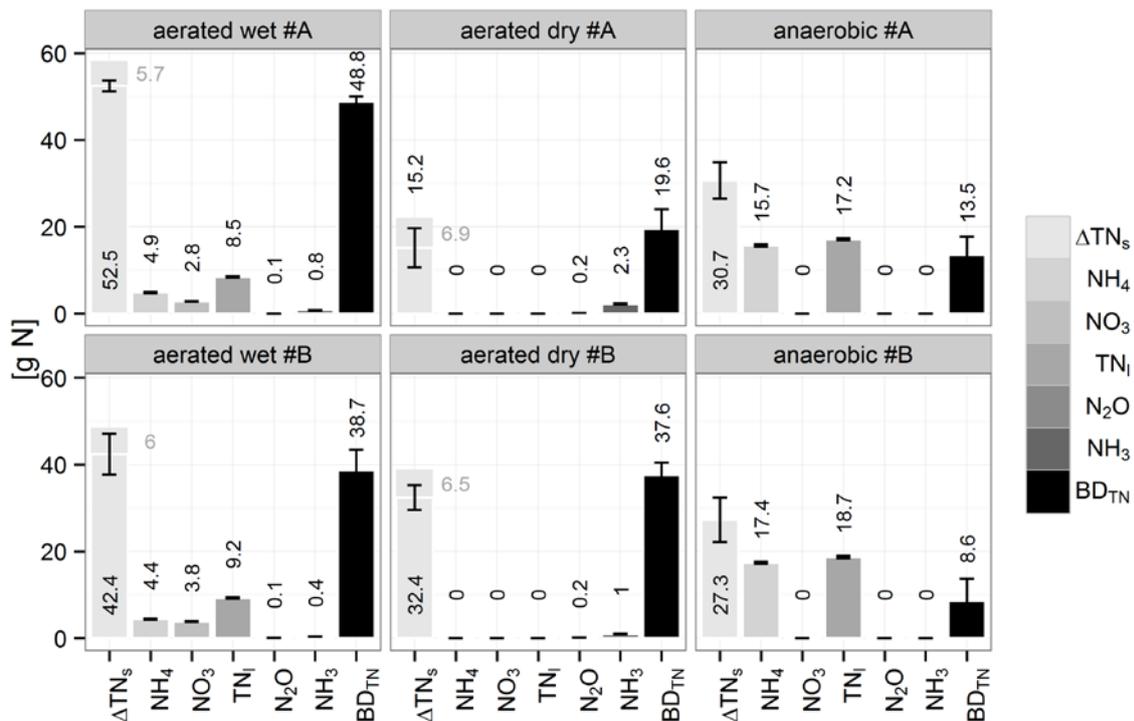


Fig. 7 Nitrogen balance of the LSR experiment (absolute values)

Notes: The numbers #A and #B denote respective replicates. The tips above the TN_s represent the removal during the second sampling campaign (amount denoted horizontally in grey). The indicated amounts for the ΔTN_s are without sampling loss. The losses of aqueous NO_3 and NH_4 are included in the TN_i for balancing (not to double-count) and are displayed for comparison only. Suffices: s solid, l liquid. BD_{TN} balance deviation, TN total nitrogen.

Interpreting the gap between of the total nitrogen balance (BD_{TN}) as gaseous N_2 loss revealed that for the aerated wet treatment the N_2 losses were highest (~17-18 % TN_{init} , Fig. 8) followed by the aerated dry (~7-13 % TN_{init}) and anaerobic treatment (4-6 % TN_{init}). For all the treatments the majority of the nitrogen remained in the solids at the end of the experiment (Fig. 8, accordingly 78, 90 and 87 % TN_{init} averaged for the aerated wet, aerated dry and anaerobic treatment). The initial TN_s did not contain NO_3 , but 10 % TN_{init} NH_4 detected after aqueous elution, and the final TN_s contained on average 9.7 % TN_{init} NH_4 for the anaerobic treatment and none for the aerated treatments. Concerning NO_3 , the final content of TN_s varied between 0 % TN_{init} for the anaerobic treatment, 3.3 % TN_{init} for the aerated wet and 15.5 % TN_{init} for the aerated dry treatment (Fig. 8).

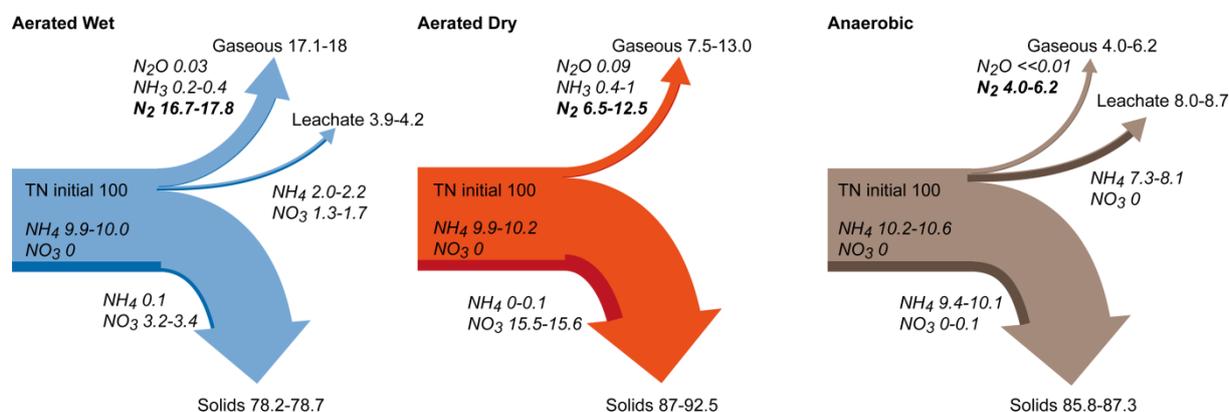


Fig. 8 Transfer coefficients for TN into the various outputs

Notes: Units are in % initial TN. For the aerated treatments, the withdrawn solid samples were subtracted from the initial TN pool. The ranges are given by the respective values from each reactor for each treatment. The gaseous N_2 flow (bold and italic) was calculated as difference between solid TN loss on the one hand and gaseous/leachate losses on the other hand. TN total nitrogen

4. Discussion

4.1. Data plausibility

4.1.1. Mass balance

Major nitrogen flows and pools were assessed, at least indirectly. For directly assessing the nitrification/denitrification pathways at different experimental in-situ aeration stages, more sophisticated experimental methods like stable isotopes (e.g. Dawson et al. 2002) would be required. The focus in this work was however to provide net nitrogen balances during the in-situ aeration of MSW.

On the input side N-fixation was not investigated whose contribution to the general N-cycle of landfills is yet to be investigated (Bodelier and Steenbergh 2014). Potential N-fixation would have increased the TN_s during the experiment but there was no indication of increase; at most N fixation could have led to an underestimation of the calculated contribution to denitrification by reducing the ΔTN_s . Nitrogen fixation depends on the enzyme nitrogenase, which is denatured in the presence of O_2

(Chapin III et al. 2002, p. 198) making a pronounced activity at least for the aerated treatments unlikely.

The rather long retention times for the leachate after a recirculation event had a strong impact on the nitrogen balance. The observation of NO_3 only being able to accumulate after BOD_5 depletion (Fig. 4) suggests that carbohydrates collected during leachate recirculation were exhausted during denitrification in the leachate itself. If the leachate had been collected directly after recirculation, higher concentration levels of NO_3 and BOD_5 would have been detected simultaneously. Accordingly, we believe that the relatively long time spans between the recirculation and the sampling events of at least 16 h for every leachate sampling induced conditions beneficial for denitrification.

Over the time course of experiment (823 days) 52 N_2O -samples for analysis for the aerated and 47 for the anaerobic LSR were taken. With the here presented interpolation, the contribution of N_2O to the overall nitrogen balance was found to be insignificant, as in total 66, 210 or 0.8 mg $\text{N}_2\text{O-N}$ were emitted for the aerated wet, aerated dry and anaerobic treatment averaged for both replicates respectively. Gaseous NH_3 was stripped continuously for the aerated cases thus providing a complete detection. The discrete leachate and solid sampling also allowed for complete balances, with the variation for the ΔTN_s being highest in comparison to the other flows (Fig. 7).

4.1.2. Anaerobic setup

During a completely anaerobic setup, denitrification or anammox would not be possible, since both pathways require partly oxidized nitrogen compounds (Fig. 1). For the anaerobic treatment in the presented case a gaseous N_2 nitrogen loss of roughly 5 % was detected, indicating that the anaerobic treatment was not entirely anaerobic, but sometimes anoxic. Especially for the later stages of the experiment, the landfill gas production markedly decreased and the gas measurement frequency was reduced. Leachate recirculation intervals were extended at the same time, to lower potential oxygen intake into the reactors. As the leachate concentrations of NO_3 (Fig. 3) as well as SO_4 (data not shown) remained low for the anaerobic treatment, and the elution tests at the end of the experiment did not show a high production of NO_3 (Fig. 6), a pronounced aeration of the anaerobic treatment was not observed. Nitrous oxide could be detected to some extent for the anaerobic treatment (Fig. 5), with a comparatively low maximum value of ~ 130 ppm or 0.013 vol%. In general the N_2O discharge was much higher for the aerobic than for the anaerobic LSR, also due to the higher gas flow rates.

