
*Urban Grass and Grass-Leaf Litter
Mixtures as Source for Bioenergy
Recovery*

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Witzenhausen, 05. Oktober 2015

Meike Piepenschneider

Preface

This thesis is submitted to the Faculty of Organic Agricultural Sciences of the University of Kassel to fulfil the requirements for the degree Doktor der Agrarwissenschaften (Dr. agr.). Three papers as first author, which are published by or accepted to international refereed journals (list of the original papers is given on the next page), are the basis for this dissertation.

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List of publications

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- Chapter 3 Piepenschneider M, Bühle L, Wachendorf M (2016) Solid Fuel Generation from Urban Leaf Litter in Mixture with Grass Cuttings: Chemical Composition, Energetic Characteristics, and Impact of Preprocessing. *BioEnergy Research*, 9, 57-66.
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Abbreviations

ADF	Acid detergent fibre
ADL	Acid detergent lignin
AR (1)	Autoregressive order 1
CO ₂ -equ	CO ₂ -Equivalences
COD	Chemical oxygen demand
DM	Dry matter
FM	Fresh matter
GC-FID	Gas chromatography with flame ionization detector
GHG	Greenhouse gas
HHV	Higher heating value
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
IFBB	Integrated generation of solid fuel and biogas from biomass
LCA	Life-cycle analysis
LHV	Lower heating value
l _N	Litre normalised to 273.15 K and 1013.25 hPa
MF	Mass flow
NDF	Neutral detergent fibre
oDM	Organic dry matter
PC	Press cake
PF	Press fluid
REML	Restricted maximum likelihood
RR	Relative reduction
RSC	Ratio of standard deviation and standard error of cross-validation
Sd	Standard deviation
VS	Volatile solids

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Chapter 1

Introduction

Background

In Germany, about 6.4 % of the final energy demand is satisfied with solid, liquid or gaseous fuels generated from biomass, which corresponds to 852 PJ a⁻¹ (Bundesministerium für Wirtschaft und Technologie 2012). While Kaltschmitt & Thrän (2009) assume an annual technical potential resulting from wood, residues and energy plants of the double energy quantity (about 1700 PJ a⁻¹) in 2020, public discussions about sense and nonsense of the utilisation of biomass in energy recovery are running high, concerning the whole range of possible arguments: technical, social, ecological and economic.

Biomass promises to be a sustainable and locally available energy source. It can be converted into marketable fuels with comparable low capital investments (Sachverständigenrat für Umweltfragen 2007). Additional advantages as the regeneration of degraded land by cultivation, as well as employment and supplementary income in rural areas may occur (Hoogwijk *et al.* 2003). On a global level, energy recovery from biomass offers the opportunity for value chains, which include developing countries (Hoogwijk *et al.* 2003).

Climate protection is one of the main advantages attributed to energy recovery from biomass. Indeed, regarding greenhouse gas (GHG) emissions, bioenergy chains show clear environmental advantage in life-cycle analysis (LCA) compared to fossil fuels (Rettenmaier *et al.* 2010). However, depending on the specific energy crop and the produced fuel, disadvantages become obvious, when taking other environmental impact categories such as eutrophication or ozone depletion into account (Rettenmaier *et al.* 2010). Additionally, GHG emission savings might be no longer existent if the boundaries of the life-cycle analysis (LCA) are extended to indirect GHG outputs. For example, global land-use changes often lead to enhanced carbon release (e. g. conversion of forest to cropland, Searchinger *et al.* 2008) though are seldom included in LCAs. Land-use changes may also occur in Germany, though in a different dimension as woodlands are effectively protected by law (Deutscher Bundestag 1975). Additionally, the area of permanent grassland did not change considerably between the years 2010 and 2015 (4.65 million ha compared to 4.68 million ha, respectively; Statistisches Bundesamt

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2015a). Nevertheless, cultivation of energy plants in Germany might enhance global land-use changes (leakage).

Next to environmental impacts of land-use changes, the pressure on agricultural land rises due to the competition between the production of food, feed, fibre and fuel (Rettenmaier *et al.* 2010). In Germany, electricity production from biomass is mainly based on biogas technology, whose main input substrate is maize (Scheftelowitz *et al.* 2015). However, maize has a comparable high impact on the environment as it regularly needs high amounts of fertiliser and pesticides. Also, significant soil erosion and nitrogen leaching occur with consequences for ground and surface water. Additionally, maize is usually cultivated as a monoculture with negative impacts on bio- and agrobiodiversity, as well as on the recreational value of the landscape (Sachverständigenrat für Umweltfragen 2007; Graß *et al.* 2013). Alternative management regimes such as double-cropping systems are suggested to minimise negative environmental effects (Graß & Scheffer 2003; Graß *et al.* 2013). Next to the attempt to produce energy plants more ecologically, the utilisation of residual biomass seems promising. Focussing on residual biomass may help to identify and exploit considerable amounts of produced though unused material. Utilisation of residual biomasses implies a more effective exploitation of already available resources. Regarding urban biomass, an utilisation of these materials meet one of the main aims in European waste politics: to reduce the amount of biodegradable municipal waste, which is disposed in landfills (European Commission 2014a).

In 2014, more than half of the generated renewable thermal energy was already provided from biogenic solid fuels arising from households and industry (Fachagentur Nachwachsende Rohstoffe e. V. 2014). However, the degree of utilisation of organic and green waste, which is in Germany regularly collected separately, accounts for only 5-10 % in a rough estimation (Mühlenhoff 2013). This is mainly due to heterogeneous quality and complex logistics (Mühlenhoff 2013). Nevertheless, this fraction accounts for 8.6 million t of fresh matter (FM) with about 4.4 million t of green waste (Funda *et al.* 2009). This quantity is currently composted (Funda *et al.* 2009) with low or even negative revenues, or burnt in waste incineration plants, which regularly take fees for acceptance (Hasse 2012). Thereby, the green waste disposer (usually the municipality) has management costs though without considerable revenues from this resource. Instead, the municipalities could use this material in energy recovery and thereby neutralise the costs for logistics, or even generate a small financial benefit. There exist

well-intentioned projects utilising green waste as solid fuel (Hasse 2012), but a widespread recovery is not given.

McCormick & Kaberger (2007) stated that no EU member country exhausts the actual bioenergy capacity. They determined barriers for bioenergy by analysing six case studies from different European countries, which comprised various input materials, technologies and outputs. Main barriers were: economic conditions because nuclear power and fossil fuels profit from subsidies and external costs are often not included in calculations; expertise and institutional capacity because interdisciplinary approaches become necessary; as well as supply chain coordination, which reliably connects all relevant actors (McCormick & Kaberger 2007). The authors concluded that there are “no absolute barriers to realising the potentials of bioenergy in the EU” but point out that mature conversion technologies exist and key barriers, which are hindering the extension of bioenergy, are rather non-technical. This thesis will partly answer, whether this statement holds true for urban green waste.