4.2. Nitrogen Transformation processes

4.2.1. Leachate NH_4 removal and nitrification

The observed NH_4 reduction after aeration start (Fig. 3) was already described in numerous in-situ aeration studies (e.g. Giannis et al. 2008; Prantl et al. 2006; Ritzkowski et al. 2006) and it was attributed to the simultaneous occurrence of nitrification/denitrification processes (Ritzkowski et al. 2006). It was also hypothesized, that nitrogen uptake in the microbial biomass could play a significant role in nitrogen transformation processes during in-situ aeration (Fellner and Laner 2011). For the aerobic degradation of a rather recalcitrant substrate (leaf litter from beech, *Fagus sylvatica* L.), Brandstätter et al. (2013) found that NH_4 was inversely correlated with microbial biomass N based on a short term incubation experiment. This observation was explained by a high microbial N demand, since fast growing microorganisms would dominate an early stage leaf litter decay system (Moorhead and Sinsabaugh 2006). The early stage leaf litter decomposition system might bear many similarities to an initial stage of an MSW in-situ aeration system, as for instance microbial growth rates were enhanced after beginning of in-situ aeration (Mellendorf et al. 2010) as well as for aerobic microbial litter decomposition. Nonetheless, occurring denitrification processes were indirectly observed via

mass balancing and also the disappearance of nitrogen species in the leachate for an elongated timespan indicates potential denitrification as will be discussed further below.

For the anaerobic treatment, the contribution of NH_4 loss via leachate to the total N-losses was relatively high (Figs. 7 and 8). In the leachate the NH_4 concentrations were slightly reduced over time, which was expected, as it is known for anaerobic landfills that the NH_4 -concentrations in the leachate can remain high for many decades to centuries (Laner et al. 2011).

The initial fraction of NH_4 in the solid phase as well as for the anaerobic treatment at the end (Fig. 8) was most certainly underestimated, since prior to detection the material was eluted with deionized water only. Since landfilled MSW exhibits a certain cation exchange capacity (Mårtensson et al. 1999), the addition of a salty solution (here 3 M KCl) led to higher NH_4 leaching (roughly double as high, Fig. 9) compared to elution with deionized water only. This indicates that the same amount of NH_4 readily leachable with deionized water additionally was attached to the organic waste matrix via ionic bonding. Since this test was only performed with material after aeration, the contribution of NH_4 to the TN_s in Fig. 8 was not corrected for.

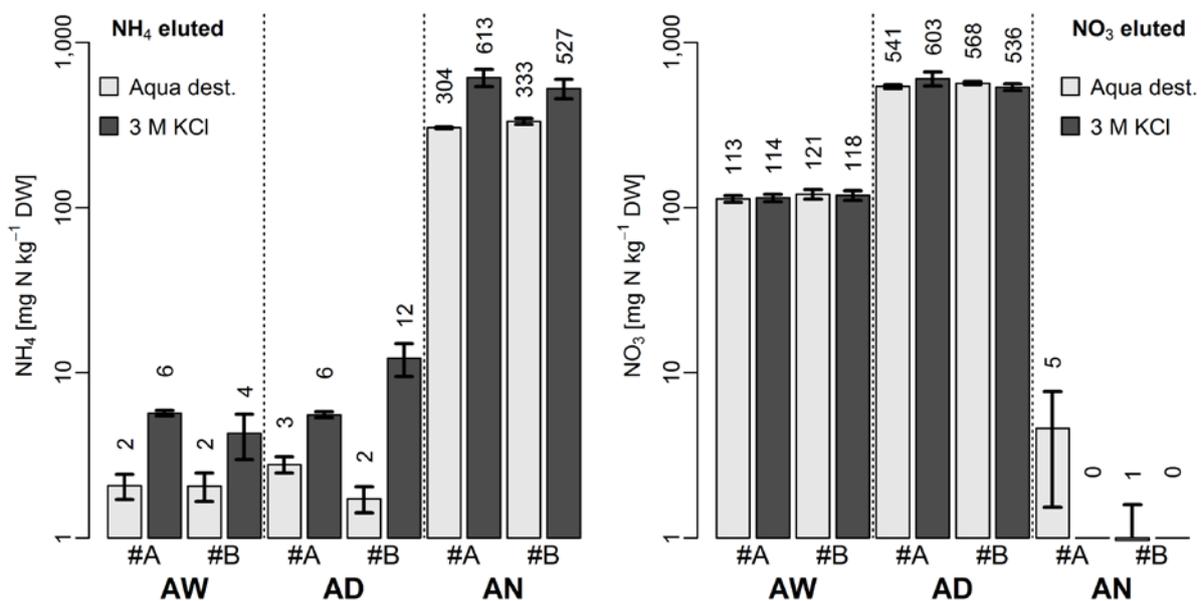


Fig. 9 Elution experiment with 3 M KCl in comparison to aqueous elution at the end of the experiment

Notes: The numbers #A and #B denote respective replicates. AD aerated dry, AN anaerobic, AW aerated wet, DW dry weight

4.2.2. Nitrous oxide formation

The observation that the N_2O losses were higher for the dry treatment than for the wet treatment was not expected a priori, since N_2O production is considered to be positively influenced by water content in natural ecosystems (Brown et al. 2012) and the production of N_2O was also found to be highly correlated with denitrification (Brown et al. 2012), which was most pronounced in this experiment for the aerobic wet treatment (Fig. 8). The observation of higher N_2O emissions in the aerobic dry treatment can probably be best explained from the view of denitrification: denitrification can mainly occur via nitrate reduction, where N_2O is an intermediate product (Davidson and Seitzinger 2006). The completion of the process with N_2 as final product is favored, if NO_3 is available, if O_2 is scarce or absent and if electron donors (mainly carbon sources) are abundantly available (Seitzinger et al. 2006).

The stronger decrease in N₂O emission for the aerated dry treatment could indicate that the substrate became increasingly oxidized and thus providing aerobic conditions and limiting N₂O formation. Also a rather heterogeneous water distribution could be observed at the end for the aerobic dry treatment, since some free water was available with rather dry areas at the top, even if the overall water content remained unexpectedly high at 21.2 % FM (fresh mass, see Brandstätter et al. 2015) at the end of the experiment. For the aerated wet treatment the decrease in N₂O after the solid sampling campaign was less pronounced presumably for other reasons: anoxic conditions might have been abundant over the whole waste matrix and with the leachate recirculation mixing processes might have established a continuing supply of substrate or nutrients for microbial activities.

The high concentrations of N₂O detected directly after the solid sampling campaign for the aerated dry treatment were analyzed in two separate laboratories, thus supporting their validity (Fig. 5). Similar observations of N₂O peaks after the turning of compost were reported in composting studies, for instance, during the composting of grass and green waste (Hellebrand 1998). Furthermore free NO₃ was described as a main driver for N₂O emissions after compost turning (Maeda et al. 2013) and the analysis of isotopic signatures allowed for the identification of denitrifying bacteria being mainly responsible for the N₂O emissions. After compost turning also an O₂ decrease in the respective heap centers was observed, leading to favorable conditions for N₂O production (Mulbry and Ahn 2014). Since for the aerated dry treatment in the presented study, there was no aqueous pathway of discharging NO₃, it could accumulate in the solid waste matrix (Fig. 6). To a certain degree, this can explain the discrepancy in N₂O emissions between the aerated wet and aerated dry treatment after the solid sampling campaign and consequently substrate mixing. However, the minor contribution of N₂O to the overall nitrogen balance should be taken into account, which is especially valid for the anaerobic treatment. We attribute the reduction of N₂O concentrations at later stages (~ after 500 days) of the anaerobic treatment to the reduction of the leachate recirculation rate (~ 440 days) and thus a reduction in unintended air intrusion.

4.2.3. Denitrification

The influence of the leachate sampling on denitrification was already discussed above. The exclusive presence of either NO₃ or BOD₅ in the leachate indicates that denitrification took place in the leachate as long as easily degradable organics were available. Towards the end of the experiment, when leachate was increasingly deprived of carbohydrates, NO₃ could be denitrified only partially, using up the degradable organics and leaving some NO₃ in the leachate. It should be noted, that neither the detected NO₃ nor the detected BOD₅ (Fig. 4) reflected the leachate situation directly after recirculation, but after a timespan (at least 16 hours) of storage at the LSR bottom. This is a possible explanation for the gap between BOD₅ depletion and not yet noteworthy levels of NO₃ between 250 and 500 days after the experiment start.

The aerated treatments differed in water content and recirculation rate. As already mentioned, higher moisture was considered to show the negative effect of water occupied pore space during in situ-aeration; indeed on the macro scale a differing porous structure of the incubated waste material could be observed (Brandstätter et al. 2015). The aerated wet treatment showed a smeary structure, while the aerated dry treatment seemed highly porous. This differing structure might have led to differing levels of air intrusion for the two distinct treatments, leading to more benevolent conditions for denitrification after water addition. Nonetheless, most likely the majority of denitrification will have occurred at the bottom of the LSR in the temporary leachate reservoir.

Another effect of the water addition and recirculation might have been a mixing of the substrate, thus improving the nutrient supply for the denitrifying microorganisms. However, if that mixing effect

would have been of great importance for all microorganisms, the aerated wet treatments should also have shown a generally higher level of C-discharge, which was not the case (Brandstätter et al. 2015). Only for a short period directly after the solid sampling the microbial activity in terms of CO₂-respiration increased for both aerated treatments, while for the aerated dry treatment it was a sharper and shorter increase followed by a rapid decrease.

4.3. Overall mass balance and resulting practical implications for in-situ aeration

At the end of the experiment the amount of N remaining in the solids (TN_s) was highest for the dry treatment (Fig. 8), since there was no nitrogenous leachate discharge as for the other treatments. However, excluding leachate losses, the nitrogen loss for the aerated wet treatment greatly exceeded the amount of nitrogen lost in the aerated dry treatment (Fig. 8), since conditions were enhancing the denitrification process in the aerated wet treatment. The presented data allowed for reasoning that the aerated wet treatment showed the highest denitrification activity, followed by the aerated dry and then by the anaerobic treatment. Nonetheless, for all treatments the majority of TN remained in the solid phase.

For future studies concerning nitrogen removal during in-situ aeration, we highly encourage a precise utilization of terms like “nitrogen removal efficiency” and taking overall nitrogen balances in account, if possible. In the presented case, nitrogen removal efficiency for NH₄ in the aerobic wet treatment would be nearly 100 % since the NH₄ concentrations depleted (Fig. 3). But, as can be seen from Fig. 8 over time, the leachate nitrogen only constituted a minor fraction of the whole nitrogen balance, with the majority of nitrogen remaining in the solids leading to a total nitrogen removal efficiency of ~ 22 % TN_{init} for the aerated wet treatment.