Regular technical opportunities to recover biomass for energetic purpose are fermentation and direct combustion. Urban green waste consists, depending on the season, of leaf litter, grass and hedge clippings and shows therefore a very heterogeneous quality. Generally, this material is characterised by comparable high fibre (Liew *et al.* 2012) and mineral concentrations (Hensgen *et al.* 2011). This composition complicates its energetic utilisation with the aforementioned technologies. On the one hand, inverse linear relations are regularly found for methane yield and lignin concentration (Liew *et al.* 2012; Prochnow *et al.* 2009b). On the other hand, minerals, in particular Cl, K, S and N, have detrimental effects during combustion as corrosion, slagging and toxic emissions appear (Oberberger *et al.* 2006; Prochnow *et al.* 2009a; Jenkins *et al.* 1998). To solve this problem, a separation of fibres and of minerals seems appropriate and can be realised with the “integrated generation of solid fuel and biogas from biomass” (IFBB) technique. During the IFBB procedure, the biomass is mashed with warm water and subsequently separated mechanically into a fibre-rich press cake and a press fluid, which contains major parts of the minerals and of easy soluble hydrocarbons (Wachendorf *et al.* 2009). These are highly fermentable and are therefore a valuable substrate for biogas production, while the press cake can be burnt in an adapted biomass boiler with a cooled burning chamber and well-controlled oxygen supply (Bühle *et al.* 2014; Oberberger *et al.* 2006; Prochnow *et al.* 2009a). The technique is well investigated for agricultural material (Hensgen

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et al. 2012), as well as for mixtures of green cut material from landscape conservation and private households (Hensgen *et al.* 2011).

The chemical composition of grass from urban roadside verges is unknown so far. This concerns the minerals, as well as potentially toxic elements (“heavy metals” as defined in chapter 2). It is widely recognised that traffic activities cause accumulation of potentially toxic elements on the road surface. During rainfall events, the elements are washed into the surrounding environment (e. g. Helmreich *et al.* 2010; Brown & Peake 2006). In a meta-analysis comprising 64 sites across Europe Werkenthin *et al.* (2014) show that element concentrations (Cd, Cr, Cu, Ni, Pb and Zn), as well as their deviations are highest at a small distance (<5 m) from the road. However, at a distance >10 m the median concentrations of the elements were close or below the assumed background values. The relevance of this contamination for urban biomass from roadside verges (mainly grass clippings) and its usability in energy recovery will be discussed in chapter 2. The concentration of minerals will be given and the influence of the IFBB procedure on the concentration levels will be presented.

As mentioned, grass clippings from urban environments barely occur in pure fractions, but in mixtures with other biomasses. The impact of the IFBB technique on typical urban green waste mixtures (grass cuttings and leaf litter) will be addressed in chapter 3.

While in German municipalities about 4.4 million t of green waste are currently collected (Funda *et al.* 2009), the actual available amount is unknown. Until now, municipalities had no reason to collect these data and additionally, a non-quantifiable amount of biomass is composted by inhabitants (Hogg *et al.* 2002) or by widely independently acting municipal entities. Therefore, the theoretical biomass potential of urban roadside verges and its characteristics regarding energy recovery options is the focus of chapter 4.

Research objectives

Utilising urban green waste for energy generation could contribute to a sustainable development of energy supply including all levels of sustainability (economic, social, ecological). A precondition for the exploitation of this, by now widely unused, resource is its technical suitability in energy recovery procedures. The suitability is, however, strongly dependant on the chemical characteristics of the material. To gain insight into the chemical composition of two important urban waste fractions (grass from roadside verges and leaf litter from park areas) samples were taken in the city of Kassel, which was assumed to be a typical major city in Germany, as well as in Europe. For example, the mean number of inhabitants in European cities in 2012 was according to Eurostat (urban audit) about 260,000 (Eurostat 2015), while Kassel has 197,000 inhabitants (Stadt Kassel 2014). In Kassel the car density is about 432 cars per 1,000 inhabitants (Frehn *et al.* 2012), the German mean is 531 and the European mean is 435 (Statistisches Bundesamt 2014).

Grass was collected from roadside verges (10 sites with a 2-cut and a 4-cut management, each) and leaf litter was taken from a major park within the city. Leaf litter was mixed with a *Lolium perenne* dominated sward with a share of 0%, 33%, 66% and 100 % of leaf litter (fresh matter based). The pure fractions, as well as the mixtures were ensiled and subsequently analysed on their chemical composition, before and after application of the IFBB technique. As for the grass from urban roadside verges, I focused on the elemental composition including possible contamination with elements originating from traffic activities and their mass flows within the IFBB procedure. As for the leaf litter-grass mixtures, the focus was on potential interactions between the fractions regarding the mass flows during the IFBB process.

Data on the fibre composition was gained from grass of roadside verges in the two mentioned cutting intensities (2-cut, 4-cut) and specific methane potential was measured in batch tests. Additionally, biomass yield was determined in two successive years. A comparison of recovery techniques (biogas and IFBB) based on the gained data allowed evaluation of the potential of urban grass biomass in energy generation.

In detail, the research objectives of this thesis were to clarify

- (i) the elemental and fibre composition, which can be expected from typical urban green wastes: grass of urban roadside verges at different maturity stages and mixtures of grass and leaf litter.

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- (ii) the influence of the IFBB procedure on the elemental composition of grass from roadside verges and of mixtures from grass and leaf litter focussing on interrelations between substrates, as well as on mass flows of heavy metals (Cd, Cr, Cu, Mn, Pb, Zn).
- (iii) the energetic and chemical characteristics of the IFBB solid fuel and press fluid produced from grass from roadside verges and from mixtures from grass and leaf litter.

To quantify the potential contribution of grass from urban areas to a sustainable energy provision, further objectives were to determine

- (iv) the biomass and methane potential of grass from roadside verges.
- (v) the potential gross energy yield from application of biogas technology or IFBB technique on grass from roadside verges.

Chapter 2

Element concentrations in urban grass cuttings from roadside verges in the face of energy recovery

Abstract

Grass from municipal roadside verges is a potential yet largely unused resource for bioenergy recovery, which is mainly due to its unknown elemental composition. Therefore, we measured the concentration of 16 elements (Ca, K, Mg, N, Na, P, S, Al, Cd, Cl, Cr, Cu, Mn, Pb, Si, Zn) in material from the city of Kassel harvested in different management intensities. The element concentrations were mainly close to reference values of agricultural or nature conservation grassland and usually within the range of literature data. Concentrations of most elements, including heavy metals (Cd, Cr, Cu, Mn, Pb, Zn), were below limiting values. Only N and Cl concentrations in the raw material exceeded the limiting values for combustion, but washing and dewatering of the biomass with the “integrated generation of solid fuel and biogas from biomass” technique resulted in concentrations in the press cake well below the limiting values. Considering the element concentrations of grass from urban roadside verges, utilisation for energy recovery may be possible, provided an appropriate technology is applied.

Introduction

Using grass for bioenergy purpose became popular in recent years, concentrating on perennial energy grasses (Prochnow *et al.* 2009a). However, grass from municipal roadside verges is increasingly seen as potential resource for bioenergy (El-Nashaar *et al.* 2009). In many cities, roadside verges are frequently mulched rather than harvested although this management stresses public budgets without compensation. Potential energy recovery technologies are combustion and biogas production. On the one hand, the utilisation of grass in combustion is, compared to wood, mainly limited by the higher concentration of elements complicating combustion. However, adapted technology can solve the problems (Prochnow *et al.* 2009a; Obernberger *et al.* 2006; Wachendorf *et al.* 2009). On the other hand, co-digestion of grass from public green areas and roadside verges is possible, but methane production can be low compared to other digestates, and the high dry matter (DM) content may cause technical problems (Hidaka *et al.* 2013; Moor *et al.* 2013). To overcome these technical difficulties, the IFBB technique was developed. The main step of this technique is the hydrothermal conditioning with subsequent mechanical dehydration of the material. Thereby, the biomass is divided into

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a fibre-rich press cake (PC) and a highly digestible press fluid (PF), which contains the easy-soluble carbohydrates and, in large part, the soluble mineral compounds. Utilising the press fluid of agricultural grass in fermentation delivered higher methane yields per volatile solids (VS) in comparison to grass silage. The press cake could be presented as high-quality solid fuel. By now, the technique is well investigated and the general reliability is proved (Wachendorf *et al.* 2009; Hensgen *et al.* 2012). The application of the IFBB technique is especially suitable for highly fibrous green material, which is less suitable for direct fermentation. In general, the fibre content increases with advancing maturity of biomass (Prochnow *et al.* 2009b). To deliver information for both recovery methods, IFBB and fermentation, grass of different maturity stages was investigated in this study (2-cut-, 4-cut-management).

Next to these technical challenges, municipalities worry about the concentration of contaminants and the unclear legal consequences. A major reason is that, in many European countries, urban grass cuttings are classified as waste, which puts any usage of this biomass into the difficult legal context of the Waste Framework Directive 2008/98/EC, which defines end-of-waste criteria. The outcome of an ongoing discussion in European politics will specify these criteria for biodegradable waste to support waste managers to adhere to the waste hierarchy and ensure that substances are more likely to be put to a useful purpose and are less likely to be disposed (European Commission 2015). Once established, these criteria will help to prevent negative effects on environment and human health, which, for example, can arise from inorganic contaminants.

From a technical point of view, inorganic contaminants can stimulate or inhibit acidogenesis and methanogenesis in biogas production, as they interfere with microorganisms' enzymes. Toxic concentrations are highly variable and depend on substrate, bacteria genre, the relative toxicity and environmental factors (Chen *et al.* 2008; Mudhoo & Kumar 2013). However, Scholwin (2009) give rather high guiding values for toxic concentrations (e.g. Cu >40 mg l⁻¹, Pb >340 mg l⁻¹) in comparison to the mean concentration in road runoff (Cu 0.19 mg l⁻¹, Pb 0.056 mg l⁻¹; Helmreich *et al.* 2010). Regarding combustion processes, inorganic contaminants are mainly of interest concerning emissions and ash utilisation, whereas no considerable detrimental effects appear during combustion (Hartmann 2009).

Hartmann (2009) observed higher concentrations of macro-elements in grass from roadside verges than in landscape conservation hay. Investigations on the heavy metal contamination

of roadside verges mainly focused on the concentration in soil usually finding decreasing levels with increasing distance from the road (Werkenthin *et al.* 2014). Werkenthin *et al.* (2014) summarised the results of 27 European studies finding that median metal concentrations (Cd, Cr, Cu, Ni, Pb, Zn) in >5 m distance from the road edge not exceeded Dutch target values. Little information exists on heavy metal bio-monitoring in single plant species. With regard to pollutant dispersion, moss bags were successfully used to monitor major and trace elements originating from street canyons in Serbia (Fumagalli *et al.* 2010) and in Italy (Nicola *et al.* 2013). In the first cut of *Lolium multiflorum*, Ylärinta (1994) found significantly higher concentrations of Zn and Pb in 22 m distance from the road but not of Cu and Cd in comparison to material from 200 m distance. In the second cut, the difference only prevailed for Pb. Higher levels of Pb and Cu, but not of Mn, have been found in tissue of close-to-road individuals in Italy (Alfani *et al.* 1996). In China, concentrations of Cd, Cr, Pb, Zn, but not of Cu, in leaves of *Sophora japonica* were significantly higher in tissue from roadside sites than from park sites (Li *et al.* 2007). However, increased metal concentrations do not automatically indicate toxic levels: Li *et al.* (2007) measured Cd concentrations of 0.1 mg kg⁻¹ DM in leaves at roadside sites, while the EU limiting value for Cd in potatoes for human diet is at a much higher level, i. e. 0.1 mg kg⁻¹ FM (The Commission of the European communities 2006). High variability in metal concentrations within plant species, plant part, sampling period, leaf age, wind direction, soil pH and soil mineral content complicates the interpretation of data (Ylärinta 1994; Alfani *et al.* 1996; Massadeh *et al.* 2009). As many investigations revealed that the concentration of several metals in plant samples is mainly due to deposition (e. g. Ylärinta 1994; Alfani *et al.* 1996; Massadeh *et al.* 2009; Fumagalli *et al.* 2010), washing tests were conducted, which showed a pronounced reduction of metals (Massadeh *et al.* 2009). There are only few studies on contamination with a view to utilisation of the material from roadside verges in bioenergy recovery and even fewer studies deal with a wide range of elements (e. g. Selig & Fischer 2003).

Thus, the aim of this study was to answer the following questions: (i) What is the elemental composition of grass from roadside verges in a typical German city? (ii) Is the elemental composition differing between 2-cut and 4-cut management and between cut numbers and is it depending on soil element concentration? (iii) Is the elemental composition of roadside grass limiting its utilisation for energy recovery with special regard on inorganic contaminants (“heavy metals” defined as Cd, Cr, Cu, Mn, Pb, Zn)? (iv) Which influence has the IFBB technique on the elemental composition?

Chapter 2

Materials and methods

Investigation sites and soil characteristics

In Kassel, a city located in the middle of Germany with about 200,000 inhabitants and an area of 107 km² 10 evenly dispersed investigation sites were established. All sites were classified by the municipal administration as roadside verges and the bordering roads as main roads“ with a traffic volume of up to 35,000 cars per working day (Figure 1). The data concerning traffic density were provided by the city administration of Kassel and are based on a traffic model that was developed from structural and network data, as well as on data from traffic monitoring. Smallest distance between site and nearest road ranged from 3 to 31 m (Table 1).