The addition of water during the in-situ aeration of old MSW did not increase the C-discharge (Brandstätter et al. 2015), but had a significant impact on the nitrogen removal efficiency: denitrification was intensified for the moist aerated setup. This observation was made for old MSW material rather low in organics (< 10 % TOC) and under a certain laboratory setup; leachate was recirculated at least 16 h prior to sampling. This experimental approach led to an intense denitrification for the aerated wet treatment.

For the field these insights would implicate, that if nitrogen removal via denitrification was the target of an in-situ aeration measure, water should be introduced to the landfill. The leachate of the aerated wet treatment was C-depleted especially at later stages of the experiment. Thus mixing mature leachate from older landfill compartments with younger leachate from compartments with less degraded waste in a common leachate pond might show beneficial effects on denitrification processes.

5. Conclusions

In this study a detailed nitrogen balance was established for a lab-scale degradation experiment of old landfilled MSW. Transformation of organic nitrogen into various nitrogen species was investigated under aerobic conditions with forced air intrusion (one set of replicates with water addition and recirculation, one without) and under an anaerobic conditions (as a reference set-up). After the degradation experiment, the majority of nitrogen remained in the solids. A minor part of the initial nitrogen content was discharged via leachate in case of the aerated treatments; while it proved to be the main pathway for nitrogen losses in case of anaerobic waste degradation. Denitrification and thus nitrogen removal was enhanced by water addition and recirculation during aeration resulting in N-losses of around 17 % of the initial total nitrogen content. Denitrification was likely to occur mainly in the leachate, also because the time lag between leachate recirculation and sampling resulted in an optimal environment for denitrification to take place, particularly in the beginning of the aeration

experiment. The mixing of solids during the one-time solid waste sampling led to an increase in N₂O emissions of the aerated dry LSR directly afterwards, which was mainly attributed to high NO₃ concentrations. The overall production of N₂O as well as ammonia volatilization was only of minor significance for the nitrogen balance and accounted for less than 4 % the total nitrogen losses for the aerated dry treatment and less than 1 % for the other treatments. The detailed account of the pools and flows of various nitrogen species in this study allowed for new insights in the nitrogen circle during in-situ aeration of MSW and thereby provides a basis for creating conditions (e.g. water addition during in-situ aeration, leachate treatment strategies) to enhance nitrogen removal during in-situ aeration of old landfills.

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Appendix IV. A closeup study of early beech litter decomposition: potential drivers and microbial interactions on a changing substrate

A closeup study of early beech litter decomposition: potential drivers and microbial interactions on a changing substrate

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Abstract

Aims Litter decomposition and subsequent nutrient release play a major role in forest carbon and nutrient cycling. To elucidate how soluble or bulk nutrient ratios affect the decomposition process of beech (*Fagus sylvatica* L.) litter, we conducted a microcosm experiment over an 8 week period. Specifically, we investigated leaf-litter from four Austrian forested sites, which varied in elemental composition (C:N:P

ratio). Our aim was to gain a mechanistic understanding of early decomposition processes and to determine microbial community changes.

Methods We measured initial litter chemistry, microbial activity in terms of respiration (CO_2), litter mass loss, microbial biomass C and N (C_{mic} and N_{mic}), non purgeable organic carbon (NPOC), total dissolved nitrogen (TDN), NH_4^+ , NO_3^- and microbial community composition (phospholipid fatty acids – PLFAs).

Results At the beginning of the experiment microbial biomass increased and pools of inorganic nitrogen (N) decreased, followed by an increase in fungal PLFAs. Sites higher in NPOC:TDN (C:N of non purgeable organic C and total dissolved N), K and Mn showed higher respiration.

Conclusions The C:N ratio of the dissolved pool, rather than the quantity of N, was the major driver of decomposition rates. We saw dynamic changes in the microbial community from the beginning through the termination of the experiment.

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Keywords Leaf litter decomposition · Microbial biomass · Microcosm · Microbial community structure analysis · Microbial respiration

Abbreviations

AK	Achenkirch
C	Carbon
Ca	Calcium
C_{mic}	Microbial biomass carbon
$C_{\text{mic}}:N_{\text{mic}}$	C:N microbial biomass

DOC	Dissolved organic carbon
dw	Dry weight
ECD	⁶³ Ni-electron-capture detector
FB-ratio	Fungal-bacterial ratio
Fe	Ferrum
FID	Flame ionisation detector
K	Potassium
K	Decomposition constant
KL	Klausen-Leopoldsdorf
Mg	Magnesium
ML	Litter mass loss
N	Nitrogen
N _{mic}	Microbial biomass nitrogen
NPOC	Non purgeable organic carbon
OR	Ort
P	Phosphorus
PE	Perg
PC	Principal component
PCA	Principal component analysis
PLFA	Phospholipid fatty acid
qCO ₂	Microbial metabolic quotient
NPOC:TDN	C:N ratio of non purgeable organic C and total dissolved N
TDN	Total dissolved nitrogen
TIN	Total inorganic nitrogen
Zn	Zinc

Introduction

Climate and substrate quality are the main drivers of leaf litter decomposition rates (Meentemeyer 1978; Prescott 1995). Specifically, the chemical composition of litter (e.g. lignin- and N-content) has been shown to strongly affect decomposition rates (Melillo et al. 1982; Prescott 2010). Usually, to assess litter decomposition rates two basic methods are used: the litter bag-technique or microcosm studies (Salamanca et al. 1998). In the present study, we controlled variation of climatic factors to a minimum by using the microcosm approach (Taylor et al. 1989), which allowed us to more exclusively focus on the impact of substrate quality and initial nutrient stoichiometry on decomposition. Even though increasing numbers of studies have dealt with decomposition rates in early stages (Prescott 2010), we propose that the importance of the dynamics of the early stages of decomposition has been widely overlooked. In the present study we

more explicitly explore the time course of very early litter decomposition. The chosen high temporal resolution allowed us to find new insight into the very early microbial and nutrient dynamics in a leaf litter system.

Initial litter composition is thought to control litter decomposition rates (Jacob et al. 2010) as well as initial nutrient content and relative amounts of labile and refractory carbon (C) (Aber and Melillo 1991; Melillo et al. 1982). During the early phase, C is relatively available and nutrients are often a limiting factor, since immobilization of the limiting nutrient (usually N) occurs regularly (Prescott 2005). Litter with greater initial N content has been shown to decompose at a faster rate because it poses a smaller discrepancy in the C:N ratio between litter and decomposer microbes, and so microbes will need to immobilize less N to decompose the litter (Aber and Melillo 1991).

During litter decomposition the C pool is subject to qualitative changes: easily accessible substances like cellulose and C-containing cell solubles are preferably decomposed, which leads to an increase in more recalcitrant C-containing molecules like lignin and lignified cellulose and a slowing of the decomposition rate (Berg 2000; Berg et al. 1993). The impact of N on decomposition is more controversial. So far, the classification of the time into “short-term” and “long-term” litter decomposition is relatively common (Berg and McLaugherty 2008). Nitrogen (N) seems to accelerate decomposition in earlier stages due to a higher microbial nutrient demand (Moorhead and Sinsabaugh 2006), whereas in later stages it is thought to decelerate litter decomposition (Gallo et al. 2004). This issue has been addressed as “microbial mining theory” (Craine et al. 2007). In a recalcitrant substrate, certain guilds of microbes have to invest more energy and therefore be able to access nutrients that are closely tied to the substrate. If enough N is available, there is no need to decompose recalcitrant substances to access nutrients, thus decomposition slows down despite high N-availability.

Other possible mechanisms for the inhibition of late stage decomposition by N additions include a proposed negative effect of N on C mineralization, or a negative effect on lignin degradation by inhibiting lignin degrading enzymes, resulting in reduced availability of the structural carbohydrates in the lignocellulose complex (Chesson et al. 1997; Henriksen and Breland 1999).

In addition to the abundant C and N, other elements have been discussed to be able to control litter decomposition, mainly Mn and P. In general, litter poor in P is suggested to have higher F/B ratios (Hieber and Gessner 2002; van der Wal et al. 2006; Güsewell and Gessner 2009). A previous study at these same sites as the current study has noted a strong impact of P on the microbial community composition (Schneider et al. 2012) and another one on the early phases of litter decomposition at other sites (Aerts and de Caluwe 1997). Similarly, Mn has been mentioned in relation to fungal decomposition, as fungi use Mn-peroxidase-enzymes for lignin degradation (Hofrichter 2002). Fungi have the ability to degrade highly recalcitrant compounds like lignin by excreting extracellular enzymes (Boer et al. 2006). Although with PLFA-analysis it is not possible to distinguish between different fungal phyla, predominant fungal phyla in the soil-litter interface (Osono and Takeda 2006), are considered to be Ascomycota and Basidiomycota. While Ascomycota have been mentioned as first colonizers during beech litter decomposition at similar Austrian sites (Schneider et al. 2012), they are regarded primarily as cellulose decomposers or sugar fungi (Osono 2007) and their ability to degrade lignin is limited. On the other hand, the succession at later stages of decomposition tends towards Basidiomycota at these same Austrian sites (Schneider et al. 2012), which have previously been shown to be controlled by the Mn content of the original litter (Berg et al. 2007). Within the decomposer community fungi and bacteria exhibit different nutrient demands and constraints on the decomposition processes, (Keiblinger et al. 2012), and thereby influence decomposition including the C use efficiency (Sinsabaugh et al. 2009; Keiblinger et al. 2010).

In the current study we asked: (i) Would higher initial N content and lower C:N ratios accelerate early stage decomposition rates (Schneider et al. 2012; Zhang et al. 2008) of lignin-rich (Melillo et al. 1982) and thus recalcitrant beech litter (Mungai and Motavalli 2006)? (ii) Which other elements in addition to, or beside, N possibly influenced the decomposition rates of beech litter? (iii) How would the litter decomposing microbial community react to changes in substrate quality during the early stage of decomposition?