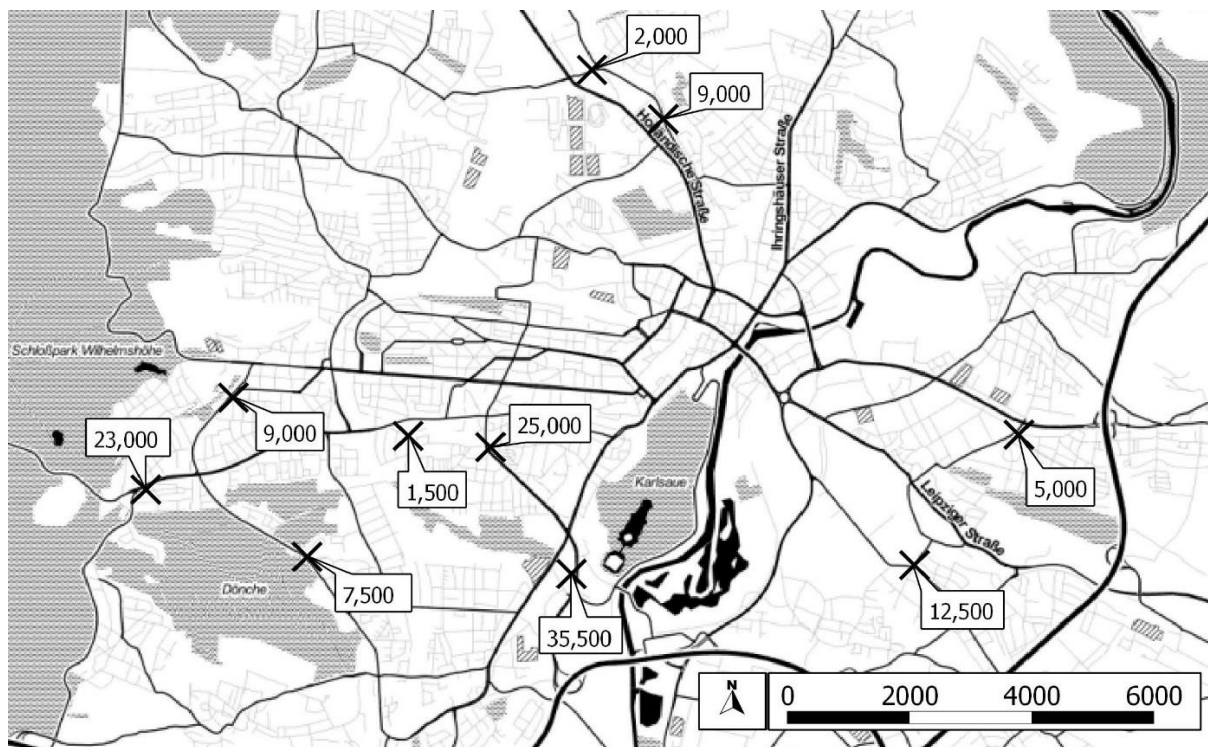


Figure 1. Locations of the 10 investigation sites within the city of Kassel. Traffic density (cars working day⁻¹) is stated according to the traffic model of the city administration of Kassel, which is calibrated with traffic censuses. Scale is given in meter. Underlying map: OpenStreetMap contributors (<http://www.openstreetmap.de>).

A botanical survey conducted in the first week of July revealed a species richness between 14 and 34 per site (Table 1). Most commonly *Agrostis stolonifera*, *Festuca rubra*, *Lolium perenne* and *Trifolium repens* occurred in coverage >10 %.

Table 1. Botanical characteristics of grassland vegetation at the 10 investigation sites in the city of Kassel (Germany) and distance to closest road.

Site	Number of species	Species with coverage >10 % of site area	Distance to closest road (m)
1	28	<i>Agrostis capillaris</i> , <i>Trifolium pratense</i>	6
2	26	<i>Agrostis stolonifera</i> , <i>Festuca rubra</i> , <i>Galium verum</i> , <i>Lolium perenne</i> , <i>Prunella vulgaris</i> , <i>Taraxacum spec.</i>	31
3	23	<i>Agrostis stolonifera</i> , <i>Decidious tree shoot</i> , <i>Lolium perenne</i> , <i>Poa pratensis</i> , <i>Trifolium repens</i>	9
4	34	<i>Agrostis stolonifera</i> , <i>Arrhenatherum elatius</i> , <i>Festuca rubra</i> , <i>Lolium perenne</i> , <i>Phleum pratense</i> , <i>Potentilla reptans</i> , <i>Veronica hederifolia</i>	3
5	27	<i>Achillea millefolium</i> , <i>Agrostis stolonifera</i> , <i>Glechoma hederacea</i> , <i>Festuca rubra</i> , <i>Holcus lanatus</i> , <i>Lolium perenne</i>	7
6	19	<i>Agrostis stolonifera</i> , <i>Glechoma hederacea</i> , <i>Festuca rubra</i> , <i>Lolium perenne</i>	5
7	23	<i>Agrostis stolonifera</i> , <i>Festuca rubra</i> , <i>Prunella vulgaris</i> , <i>Trifolium repens</i>	5
8	14	<i>Achillea millefolium</i> , <i>Agrostis stolonifera</i> , <i>Lolium perenne</i> , <i>Trifolium repens</i>	8
9	18	<i>Achillea millefolium</i> , <i>Agrostis capillaris</i> , <i>Festuca rubra</i> , <i>Stellaria graminea</i>	11
10	22	<i>Agrostis capillaris</i> , <i>Holcus lanatus</i> , <i>Lolium perenne</i>	9

At six points at each site soil samples were taken in 0-30 cm depth, dried at room temperature and subsequently sieved to 2 mm. For each site, a mixed sample was produced and kept cool at 4 °C until analysis. Soils had a pH between 5.8 and 7.5 (Table 2). Element concentrations differed, but no obvious contamination was determined comparing concentrations with standard literature values (Scheffer *et al.* 2010). Only at site 3 Zn and Pb concentrations were higher than assumed as background value, though still low compared with concentrations of industry-contaminated soils (Scheffer *et al.* 2010).

Table 2. Soil conditions at the 10 investigation sites in the city of Kassel (Germany) in 0-30 cm depth.

	Site										Mean±Sd
	1	2	3	4	5	6	7	8	9	10	
pH	5.8	7.5	7.3	7.4	6.1	7.3	7.3	7.5	6.0	6.5	6.9±0.64
Ca (g kg ⁻¹)	3.12	21.55	9.13	8.46	3.34	13.59	11.75	15.41	4.16	6.18	9.7±5.7
K (g kg ⁻¹)	1.79	2.76	3.80	2.65	1.93	3.76	3.15	4.83	2.57	2.50	3.0±0.9
Mg (g kg ⁻¹)	2.88	4.22	4.77	2.95	2.43	5.96	5.48	10.66	7.30	4.65	5.1±2.3
Na (mg kg ⁻¹)	277	494	253	339	185	832	380	1067	323	298	445±269
Al (g kg ⁻¹)	13.37	12.91	17.09	12.83	10.88	15.44	15.85	17.96	17.10	13.57	14.7±2.2
Cd (mg kg ⁻¹)	0.27	0.38	1.70	0.28	0.26	0.24	0.21	0.49	0.25	0.23	0.43±0.43
Cl (mg kg ⁻¹)	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Cr (mg kg ⁻¹)	35	29	37	26	22	34	34	46	67	43	37±12
Cu (mg kg ⁻¹)	15	30	35	22	28	20	18	58	22	18	27±12
Mn (mg kg ⁻¹)	474	343	452	410	443	432	587	445	593	469	465±72
P (mg kg ⁻¹)	55	59	70	66	62	101	83	100	94	72	76±16
Pb (mg kg ⁻¹)	30	33	199	33	50	33	41	116	38	43	62±52
Zn (mg kg ⁻¹)	59	145	1492	94	81	81	62	254	70	67	241±421
N (%)	0.11	0.16	0.15	0.16	0.17	0.15	0.11	0.26	0.18	0.15	0.16±0.04
C/N ratio	12.63	16.30	17.30	15.96	14.86	15.44	15.54	17.21	13.09	13.33	15.17±1.51

Sd, Standard deviation

Plant sampling and processing

At all sites, a 4-cut and 2-cut mowing regime was established of 40 m² each. Plant samples were taken in calendar weeks 27 and 39 for the 2-cut and 4-cut regime and additionally in weeks 21 and 33 for the 4-cut regime. Samples were cut in triplicates at 5 cm height with scissors by hand. They were kept cool and were immediately dried at 65 °C for 48 to 156 h depending on their water content. Samples were ground with a cutting mill (SM 1, Retsch) to 5 mm and subsequently with a sample mill (1093 Cyclotec, Foss) to pass a 1 mm sieve. From plots of the 2-cut regime material was pooled and ensiled in 30 l barrels for being processed with the IFBB technique. After sampling, the plots were mowed with a flail mower (AS Motor 570 SM) and the not required biomass was removed from the plots. Ensiling lasted for 6 weeks minimum.