To answer these questions, we closely examined nutrient sinks and sources, respiration and microbial community composition weekly over the course of the 8 week experiment. We also focused on interactions

between fungi and bacteria in relation to changes in substrate quality, as for terrestrial litter decomposition fungal/bacterial interaction studies (e.g. Rousk and Baath 2007; Schneider et al. 2010) are not as well investigated as in comparison for aquatic litter decomposition (Das et al. 2007; Mille-Lindblom and Tranvik 2003; Schlief and Mutz 2007).

Material and methods

Sample sites

In autumn 2007 we collected fresh beech (*Fagus sylvatica* L. (1753)) litter from the surface of the forest floor from four different sites in Austria: Achenkirch, Tyrol (AK), Klausen-Leopoldsdorf, Lower Austria (KL), Perg, Upper Austria (PE) and Ort, Gmunden, Upper Austria (OR), which varied in elemental nutrient stoichiometry. Achenkirch is a Tyrolean Spruce-Beech (*Picea abies* L., H.KARST. (1881)) forest on Rendric Cambisol with a pH of 7.0. The coordinates of AK are 47°35' N and 11°39' E (Ambus et al. 2006). Klausen-Leopoldsdorf is situated in the Vienna Woods, with the coordinates 48°07' N and 16° 03' E. The soil type is Dystric Cambisol with a pH of 4.6 (Kitzler et al. 2006b). The coordinates of OR are 47° 51' N and 13°42' E. The forest consists mostly of beech but also of Norway spruce and fir (*Abies alba* MILL. (1768)). The soil is a Dystric Cambisol on carbonate rock. The coordinates of PE are 14°54' N and 48° 21' E. The site is dominated by beech, but it also contains conifers (*Picea abies*, also *Abies alba*) and the soil type is Cambisol (eBOD, BFW, Austria, based on the digital soil map of Austria, 1 km-grid).

Experimental setup

Before being put into microcosms, the air-dried beech litter was shredded and sieved with only the fraction from 1 mm² to 1 cm² included in the experiment. Every microcosm consisted of a PVC cylinder (Ø 10×10 cm height) with a grate two cm above the bottom. Before the start of the experiment, dry litter was re-wetted with deionized water to reach a water content of 60 % and left to equilibrate for 2 days. Into each microcosm 38 g of moist litter were then filled and incubated at 20±2 °C. Water content was adjusted weekly. To prevent drying, the microcosms were

covered with a perforated polyethylene foil fixed to a two cm ring of drainage pipe and a moist sponge cloth was laid underneath. After destructive sampling of the microcosms the litter was chopped into small pieces with a two-bladed mincing knife and homogenized.

In total 60 microcosms, 15 for litter from each site were established. Every week respective samples were taken out of one single cylinder, with three exceptions: in week zero samples were gathered from the original litter pool ($n=1$). In week four, four microcosms ($n=4$), and in week eight five ($n=5$) microcosms were available. This approach resulted in an unbalanced statistical design.

The number of subsamples for the used methods is given at the respective section. Gas sampling was conducted every week in four separate microcosms per site. At week eight these microcosms also were analysed for NH_4^+ , NO_3^- , microbial biomass C (C_{mic}) and N (N_{mic}) and PLFAs. PLFA analyses were conducted three times during this 8-week experiment, whereas all other analyses were performed weekly.

Elemental analyses

Ten g of fresh litter from every cylinder was oven dried overnight at 105 °C and milled to a fine powder to obtain homogenous samples. Prior to the start of the experiment an elemental analysis of the collected litter with six subsamples per site was performed. The milled samples were wet oxidized ($\text{H}_2\text{SO}_4 + \text{HNO}_3$) in a microwave oven (Henschler 1988) and elements (P, K, Ca, Mg, Fe, Mn, Zn) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Carbon and N-contents were measured with a Leco CN2000 elemental analyzer (LECO corp. St Joseph, MI, USA) initially and during the experiment for every microcosm.

Gas fluxes

Microcosms were opened 2 min before gas sampling. Two airtight covers were then used for gas sampling, one with a hole and a septum sealed by means of silicone (Baysilone medium viscous; Bayer corp., Leverkusen, Germany) to the top of the microcosm. A 2 mm polyurethane band was adjusted inside the covers and parafilm outside for

air-tight sealing. After sealing the microcosms we sampled 10 ml headspace air of the gas tight microcosms. Over a time course of 20 min gas samples were taken every five minutes and gas samples were analysed by gas-chromatography with a 6890 N GC-System (Agilent, Santa Clara, CA, USA) connected to an automatic headspace-sample injection system (Dani HSS 86.50 Dani, Cologno Monzese, Italy). Measurements and calculations of CO_2 and N_2O were conducted as described by Kitzler et al. (2006a), and of CH_4 as in Schauffler et al. (2010).

$\text{NH}_4^+/\text{NO}_3^-$, C_{mic} and N_{mic} ; NPOC and TDN –measurement

Litter was extracted in two subsamples per microcosm in a 1:20 w/v ratio in 0.1M KCl-solution shaking at vigorous agitation for 1 h for analyses of NO_3^- and NH_4^+ which were conducted according to Kandeler (1996) with minor modifications, and detected with a μ Quant mQx200 well plate reader (Bio-Tek Instruments, Inc., Vermont, USA) at a wavelength of 660 nm for NH_4^+ and 210 nm for NO_3^- . The determination of N_{mic} and C_{mic} was performed from two subsamples per microcosm via chloroform fumigation extraction (Öhlinger 1996). An extractability factor was not applied for calculation of microbial biomass. Non purgeable organic C (NPOC) and total dissolved N (TDN) were determined from a 1:20 w/v extract in 1M KCl with a TOC/TN analyser (TOC-V CPH E200V, linked with a TN-unit TNM-1 220 V, Shimadzu Corporation, Kyoto, Japan). Sample extracts were stored frozen at -20 °C prior to analysis.

Phospholipid fatty acids PLFA

Phospholipid fatty acid analyses were performed at three time points (initially out of the litter pool ($n=1$), after four ($n=4$) and 8 weeks ($n=5$)). For every PLFA analysis, three subsamples were extracted from 1 g subsamples using a modified Bligh and Dyer technique, as described by Hackl et al. (2005), referring to Frostegard et al. (1991) and detected with a FID on a HP 6890 Series GC-System and a 7683 Series injector and auto sampler on a HP-5 capillary column. For identification of the fatty acid methyl esters an external standard (Bacterial acid methyl esters mix from SUPELCO, St. Louis, Missouri, USA) was used. For quantification of the peaks methyl non-adeconoate fatty

acid (19:0) was added as internal standard. The GC-injection volume was 0.2 μl . PLFA nomenclature is based upon Frostegard et al. (1993). The PLFAs i14:0, i15:0, a15:0, i16:0, i17:0, a17:0 were chosen to represent gram + bacteria. The PLFAs 16:1 ω 7, 16:1 ω 9, 17:1 ω 9, cy17:0, 18:1 ω 11, and cy19:0 were used as biomarkers of gram- bacteria (Fierer et al. 2003). 18:2 ω 6 was regarded as fungal marker (Zelles 1997) and 10Me16:0, 10Me17:0 and 10Me18:0 were applied as biomarkers of actinomycetes (Frostegard et al. 1993). 14:0, 15:0 and 17:0 were for unspecific bacteria. The sum of markers for gram+, gram- and unspecific bacteria accounted for total bacteria. The ratio fungal/bacterial PLFA was calculated with 18:2 ω 6 divided through the amount of bacterial PLFA (Frostegard and Baath 1996). 20:4 ω 6 and 20:2 ω 6 were regarded representative of protozoa (White et al. 1996).

Statistical analyses

One-way ANOVAs followed by Tukey's HSD test were used to evaluate differences between litter from the four sites. The program used for most of the graphs, regressions and non-parametric Spearman correlations was R 2.9.0 (R_Development_Core_Team 2009). ANOVAs and Pearson correlations of normally distributed data were carried out with STATGRAPHICS Centurion XV (StatPoint Technologies, Virginia, USA). Where a prerequisite for ANOVA in terms of homogeneity of

variance was violated, as tested by Levene's test, non-parametric Kruskal-Wallis tests were calculated. Two principal component analyses (PCA) were calculated with and without PLFA results using the program SIMCA-P 11.0 (Umetrics, Umeå, Sweden).

Results

Litter elemental composition

Beech litter from the four sites significantly differed in nutrient stoichiometry (C:N, C:P, N:P) and in nutrient content for certain elements (P, K, Mg, Mn) as shown in Table 1. Initial C:N-ratios ranged from average 48.7 (AK) to 57.6 (PE) with significant differences between OR, PE and either AK or KL. The C:N-ratios significantly decreased over time in litter from the four sites from 51.8 at week zero to 47.0 at week eight. For single sites, no significant differences were found between the weeks. Averaged over the whole experiment, the highest C:N-ratio was found for PE (51.4), followed by OR (50.3), KL (46.9) and AK (43.9).