Silage was processed with IFBB technology as described by Hensgen *et al.* (2011). Hydrothermal conditioning was conducted with a silage:water ratio of 1:4 and a temperature of 40 °C for 15 min. The material was subsequently dewatered with a screw press (type AV, Anhydro Ltd., Kassel, Germany), which had a pitch of 1:6 and a rotation speed of 6 revolutions per

minute. The resulting solid fraction (PC) was dried at 65 °C for 48 h minimum and afterwards ground in the same procedure as that of the raw plant material.

Laboratory analysis

Analysis of Cl

For Cl⁻ analysis in the plant material, 40 ml 0.15 M HNO₃ was added into an Erlenmeyer flask containing 1 g of plant material, and the mixture was shaken manually. For Cl⁻ analysis in soil, 50 ml 0.15 M HNO₃ was added into an Erlenmeyer flask containing 10 g of soil and the mixture was left on a shaking plate for 30 min. The suspensions were filtered over filter paper and the filter was then rinsed with 20 ml 0.15 M HNO₃. The amount of chlorides present in the samples was subsequently determined via a potentiometric titration of the extract with silver nitrate (AgNO₃) using a Metrohm 718 STAT titrino apparatus (Metrohm), after standardisation of AgNO₃ with 0.01 N NaCl. The chloride concentration of the samples was calculated using the formula:

$$\text{Cl}^- = \frac{V * C * M_w}{M_s},$$

where V is the volume of silver nitrate used during titration,

C is the normality of silver nitrate,

M_w is the atomic weight of chloride

M_s is the sample mass.

Analysis of Ca, K, Mg, Na and P, as well as Al, Cd, Cr, Cu, Mn, Pb and Zn

For the determination of Ca, K, Mg, Na and P, as well as Al, Cd, Cr, Cu, Mn, Pb and Zn plant samples were pre-treated by open microwave. Dried plant material (0.25 g) was transferred to a plastic microwave digestion vessel. HNO₃ (3.5 ml) and H₂O₂ (3.5 ml) were added successively under a fume hood and the mixture was allowed to react at room temperature overnight (minimum 12 h) before microwave digestion. Next, the samples were diluted until 25 ml and filtered on an acid resistant filter into a 50 ml volumetric flask. The filtrate (open microwave extract) was analysed for Ca, Mg, Na and K, as well as for Al, Cd, Cr, Cu, Mn, Pb and Zn with inductively coupled plasma – optical emission spectrometry (ICP-OES: Varian vista MPX, Varian Palo Alto). For P analysis in plant samples, 1ml of the previously described open microwave extract, 5ml of water, 1 ml Scheel solution I and 1 ml Scheel solution II were successively

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added to a test tube. The mixture was shaken for homogenisation and allowed to react for 15 min. Then, 2 ml of Scheel solution III was added and the mixture was shaken again and allowed to react for 15 min. The same procedure was followed for the standards of 0, 25 and 50 mg P l⁻¹. The absorbance was measured at 700 nm with a Jenway 6400 spectrophotometer absorbance, designed and manufactured by Jenway LTD (Ranst 1999).

For the determination of Ca, Mg, Na and K, as well as of Al, Cd, Cr, Cu, Mn, Pb and Zn in soil samples, 1 g of dried soil was transferred into an Erlenmeyer flask. A minimum amount of water (2-3 ml) was added to moisten the soil. Next, 7.5 ml of concentrated HCl and 2.5 ml of concentrated HNO₃ were added successively under a fumehood for *aqua regia* digestion. The container was covered with a watch glass and the mixture was allowed to react at room temperature overnight (minimum 12 h). Then, the mixture was boiled for 2 h and allowed to cool to ambient temperature. The extract was filtered on an acid resistant filter into a 100 ml volumetric flask. The Erlenmeyer flask was rinsed repeatedly and the residue was transferred to the filter with an aqueous solution of 1% HNO₃. The combined filtrate (*aqua regia* extract) was analysed with ICP-OES (Ranst 1999) but with ICP-mass spectrometry for Cd. For P analysis of soil samples, 1 ml of *aqua regia* extract, 5 ml of water, 1 ml Scheel solution I and 1 ml Scheel solution II were successively added to a test tube. Then, the same procedure as for P analysis in plant samples was conducted.

Analysis of N, S and Si

Nitrogen concentration in soil and plant samples was measured using 150 mg of dried material in an elemental analyser (Vario MAX CHN Elementar Analysensysteme GmbH). Sulphur and Silicon concentration was measured in plant samples of the 2-cut regime only. Samples were prepared with pressure digestion and analysed according to DIN EN ISO 11885 with ICP-OES.

Statistics and calculations

Statistical analyses was conducted with R 2.15.3 (R Core Team 2013) concerning descriptive statistics and Mann-Whitney *U* test was used to detect differences in element concentrations between regimes and effects of IFBB procedure. For further inferential statistics, SAS 9.2 was applied using the mixed model procedure MIXED due to repeated measurements with harvest dates nested within sites as repeated measures factor. The type of covariance structure was set as autoregressive order 1 (AR 1), which is commonly used for low numbers of equally

spaced observations, as it assumes the same correlation for all pairs of observation (Littell *et al.* 2006). The Restricted Maximum Likelihood (REML) method was used to estimate the covariance parameters and standard errors, and *F*-statistics of the covariance model was corrected by Satterthwaite approximation. Differences in element concentrations between single harvests within a regime (4-cut or 2-cut) were calculated using differences of least-square means taking the covariance structure of data into account. Due to Satterthwaite approximation, denominator degrees of freedom are variable and thus, the conservative studentized maximum modulus method was used to adjust least-square means statistics (SAS Institute Inc. 2015).

Relative reduction of elements due to dewatering was calculated as

$$RR = \frac{\text{Concentration of } x \text{ in silage} - \text{Concentration of } x \text{ in press cake}}{\text{Concentration of } x \text{ in silage}}$$

where *x* is the measured element.

Massflow was calculated as

$$MF = \frac{\text{percentage of } DM_{\text{press cake}} \text{ in mash} * DM_{\text{press cake}} * \text{Content}_x \text{ in press cake}}{DM_{\text{mash}} * \text{Content}_x \text{ in silage}}$$

where *x* is the measured element.

Results and discussion

Element concentrations compared to reference and limiting values

The concentrations of Ca and P in grass cut in 2- or 4-cut-regime and of Mg in 4-cut regime were higher than in agricultural or conservation grassland (Table 3). However, concentrations were within ranges that were observed in other herbaceous material from roadside verges. There are no limiting values in German legislation for the concentration of those elements; nevertheless, according to the non-industrial standard DIN EN 14961-6:2012 for pellets from non-woody material class B, a total ash concentration of 10 % is limiting (DIN Deutsches Institut für Normung e. V. 2012). This value was met by the measured ash contents.