Total N content was highest in AK (1.17 %) and lowest in litter from PE (0.93 %) for the duration of the experiment. The initial Mn-, Ca-, P-, and K-contents were significantly different for all sites (Table 1). The initial K-content was highest in KL (0.395 mg kg⁻¹), followed by PE, OR and AK

Table 1 Initial beech litter chemistry of four different sites

		AK	KL	OR	PE
C	(%)	50.94 ^c (0.04)	49.42 ^b (0.18)	48.65 ^a (0.14)	49.59 ^b (0.16)
N	(%)	1.05 ^c (<0.01)	0.97 ^b (<0.02)	0.90 ^a (<0.01)	0.86 ^a (<0.02)
P	(%)	0.030 ^a (<0.001)	0.033 ^b (<0.001)	0.045 ^c (<0.001)	0.056 ^d (<0.001)
K	(%)	0.099 ^a (0.002)	0.395 ^d (0.003)	0.179 ^b (0.002)	0.212 ^c (0.002)
Ca	(%)	1.48 ^c (0.02)	1.30 ^b (0.02)	2.03 ^d (0.02)	1.16 ^a (0.01)
Mg	(%)	0.23 ^d (<0.01)	0.16 ^b (<0.01)	0.16 ^c (<0.01)	0.13 ^a (<0.01)
Fe	(mg kg ⁻¹)	121.9 ^a (3.7)	175.5 ^b (4.5)	240.9 ^c (16.8)	181.5 ^b (8.5)
Mn	(mg kg ⁻¹)	103.8 ^a (2.6)	985.2 ^d (18.3)	521.2 ^c (19.0)	292.8 ^b (9.4)
Zn	(mg kg ⁻¹)	32.3 ^a (0.9)	39.0 ^b (1.6)	34.1 ^a (0.6)	41.2 ^b (0.8)
C:N		48.7 ^a (0.3)	50.9 ^a (0.7)	54.2 ^b (0.4)	57.6 ^c (0.8)
C:P		1707 ^d (18)	1494 ^c (34)	1090 ^b (16)	892 ^a (2)
N:P		35.0 ^d (0.2)	29.1 ^c (0.4)	20.1 ^b (0.2)	15.8 ^a (0.2)

Values represent means, with +/- SE in parentheses, different letters indicate significant differences between sites after Tukey's HSD test ($p < 0.05$, $n = 6$)

AK Achenkirch, KL Klausen-Leopoldsdorf, OR Ort and PE Perg

(0.099 mg kg⁻¹). Initial Ca-content was highest in litter from OR (2.03 %) and lowest for PE (1.16 %) and P was highest in PE (0.056 %) and lowest in AK (0.03 %). Manganese was highest in KL (985.2 mg kg⁻¹), followed by OR, PE and AK (103.8 mg kg⁻¹).

Litter mass loss (ML)

Final mass loss was significantly highest with 8.8 % in KL, the site with highest respiratory activity, with 6.6 % in OR, 6.9 % in PE and 7.1 % in AK (Fig. 1a) without significant differences between these three other sites. The cumulative mass loss between week 0 and 1 was slightly negative. This can possibly be contributed to the fact, that watering during the experiment was applied 1 day before the harvesting procedure and thus could have slightly increased the weight of the microcosms. The calculated cumulative C-loss obtained by gravimetric method at week eight ranged between 30.7 mg C g⁻¹ DW (OR) and 43.9 mg C g⁻¹ DW (KL).

NH₄[±] and NO₃⁻-concentrations

Initial NH₄⁺-N concentration was highest in AK and lowest in KL, decreased in the first weeks and

remained at a low level during the later stage of the experiment (Table 2, Fig. 1b). Generally NO₃⁻ decreased in the beginning and started to increase after 6 weeks (Table 2). The site highest in respiration (KL) revealed lowest initial NH₄⁺ concentrations but highest concentrations of NO₃⁻. Total inorganic N (NH₄⁺+NO₃⁻, TIN, Table 2, Fig. 1c) declined over time with an initial average of 425 μg N g⁻¹ dw to 66.1 μg N g⁻¹ dw at week eight, and it was generally highest for microcosms of OR (465 μg N g⁻¹ dw to 116 μg N g⁻¹ dw).

Gas fluxes

Respiration declined during the experiment (Fig. 1d) with highest initial values in KL (104.4 μg C g⁻¹ dw h⁻¹). During most of the experiment respiration was significantly higher in KL than in litter from the other sites and AK was lowest. Respiration showed the opposite pattern than initial NH₄⁺ concentration between sites (KL>PE>OR>AK). During the experiment there was no significant N₂O and CH₄ production and/or consumption.

The cumulative C-loss after 8 weeks via respiration showed values between 234 mg (AK) and 631 mg

Fig. 1 Time course of **a)** Mass Loss %, **b)** NH₄⁺-N, **c)** total inorganic N (TIN) and **d)** respiration. An ANOVA was conducted for week 4 and 8 to detect significant differences between the four sites. Where brackets indicate a violation of the prerequisite of homogenous variances, a non-parametric Kruskal-Wallis test was computed (ns $p > 0.05$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$). AK Achenkirch, KL Klausen-Leopoldsdorf, OR Ort, PE Perg

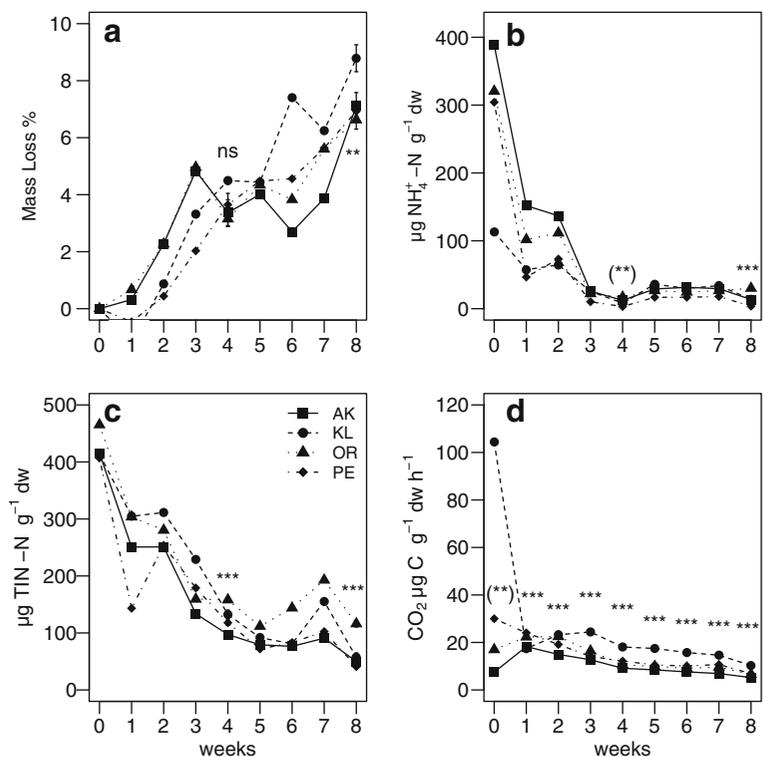


Table 2 Nitrogen and carbon pools averaged over all four sites during 8 weeks

Weeks	N	C	NH ₄ ⁺	NO ₃ ⁻	TIN	NPOC	TDN	C _{mic}	N _{mic}
0	150.8 (4.3)	7421 (66)	4.22 (0.44)	2.16 (0.43)	6.38 (0.10)	147.6 (3.6)	16.33 (0.98)	18.64 (2.67)	1.22 (0.26)
(%)	100	100	2.80	1.43	4.23	1.99	10.83	0.25	0.81
1	155.3 (4.9)	7607 (130)	1.37 (0.19)	2.47 (0.29)	3.84 (0.28)	84.7 (4.8)	9.15 (0.27)	33.20 (1.97)	2.67 (0.23)
(%)	100	100	0.88	1.59	2.47	1.11	5.89	0.44	1.72
2	157.7 (5.3)	7478 (127)	1.46 (0.13)	2.69 (0.22)	4.15 (0.11)	68.3 (4.2)	7.71 (0.13)	45.35 (2.27)	4.92 (0.26)
(%)	100	100	0.92	1.71	2.63	0.91	4.89	0.61	3.12
3	150.0 (5.2)	7309 (122)	0.31 (0.03)	2.29 (0.17)	2.60 (0.16)	58.1 (4.3)	3.59 (0.20)	45.09 (2.25)	4.89 (0.25)
(%)	100	100	0.21	1.53	1.73	0.80	2.40	0.62	3.26
4	151.3 (5.2)	7321 (119)	0.15 (0.02)	1.71 (0.07)	1.86 (0.08)	58.9 (4.1)	3.21 (0.14)	41.52 (2.29)	5.24 (0.30)
(%)	100	100	0.10	1.13	1.23	0.80	2.12	0.57	3.47
5	150.4 (5.5)	7204 (146)	0.40 (0.03)	0.91 (0.05)	1.30 (0.05)	56 (4.9)	3.15 (0.22)	42.98 (0.58)	4.70 (0.17)
(%)	100	100	0.27	0.60	0.86	0.78	2.09	0.60	3.13
6	150.2 (5.7)	7175 (148)	0.38 (0.03)	1.02 (0.11)	1.40 (0.10)	54.4 (4.1)	3.01 (0.17)	53.03 (1.43)	5.30 (0.17)
(%)	100	100	0.25	0.68	0.93	0.76	2.01	0.74	3.53
7	150.6 (5.4)	7128 (158)	0.39 (0.03)	1.55 (0.15)	1.95 (0.15)	59.8 (5.3)	3.80 (0.27)	46.30 (0.63)	4.41 (0.10)
(%)	100	100	0.26	1.03	1.29	0.84	2.53	0.65	2.93
8	148.9 (5.3)	6946 (134)	0.21 (0.04)	0.72 (0.07)	0.93 (0.11)	51.9 (5.2)	2.99 (0.22)	33.95 (2.14)	5.04 (0.24)
(%)	100	100	0.14	0.48	0.62	0.75	2.01	0.49	3.38

Values represent means of all sites with \pm SE in parentheses, units are mg per microcosm. For week zero a litter amount of 15 g dw was estimated, since the samples were taken out of the original litter pool. The percentage is given for each week while elemental C and N analyses were regarded as 100 %

TIN total inorganic nitrogen, TOC total organic carbon, TDN total dissolved nitrogen, C_{mic} microbial biomass C, N_{mic} microbial biomass N ($n=4$)

(KL). Linear regressions were calculated for C-loss from CO₂-respiration and C-loss from the gravimetric mass-loss determination over all time points, with coefficients of determination (r^2) ranging from 0.68 (AK) to 0.92 (KL). The final C-loss was on average 1.6-fold higher from the gravimetric (together with the elemental analysis) determination method than from the respiration.

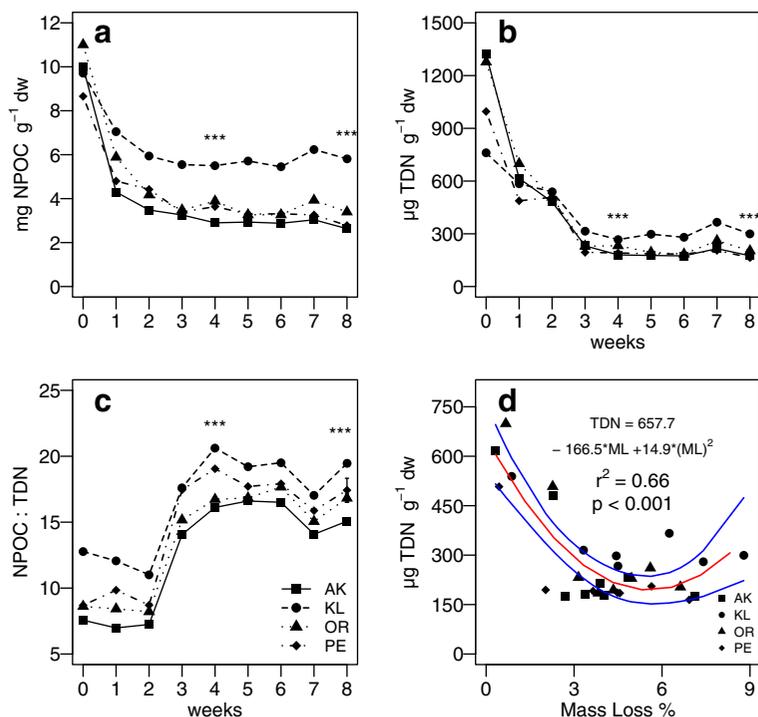
NPOC, TDN, C_{mic} and N_{mic} content

Non purgeable organic C and total dissolved N (NPOC and TDN, Table 2, Fig. 2a and b) decreased over time, with significant differences between litters

from different sites at week four and eight. A strong positive relation between NPOC and TDN was observed by single linear regression analysis ($p < 0.001$, $r^2 = 0.78$). The time course of NPOC was similar to that of TDN, except that TDN was highest for KL and lowest for AK most of the time. The C:N ratio of non purgeable organic C and total dissolved N (NPOC:TDN) increased between start and end of the experiment for all sites, and its time course is shown in Fig. 2c.

Linear regression analysis for each separate site revealed a strong positive correlation between DON (= TDN - inorganic N) and NH₄⁺ (with r^2 -values ranging from 0.60 (KL) to 0.97 (AK)) as well as a

Fig. 2 Time course of **a**) non-purgeable organic carbon (NPOC) **b**) total dissolved nitrogen (TDN), **c**) ratio of NPOC and TDN (NPOC:TDN). The remaining graph **d**) represents a quadratic regression between TDN and the cumulative litter mass loss (ML). The values for TDN between **b**) and **d**) differ, since the first week was not used for mass loss determination. The outer lines of the regression curves indicate a 95 % confidence interval and the line in between is the regression line. An ANOVA was conducted for week 4 and 8 to detect significant differences between the four sites. (ns $p > 0.5$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$). AK Achenkirch, KL Klausen-Leopoldsdorf, OR Ort, PE Perg



quadratic regression revealed a strong correlation between TDN and mass loss calculated with mean values over all sites (Fig. 2d, $n=30$, without week zero and two slightly negative values after week 1, $p < 0.001$, $r^2 = 0.66$). Also for NPOC:TDN and litter mass loss ($p < 0.001$, $r^2 = 0.57$) a quadratic regression was calculated.

For C_{mic} and N_{mic} (Table 2, Fig. 3a and b) a similar trend over time was observed and they were well correlated (Spearman's $r = 0.66$, $p < 0.001$). Initially N_{mic} was low but sharply increased in the first 3 weeks. For the time period of the whole experiment C_{mic} and N_{mic} mostly was highest in KL. The C:N-ratio in microbial biomass ($C_{mic}:N_{mic}$) declined over time starting from 18.1 in week 0 to 6.7 in week 8 for all sites. The course of N_{mic} inversely matched the development of NH_4^+ and a highly significant quadratic relationship was observed between those two variables (Fig. 3c). This suggests that most of the NH_4^+ was incorporated into microbial biomass within the first week.

For receiving a short outline, we provided a table with the examined nutrient pools during the time course of the experiment (Table 2). The proportions of NPOC (below 2 %), TDN (below 11 %), C_{mic} (below 1 %) and N_{mic} (below 5 %) in comparison to the total C and N amount of the litter, averaged for litter across all sites, were small.

Microbial metabolic quotient

The microbial metabolic quotient (qCO_2) was calculated as respiration divided by C_{mic} (Fig. 3d). A decrease during the time course of the experiment was observed with values ranging from 45.34 mg $CO_2-C g^{-1} C_{mic} h^{-1}$ (KL) at week zero to 1.98 (AK) at week eight. Since respiration was measured in four separated microcosms, an ANOVA only was conducted for week eight. A strong positive relationship for the duration of the experiment over all sites was noticed between qCO_2 and log-transformed TIN ($p < 0.001$, $r^2 = 0.70$).

Multivariate relationships

A PCA was computed with NO_3^- , NH_4^+ , respiration, NPOC, TDN, C_{mic} and N_{mic} (Fig. 4a). The arithmetic mean was calculated for each harvest time point and litter site, resulting in 36 observations and seven variables. The analysis revealed two principal components (PC). The first one was mainly explained by TDN (+0.94), N_{mic} (-0.80), NH_4^+ (+0.75) and C_{mic} (-0.51) and it explained 59.6 % of the variation and the second one by NO_3^- (+0.71), respiration (+0.56) and C_{mic} (+0.26) and it explained 23.8 % of the

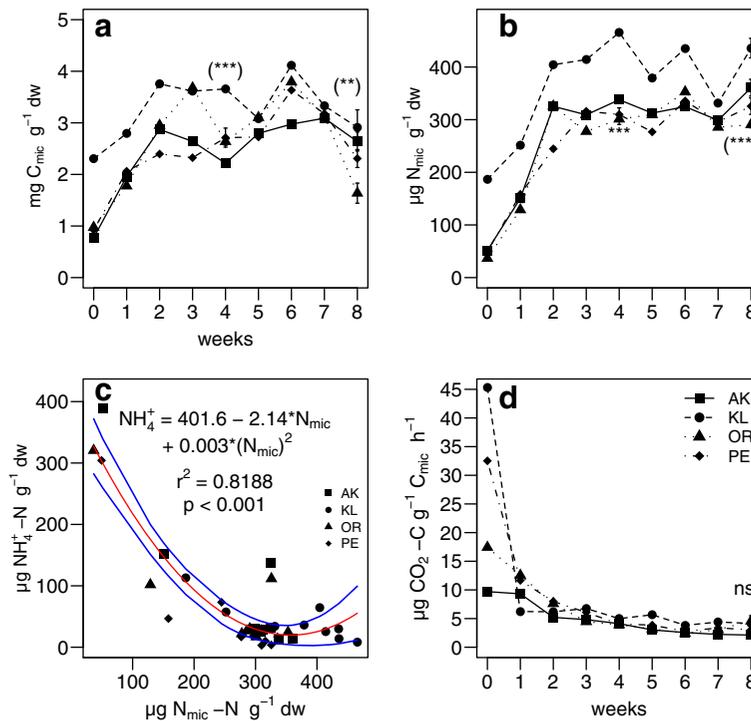


Fig. 3 Time course of **a**) microbial biomass C (C_{mic}), **b**) microbial biomass N (N_{mic}) and **d**) the microbial metabolic quotient ($q\text{CO}_2$). The remaining graph **c**) represents a quadratic regression between NH_4^+ and microbial biomass N (N_{mic}). The outer lines of the regression curves indicate a 95 % confidence interval and the line in between is the regression line. In **a**) and **b**) an ANOVA was conducted for week four and eight to detect

significant differences between the four sites, and in **d**) for week eight only. Where brackets indicate a violation of the prerequisite of homogenous variances, a non-parametric Kruskal-Wallis test was computed (ns $p > 0.5$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$). AK Achenkirch, KL Klausen-Leopoldsdorf, OR Ort, PE Perg

variation. Figure 4a shows that “time” was a more separating factor than “site”, indicating the stronger influence in comparison. Respiration and consequently litter mass loss was also influenced by TIN, as a strong negative correlation between TIN and Litter mass loss was detected ($p < 0.001$ and $r^2 = 0.60$). As expected, TIN was correlated with NPOC:TDN ($p < 0.001$, $r^2 = 0.56$) and furthermore with TDN ($p < 0.001$, $r^2 = 0.71$), since the TIN provides a portion of the TDN ranging from 19 % (KL, week 8)–92 % (PE, week 3) over the whole experiment. Litter from KL showed the highest respiration and lowest NH_4^+ -concentration.

Phospholipid fatty acids

PLFA data were classified into actinomycetes, fungi, gram + and gram- bacteria, and protozoa. Initially gram- bacteria dominated all microbial communities and only fungi and actinomycetes were significantly different among litters from different sites (Table 3).

The total amount of PLFAs did not change significantly with time. In week zero $54.3 \text{ nmol g}^{-1} \text{ dw} \pm 0.7$ (SE, $n = 12$), in week four $56.1 \pm 0.6 \text{ nmol g}^{-1} \text{ dw}$ (SE, $n = 16$) and in week eight $53.3 \pm 1.4 \text{ nmol g}^{-1} \text{ dw}$ (SE, $n = 20$) total PLFAs were measured.