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However, in other studies higher ash contents were detected (Hartmann 2009; Delafield 2006), likely due to the harvesting technique, which highly influences the amount of collected soil particles (Heckman & Kluchinski 1996, for leaf litter). Phosphorus and nitrogen concentrations differed between the 2-cut and the 4-cut regime with higher concentrations in the 4-cut regime (Table 4). This might be because the material of the 4-cut management is less mature in general and, thus, does contain less carbohydrates, whereas minerals, crude protein and crude fat have a relatively higher portion (Prochnow *et al.* 2009b). Nitrogen and potassium concentrations in both cutting regimes exceeded the agricultural reference values and partly those values found in grass from roadside verges. High K values may refer to the extraordinary dry weather conditions of the summer 2013 (precipitation from June to August was about 48% lower than the last decade's average value; Deutscher Wetterdienst 2014). This complies with results of Iannucci *et al.* (2002), who found increased K concentrations in drought-stressed *Trifolium* species. The N concentration in material from the 4-cut regime missed the limiting value of the DIN EN 14961-6:2012 (2 %) narrowly. High N concentrations with values >2 % in urban grass samples are common, as lawns are known to function as N sink (Raciti *et al.* 2008). During combustion, N can form NO_x emissions, which are not desirable regarding climate protection and human health. However, existing technique can reduce NO_x emissions: Prochnow *et al.* (2009a) and Obernberger *et al.* (2006) list among others steam air recirculation, appropriate air and fuel staging, as well as advanced air supply systems and boiler geometry as appropriate measures.

The S concentration measured in this study was lower than the reference values and met exactly the DIN limiting value. For Na, Al, Mn and Si, the prevailing norms give no limiting values, but measured concentrations fell within the range of or in case of Na below the reference values from agricultural or conservation grass, and for Na and Mn also in the range of grass from roadside verges as reported in the literature. Concentrations of Cl are known to be high in herbaceous material (Obernberger *et al.* 2006). We measured concentrations of about 5 g kg⁻¹ which met the reference values but highly exceeded the limiting value of the prevailing DIN. Obernberger *et al.* (2006) give a guiding concentration of 1 g kg⁻¹ for an unproblematic combustion.

Table 3. Element concentrations (conc.) in biomass harvested on roadside verges in the city of Kassel (Germany). Shown are mean values for the 2-cut and the 4-cut regime. Literature values from agricultural or conservation grassland, as well as from grass of roadside verges are given for comparison. Limiting values are presented wherever available.

Element	Mean conc. *		Conc. in agricultural or conservation grass	Conc. in grass from roadside verges	Limiting value
	2-cut	4-cut			
Ca (g kg ⁻¹)	6.86	7.22	3.8 ^a	20.38 ^a 6.3 ^d	-
K (g kg ⁻¹)	22.81	26.1	19.4 ^a	13 ^a 18.2 ^d	-
Mg (g kg ⁻¹)	1.68	1.92	1.7 ^a	6.3 ^a 1.9 ^d	-
N (%)	1.59	2.09	0.87 ^a	1.49 ^a 2.03 ^d	2 ⁱ
Na (mg kg ⁻¹)	133.6	136.19	1000 ^b	203-2300 ^e	-
P (g kg ⁻¹)	3.57	4.22	1.7 ^a	6.3 ^a 2.4 ^d	-
S (%)	0.2	-	1.4 ^a	1.9 ^{a, d}	0.2 ⁱ
Al (mg kg ⁻¹)	79.15	61.80	7-3410 ^c	-	-
Cd (mg kg ⁻¹)	<0.4	<0.4	0.03-1.26 ^c	0.02-0.64 ^f 0.12-0.25 ^g 0.01-1.08 ^h	0.5 ⁱ 1.5 ^{k, l}
Cl (g kg ⁻¹)	4.76	5.64	5 ^a	8.8 ^a	3 ⁱ
Cr (mg kg ⁻¹)	0.58	0.59	0.5-3.4 ^c	0.17-0.3 ^g 0.6-54 ^h	50 ⁱ 100 ^l
Cu (mg kg ⁻¹)	7.11	7.63	7.4-15 ^c	4.7-19.3 ^f 5.13-8.13 ^g 4-62 ^h	20 ⁱ 100 ^l
Mn (mg kg ⁻¹)	92.1	78.45	35-106 ^c	14.6-212.6 ^f 170 ^d	-
Pb (mg kg ⁻¹)	<4	<4	2.4-7.8 ^c	0.9-11.7 ^f 0.21-0.29 ^g 3-144 ^h	10 ⁱ 150 ^{k, l}
Si (g kg ⁻¹)	6.08	-	3-12 ^c	-	-
Zn (mg kg ⁻¹)	34.39	43.56	15-80 ^c	13.7-130 ^f 1.7-14.7 ^g 25-256 ^h	100 ⁱ 400 ^l
Ash content (%)	8.98	9.84	5.7 ^a	23.1 ^a 11.7 ^d	10 ⁱ

- not determined or available; *yield weighted mean; ^aHartmann 2009; ^bObernberger *et al.* 2006, grass in general; ^cKabata-Pendias 2011, preferable values refer to Germany or similar climate; ^dDelafield 2006, values measured in Wales; ^eBryson & Barker 2002, values measured in Massachusetts; ^fGarcia & Millán 1998, values measured in Spain; ^gModlingerová *et al.* 2012, values measured in *Achillea millefolium* in Czech Republic; ^hSeling & Fischer 2003; ⁱDIN Deutsches Institut für Normung e. V. 2012; ^kBundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz 2012, legislation about fertilising; ^lBundesministerium für Umwelt, Naturschutz und Reaktorsicherheit 1998, legislation about using bio-waste on agricultural soil

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To achieve proper Cl concentrations, a pre-combustion treatment would be necessary (e.g. leaching, Tonn *et al.* 2011; washing and fractionating, King *et al.* 2012; IFBB processing, Bühle *et al.* 2012a). Concentrations of Cd and Pb were below the detection limits of 0.4 mg kg^{-1} and 4 mg kg^{-1} , respectively, in 99 % of samples and thus, below the limiting value of the DIN and the legal limiting value for fertilisers (Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz 2012). Concentrations of Cr, Cu and Zn fell within the range of the reference values and are far from exceeding the limiting values. In summary, biomass from roadside verges from the city of Kassel had a very similar elemental composition in comparison to agricultural or conservation grass. Especially, concerns about inorganic contaminants were found not to be valid. In contrast, the inorganic contamination was low in general. This is confirmed by results of Seling & Fischer (2003), who came to the same conclusion when investigating contaminants in grass cut from roadside verges for compost purpose.

Differences between cuts

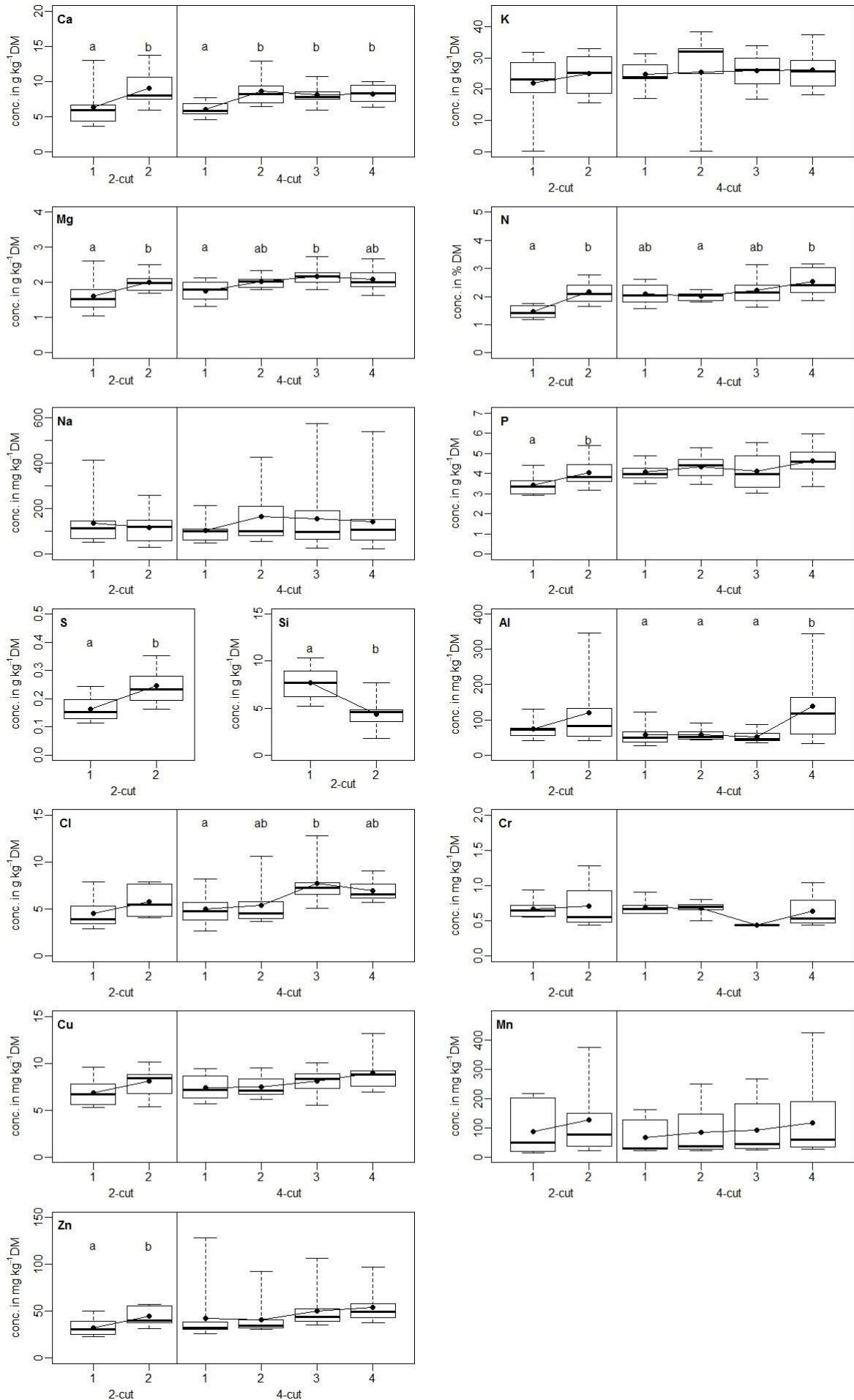
In the 2-cut regime, the concentrations of Ca, Mg, N, P, S and Zn were significantly higher in the second cut, while the Si concentration decreased (Table 4, Figure 2). This is in agreement with recent studies, which showed a negative correlation between Si concentrations and the concentrations of Ca and Zn (Brackhage *et al.* 2013), as well as of P and Si (El-Nashaar *et al.* 2009). Ca and Si are structural constituents of the cell wall and Si is known as an important element mitigating environmental stress factors, such as drought (Brackhage *et al.* 2013). In the 4-cut regime single cuts differentiated regarding the concentration of Ca, Mg, N, Al and Cl. For Mg and Cl, the first cut had a lower concentration than the third cut when the weather was particularly dry and might have induced an increase in the concentration of inorganic solutes (Iannucci *et al.* 2002).

Table 4. Levels of significance for the effects of cutting frequency, cut number within regimes and hydrothermal conditioning, as well as of the relationship between soil element concentration and plant element concentration and removal, respectively.

Element	Cutting frequency	Cut number		Hydrothermal conditioning	Linear regression plant concentration vs. soil concentration (p-value, R ² , slope in % plant per % soil)		Linear regression element removal vs. soil concentration (p-value, R ² , slope in kg ha ⁻¹ per % soil)	
		2-cut regime	4-cut regime		2-cut regime	4-cut regime	2-cut regime	4-cut regime
Ca	ns	<0.5	<0.01	<0.01	ns	ns	ns	ns
K	ns	ns	ns	<0.001	ns	ns	ns	ns
Mg	ns	<0.5	<0.01	<0.001	ns	ns	0.05, 0.57, 1.6	ns
N	<0.01	<0.001	<0.5	<0.001	ns	<0.05, 0.52, 4.8	<0.01, 0.73, 1125	<0.01, 0.61, 693
Na	ns	ns	ns	<0.001	ns	ns	ns	ns
P	<0.01	<0.5	ns	<0.001	ns	ns	ns	ns
S	-	<0.01	-	<0.001	-	-	-	-
Al	ns	ns	<0.01	ns	ns	ns	ns	ns
Cl	ns	ns	<0.01	<0.001	ns	ns	ns	ns
Cr	ns	ns	ns	<0.001	ns	ns	ns	ns
Cu	ns	ns	ns	<0.05	ns	ns	ns	ns
Mn	ns	ns	ns	ns	ns	ns	ns	ns
Si	-	<0.001	-	<0.01	-	-	-	-
Zn	ns	<0.01	ns	<0.01	ns	<0.001, 0.97, 0.05	ns	ns
Ash	ns	-	-	<0.01	-	-	-	-

ns, not significant; - not determined

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↑
Figure 2. Concentrations (conc.) of elements in biomass harvested on roadside verges in the city of Kassel (Germany) shown for each cut of the 2- and 4-cut regime. Dots indicate arithmetic means, line in the box indicates median and whiskers give minimum and maximum values. Different letters indicate significant differences among cuts.

Effect of the IFBB procedure

The IFBB treatment reduced the content of most elements and total ash. Especially, the high Cl and K concentrations, which are particularly detrimental to combustion processes (Oberberger *et al.* 2006), could be significantly reduced by more than 80 % on average (Figure 3, Table 4). To a lesser extent, concentrations of Ca, Mg, Na, N, P and Zn were reduced with mass flows between 19 and 53 % into the press cake. These results were similar compared with values achieved with material from semi-natural grasslands (Hensgen *et al.* 2012), though the element mass flow into the press cake was slightly lower in our study for most elements but S. The concentrations of Mn decreased in the press cake, but the reduction was not statistically significant, while the concentration of Al did not change by the treatment and Cu and Cr contents even increased. This is probably due to the fact, that we used standard machinery configurations of stainless steel both during mashing and dewatering, which is alloyed with Cr and may contain other metals as well. In the operating procedure, abrasion takes place and may increase the concentration of single elements in comparison to the silage. Although we used Cr- and Cu-enriched materials, the limiting values of the DIN EN 14961-6:2012 were met in the press cake (Table 3).

As organic components escape in gaseous form during combustion, elements are concentrated in the remaining ashes. Cd, Pb and Zn are particularly volatile causing highest concentrations in the fine fly ash fraction compared to bottom or coarse fly ash: 35 to 65% of total Cd and 35 to 55% of total Zn and can be found in this fraction, which has to be disposed of.