However, the relative abundance among certain microbial groups did change with time, as revealed by one-way ANOVA. During the first 4 weeks of the experiment all groups except gram- bacteria increased. This was followed by a general decrease of all groups, with exception of actinomycetes and gram + bacteria, which both increased in microcosms of OR. For litter from all sites fungi increased in the first 4 weeks. From weeks four to eight, however, differences in the relative abundance of different microbial groups differed among litters. For example: litter of two sites gained in fungal biomass (AK, KL) while other two declined (OR, PE). In general, however, fungi showed a significant increase throughout the course of the experiment (ANOVA, $p < 0.001$).

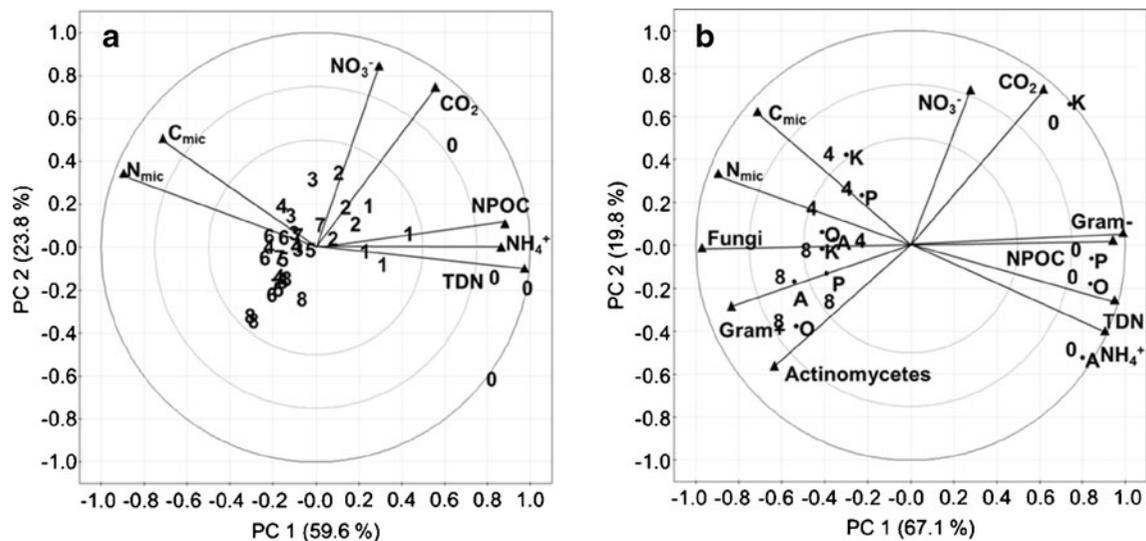


Fig. 4 Principal component analysis of **a**) inorganic N-pools, CO_2 -respiration, non purgeable organic C, total dissolved N, microbial biomass C and N and **b**) the same variables including PLFA data. Data points (indicated as numbers in **a**) and points in **b**) represent litter samples from four sites at **a**) eight (week 0–8), respectively **b**) three (week 0, 4, 8) time points. The variables NH_4^+ , NO_3^- , CO_2 and N_{mic} have been log-transformed prior to

PCA calculation for **a**) and NO_3^- and CO_2 for **b**). Explanation of variance by means of individual principal components (PC) is shown through percentages. Numbers indicate time and letters sites. C_{mic} microbial biomass C, N_{mic} microbial biomass N, TDC total dissolved C, TDN total dissolved N, *A* Achenkirch, *K* Klausen-Leopoldsdorf, *O* Ort, *P* Perg

In the microcosms of OR most gram + bacteria and actinomycetes were found. Gram- bacteria decreased

on average for all sites from $43.4 \text{ nmol g}^{-1} \text{ dw}$ at week zero to $30.3 \text{ nmol g}^{-1} \text{ dw}$ in week eight, and fungi

Table 3 PLFA-contents of beech leaf litter of four sites at three time points

Site	Actinomycetes	Fungi	Gram +	Gram -	Protozoa	FB-Ratio	Total PLFAs
Week 0 (<i>n</i> =3)							
AK	0.20 ^b (0.03)	9.93 (0.76)	1.20 ^a (0.09)	42.41 (2.70)	0.264 (0.022)	0.22 (0.03)	54.01 ^{ab} (1.81)
KL	0.01 ^a (0.01)	7.63 (0.09)	0.83 ^a (0.01)	42.39 (0.10)	0.213 (0.014)	0.17 (<0.01)	51.07 ^a (0.08)
OR	0.29 ^b (0.04)	9.62 (0.71)	2.54 ^b (0.23)	43.54 (1.75)	0.318 (0.042)	0.20 (0.02)	56.31 ^b (0.76)
PE	0.21 ^b (0.03)	8.71 (0.16)	1.30 ^a (0.05)	45.28 (0.28)	0.329 (0.016)	0.18 (<0.01)	55.83 ^b (0.04)
Week 4 (<i>n</i> =4)							
AK	0.32 ^c (0.01)	18.12 ^{ab} (0.25)	4.41 ^c (0.13)	30.60 ^a (0.75)	0.499 ^b (0.018)	0.48 (0.01)	53.95 (0.85)
KL	0.24 ^b (<0.01)	18.27 ^{ab} (0.17)	3.85 ^b (0.06)	34.28 ^b (0.95)	0.427 ^a (0.005)	0.45 (0.01)	56.74 (1.47)
OR	0.41 ^d (<0.01)	18.77 ^b (0.17)	7.11 ^d (0.15)	31.05 ^{ab} (0.88)	0.466 ^{ab} (0.004)	0.46 (0.01)	57.81 (0.95)
PE	0.22 ^a (<0.01)	17.68 ^a (0.27)	3.36 ^a (0.09)	33.50 ^{ab} (0.74)	0.892 ^c (0.023)	0.45 (0.01)	55.65 (1.00)
Week 8 (<i>n</i> =5)							
AK	0.37 ^{ab} (<0.01)	18.88 (0.08)	5.35 ^a (0.10)	28.69 ^a (0.46)	0.474 ^a (0.026)	0.52 (<0.01)	52.93 ^a (0.09)
KL	0.42 ^b (0.03)	18.33 (1.49)	4.79 ^a (0.20)	30.90 ^{bc} (0.59)	0.491 ^a (0.015)	0.48 (0.05)	54.92 ^{ab} (0.75)
OR	0.71 ^c (0.02)	17.05 (1.09)	9.14 ^b (0.37)	29.68 ^{ab} (0.37)	0.489 ^a (0.013)	0.45 (0.04)	57.39 ^b (0.60)
PE	0.31 ^a (0.01)	16.72 (1.16)	5.28 ^a (0.30)	31.79 ^c (0.56)	0.858 ^b (0.055)	0.42 (0.04)	54.96 ^{ab} (0.58)

Accounting PLFAs have been summed up to result in the assigned groups. Values represent means with +/- SE in parentheses, different letters indicate significant differences between sites for each time point after Tukey's HSD test ($p=0.05$). Except for FB-Ratio all units are $\text{nMol PLFA g}^{-1} \text{ dw}$

FB-Ratio fungal bacterial ratio, AK Achenkirch, KL Klausen-Leopoldsdorf, OR Ort, PE Perg

increased from 9.0 to 17.6 nmol g⁻¹ dw. Significant correlations were observed for gram + bacteria and actinomycetes (Pearson's $r=0.91$, $p<0.001$), gram + with gram- bacteria (Spearman's $r=-0.83$, $p=0.001$) and fungi and gram- bacteria (Spearman's $r=-0.75$, $p<0.01$). A PCA was conducted, containing all the PLFA groups and respiration, NH₄⁺, NO₃⁻, TDN, NPOC, N_{mic} and C_{mic} (Fig. 4b). Prior to performing the PCA, the arithmetic mean of the data set was calculated for three harvests (at week zero, four and eight) and each site, resulting in 12 observations and 11 variables. Three PCs were calculated. The first PC was mostly explained by gram- bacteria (+0.97), fungi (-0.94), TDN (+0.90), NPOC (+0.89), NH₄⁺ (+0.82), N_{mic} (-0.80), gram + bacteria (-0.69) and C_{mic} (-0.51), the second one by CO₂ (+0.53), NO₃⁻ (+0.52) and actinomycetes (-0.31). The third PC explained less than 1 % of total variation. Microbial community composition changed rapidly within the first 4 weeks, whereas only minor shifts occurred from week four to eight. The PCA also showed, that week zero was more different than week four and eight, which grouped closer together (Fig. 4b).

The results of the PCA revealed certain interrelationships between microbial community data and litter chemistry. Actinomycetes and fungi were negatively correlated with respiration. Gram- bacteria were positively and fungi negatively correlated with TDN and NH₄. The concentration of NH₄⁺ was highest in the first week and decreased over time as did gram- bacteria. Factors on the qCO₂ cannot be easily derived from the picture. There was a strong negative correlation between fungal-bacteria ratio (FB-ratio) and C_{mic}:N_{mic} (Spearman's $r=-0.62$, $p<0.05$) as well as with TIN (Spearman's $r=-0.59$, $p<0.05$). The qCO₂ was strongly negatively correlated with fungi (Spearman's $r=-0.75$, $p<0.01$) and positively with gram- bacteria (Spearman's $r=0.85$, $p<0.001$).

Discussion

The influence of N on early beech litter decomposition (i)

During the early stages of decomposition, microbial N limitation can occur due to high microbial N demand (Moorhead and Sinsabaugh 2006). Thus, N is proposed to accelerate decomposition during the early stages. We were not able to explain differences in

respiration rates among leaf litter from the four sites neither by initial bulk N-content nor by bulk C:N-ratios as suggested by Zhang et al. (2008), which would negate our first research question (i) "Would higher initial N content and lower C:N ratios accelerate early stage decomposition rates?". This might be attributed to the fact, that the present experiment is using only litter from four sites for evaluating this impact. We therefore tried to evaluate different influencing factors on respiration.

A strong correlation of respiration and C:N ratio of soluble C and N was observed in previous decomposition studies dealing with tropical tree species (Bernhard-Reversat 1999), and also for a decomposition study from temperate climate (Marstorp 1996). In addition, it has been mentioned, that mainly soluble carbon compounds (e.g. unshielded cellulose and hemicelluloses) are decomposed in early stages of decomposition (Berg and McClaugherty 2008). Since beech litter is considered to be rich in lignin (Melillo et al. 1982), a larger portion of cellulose may be shielded, increasing the influence of the soluble fractions during decomposition. We found that respiration was highest in leaf litter of sites with a high NPOC:TDN ratio, which is consistent with the idea, that this soluble C:N is a good indicator for the degradability of litter organic compounds (Bernhard-Reversat 1999). The influence of soluble compounds on litter decomposition has often been underestimated compared to litter chemistry stoichiometry (Cleveland et al. 2004). Moreover, an amount of about 10–40 % of DOC (comparable with our NPOC) is quickly degraded within a period of days to a few months (Silveira et al. 2011). Our results emphasize the relationship between soluble compounds and respiration although the relationship between litter mass loss and TDN was even stronger.

Higher microbial N demand (Moorhead and Sinsabaugh 2006) at early stages was on the one hand supported by our study by the quick incorporation of NH₄⁺, on the other hand a limitation of total N was not observed. The strong influence of soluble C and N together on this early stage decomposition could possibly explain this discrepancy: the bulk C:N ratio in our beech litter was about fourfold higher than the more influencing NPOC:TDN. In comparison to the C_{mic}:N_{mic} the NPOC:TDN was quite low in the beginning (0.6) and increased to 2.6 after 8 weeks for all sites. The bulk C:N stayed at a comparably similar

level between start and ending of our experiment. This comparison supports the observation, that the bulk N of our litter was not limiting decomposition after 8 weeks (i). There was no correlation found between the bulk C:N and NPOC:TDC. The linear correlation of TDN with mass loss was strongly affected by the factor time, and sites neither highest in TDN nor in NPOC showed highest respiration in the beginning, where respiration was highest, whereas this was the case for the NPOC:TDN ratio.

Since the litter from the site KL showed the highest respiration and lowest NH_4^+ -concentration, previous immobilization of NH_4^+ may have led to a negative relationship between NH_4^+ -concentration and respiration. On the contrary we observed that sites with a higher proportion of NH_4^+ in the TIN-pool resulted in lower respiration rates.

These findings are supported by quick incorporation of NH_4^+ that supposedly resulted in a transformation from inorganic N to organic amino compounds like glutamate or glutamine (Tempest and Meers 1973). This further indicates that although inorganic N, mainly as NH_4^+ , might have been utilized by microbes and accumulated into microbial biomass, higher amounts of NH_4^+ did not accelerate microbial respiration. This effect had been mentioned earlier as “ammonia metabolite repression” of fungi (Keyser et al. 1978). In the previous study NH_4^+ was reported to be able to repress the synthesis of some fungal enzymes. If this mechanism for repressing expression of enzymes can also occur in a bacterial dominated microbial community our observation would indicate that the inhibition of fungal derived enzymes would slow down litter decomposition rates already at an early stage, as they are considered to be the main degraders of recalcitrant compounds in leaf litter (Keyser et al. 1978).

On average the gravimetric C-loss was 1.6-fold higher than C-loss via CO_2 after 8 weeks (the average r^2 for each site was 0.83). We expected a similar C-loss between both methods for calculating C-loss. A possible reason for the observed differences could be that mass loss was obtained from all microcosms after destructive sampling, calculated on a dry weight basis, whereas C-loss from respiration was measured in four particular microcosms only. Regardless the gravimetric and respiration C-loss were related with a 1.6-fold factor, this is a clear indication, that respiration and mass loss are closely coupled together and respiration is an appropriate measure for decomposition rate.

The influence of initial elemental content (ii)

Other nutrients beside N could have had an effect on decomposition rates. For example Mn as a component of the exoenzyme manganese peroxidase (Berg et al. 2007) could have been an important driver for decomposition, as litter from the most active site K also showed the highest Mn content. Also P, which is known to be able to influence decomposition rates (Hobbie and Vitousek 2000) as well as Calcium (Ca), since Ca stabilizes plant cell walls (Demarty et al. 1984) and therefore possibly reduces accessibility to nutrients for microbial decomposers.

While for Austrian beech litter a critical value of 1800 for the C:P ratio was proposed, above which P mineralization is inhibited (Mooshammer et al. 2011), the highest measured C:P ratio in this study was only 1708 for AK. Therefore it is assumed, that P was not limiting litter decomposition in this experiment, although litter from AK had lowest P concentration as well as respiration rates. This indicates, that the P concentration still might have influenced microbial activity – but as AK and OR showed highest concentrations of Ca and lowest respiration, a negative influence of Ca on decomposition also cannot be excluded. Potassium was significantly highest in concentration at the most active site KL. In addition it has been shown previously that the K-content stimulated litter decomposition rates of living plants of several British herbaceous species (Cornelissen and Thompson 2008). However, litter from four sites varying in several elemental concentrations might be too less to get clear predictions of a single element on litter decomposition rates.

Microbial community changes (iii)

Gram- bacteria initially dominated the microbial community followed by gram + bacteria and fungi, although gram- bacteria continued to have the highest relative abundance until the end of the experiment. These results matched our expectations, as bacteria are in general able to degrade easily accessible compounds available during the initial stages of decomposition. Bacteria in general are followed by an increase in fungal abundance after depletion of the easily accessible compounds as fungi are more specialized on the more recalcitrant fraction for degradation (Bossuyt et al. 2001; McMahon et al. 2005; Six et al. 2006).

Similar shifts in microbial community composition were recorded for soils under an alpine grass and during primary succession (Tscherko et al. 2004), where initially dominating gram- bacteria were later succeeded by gram + bacteria and fungi. However, the data from this experiment were exclusively derived from decomposing leaf litter excluding soil. In addition the time course of this experiment was much shorter than most other decomposition studies and we assume that the substrates available in the early stages of decomposition will differ widely from most other decomposition experiments and also from litter studies including soil.

Whereas chloroform fumigation data indicated a steady increase in microbial biomass, there was no increase in total PLFA amount over the whole experiment. While in studies from other terrestrial decomposition experiments (Bailey et al. 2002; Leckie et al. 2004) a correlation between PLFA data and microbial biomass by chloroform fumigation was found, this was not observed in the present study. Bacteria are believed to contain more PLFAs per g biomass compared to fungi (Joergensen and Wichern 2008) and the observed decrease of gram- bacteria and increase of fungi over time could be another reason for not finding a correlation between total PLFA and C_{mic} .

It would have been expected, that with increasing fungal biomass, the microbial C:N ratio would increase as well (Campbell et al. 1991). In the present study, the $C_{mic}:N_{mic}$ decreased, averaged for all sites, over time from 19.0 in week zero to 6.6 in week eight. The relatively high ratio in week zero could possibly be addressed to dormant bacteria or fungal spores, since soil microorganisms appear to be largely dormant (P. Lavelle et al. 1995). The reason for the lower ratio in the last week may be due to a decrease of C_{mic} . Except for these 2 weeks the ratio seemed to be quite stable during the overall experiment (the average for all sites from week two to week eight was 9.9), which would be in accordance to the demand of microbial homeostasis (Cleveland and Liptzin 2007). Even though it has been mentioned that indicators for fungal biomass were correlated with $C_{mic}:N_{mic}$ ratio (Joergensen and Emmerling 2006), this was not always the case (e.g. Salamanca et al. 2002).

As microbial biomass was not related to respiration and litter mass loss in our experiment, the metabolic quotient (a combined factor) might provide a better insight. In the early stages respiration was highest, but

microbial biomass was lowest indicating a decrease of qCO_2 over all sites during the time course of the experiment. This is consistent with the decrease of the gram- bacteria and the increase of fungi, which are supposed to have a lower qCO_2 (Grayston et al. 2001). Moreover, the coherency of qCO_2 , TIN and FB-ratio also indicated an impact of easily available N, primarily of NH_4^+ , on qCO_2 . Higher values of qCO_2 in earlier stages of this experiment with a higher gram- bacteria content indicated lower C-use efficiency. During later stages with increased dominance of fungi, the C-use efficiency would be expected to increase (Keiblinger et al. 2010), and therefore qCO_2 to decrease. Litter quality was already defined as a decreasing function of time elsewhere (e.g. d'Annunzio et al. 2008), and in our early stage experiment many observed effects between the sites were superposed by the occurring time course. A previous study also observed that the combined “time-site” factor had a highly significant effect on extracellular enzyme activities (Keiblinger et al. 2012), which are of major importance in the breakdown of recalcitrant plant material. The response time of the microbial community was remarkably short: The microbial community structure significantly changed between week zero and week four. The differences between week four and week eight were only in a minor range in comparison indicating an early adaptation from week zero to week four. The already noticeable succession towards fungi after 4 weeks confirmed a strong impact of the more labile C- and N-pools on the microbial community as well as on the process of litter decomposition, since those pools also underwent the most pronounced changes in the very first weeks of the experiment in accordance with the stronger microbial respiration at the beginning.

Conclusions

During early stages of litter decomposition, the influence of NPOC:TDN on litter decomposition had a stronger effect on decomposition rates than bulk elemental stoichiometry. While it was expected that beech litter enriched in total N would show highest decomposition rates, in the present experiment this was not the case. Furthermore, sites lower in initial NH_4^+ -N showed less respiration and mass loss. Initial beech litter elemental contents could have a possible

influence on decomposition since Mn and K, were highest in litter from the most active site (KL) and lowest in litter from the least active site (AK).

This experiment was unique in terms of temporal resolution in early stages of litter decomposition combined with a broad range of measurements of ecophysiological parameters. Over this short period of incubation (8 weeks), our data suggest that the factor “time” was more predictive than the factor “site”, indicating that major changes occurred during the initial stages of decomposition, as had been observed for the microbial community structure. The shift from a generally bacterial dominated regime to an increase of fungal PLFAs was related with a decrease of respiration and an increase in metabolic quotient.

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