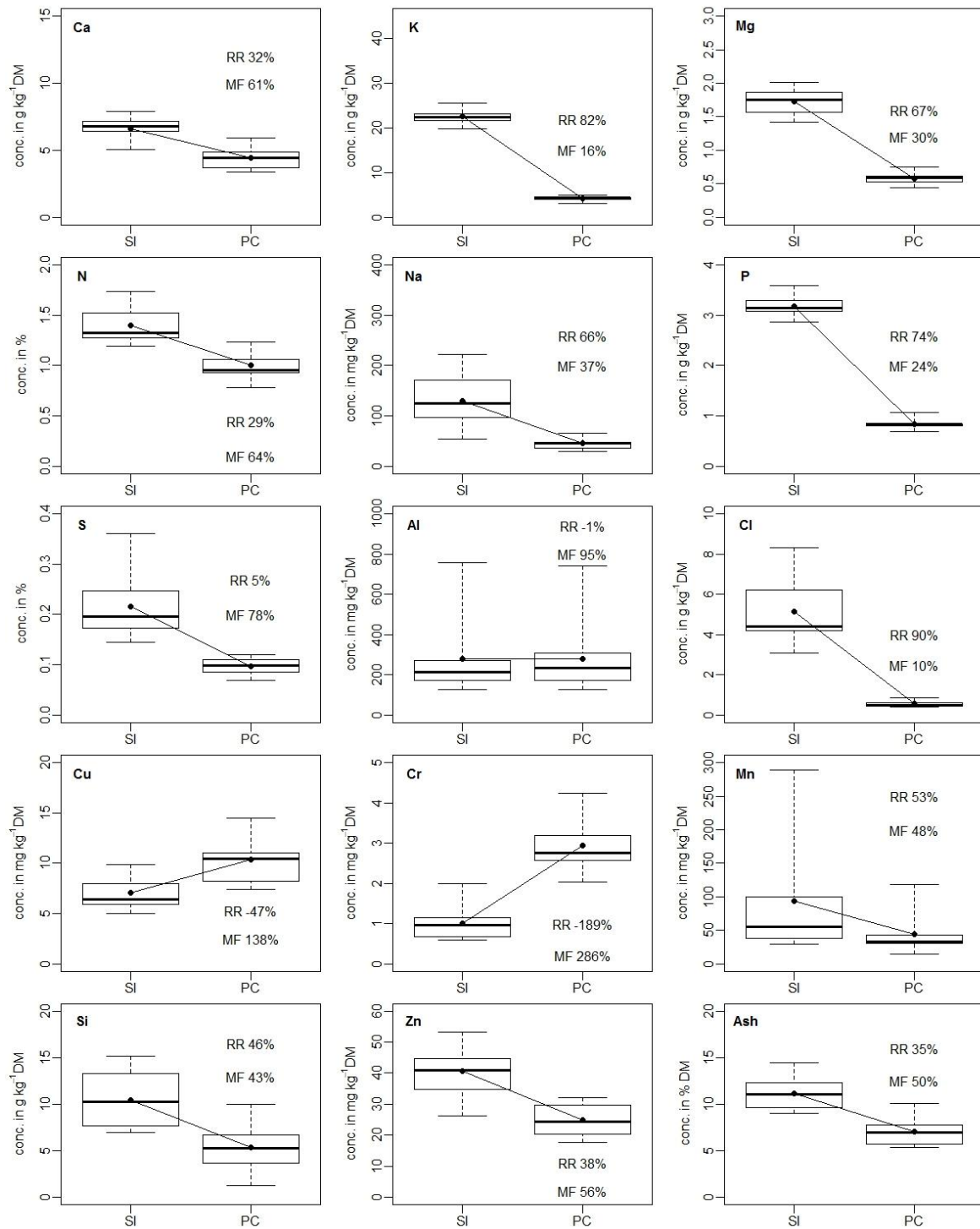


Figure 3. Element concentrations in silage (SI) and IFBB press cake (PC) produced from biomass harvested on roadside verges in the city of Kassel (Germany). Dots indicate arithmetic means, the line in the box indicates median and whiskers give minimum and maximum values. RR refers to the relative reduction of element concentration through the IFBB process, and MF indicates the actual mass flow of elements into the PC.

Bottom ash, in contrast, is rich in minerals and least volatile trace elements (e. g. Cr, Obernberger & Supancic 2009). Although the IFBB process enriched the solid fuel with Cu and Cr, concentrations in the press cake were in the range of the agricultural reference values for untreated grass. Corresponding to the decrease of Ca, Mg, Na, N, P and Zn concentrations in the press cake, concentrations of these elements increased in the dry matter of press fluid. During anaerobic digestion of press fluid, concentrations may further increase due to the conversion of organic matter into biogas. For the press fluid in this study, we calculated an increase in Zn concentration from 138 to 351 mg kg⁻¹ DM, which is well below the limiting value of the German bio-waste regulation.

Relations to soil element concentration

Linear regressions between soil concentrations of single elements and the corresponding plant concentrations and element removal, respectively, revealed few significances. This is in agreement with El-Nashaar *et al.* (2009) who also observed high variance of element content in grass species independent of soil element concentrations for Cl, S, Si, P and K. In the 4-cut-regime, the Zn concentration of soil and plant was linked, as well as in the 2-cut regime, the Mg concentration of soil and the element removal. It is noteworthy that, in both cases, results are based on one single exceptionally high soil value at one site and a corresponding high plant concentration and high element removal, respectively. Soil N concentration was related to N concentration of plants in the 4-cut-regime (R^2 0.52), as well as with element removal in the 2- and 4-cut-regime with an R^2 of 0.73 and 0.61, respectively. Conducting a pulse-labeling experiment, Raciti *et al.* (2008) also detected a close relationship between N concentrations in plant material from lawns and N concentrations in soil organic matter.

Challenges in urban environments

Although bioenergy recovery of city greens seems to be possible in regard of the element concentrations, there still exist knowledge gaps if such process chains can be organised in a financially feasible manner and greenhouse gas neutral or even saving. One of the main drivers for costs and greenhouse gas releases might be the complex logistics in cities. In contrast to typical agricultural areas, where the farm-field distance is a negligible criteria for primary energy savings (Bühle *et al.* 2012a), green areas in cities are frequently fragmented and dispersed: according to the city administrations' database, about 65 % of green areas are <0.1 ha. The increase in transport associated with the utilisation of municipal biomass may increase public's fear of enhanced traffic and, thus, may further complicate the biomass recovery.

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Hence, an interdisciplinary approach would be necessary to investigate the technical feasibility, environmental sustainability and social acceptability of such a complex process chain.

Conclusions

The concentration of 16 elements (Ca, K, Mg, N, Na, P, S, Al, Cd, Cl, Cr, Cu, Mn, Pb, Si, Zn) was measured with ICP-OES in biomass from urban roadside verges within the city of Kassel managed in 2-cut and 4-cut regimes. The elemental composition in the raw material was, with exception of N, independent of soil element concentrations and was similar to the composition of agricultural or conservation grassland. Though, some macro-nutrients occurred in higher concentrations, possibly due to the exceptional dry weather conditions. However, concentrations of trace elements including inorganic contaminants did not exceed values from literature for agricultural or landscape conservation biomass and also met the limiting values of official regulations. The only exception was the Cl concentration, which was higher than the reference values in both, grass from roadside verges and agricultural or conservation grass. Although significant for N and P, differences in element concentrations between cutting regimes were small. Element concentrations differed among cuts but maximum values were often below the limiting values except for N, S, Cl and a single Zn value. However, compared to the raw material, N, S, Cl and Zn concentrations in the press cake could be significantly reduced by the IFBB procedure. In view of the public's increasing awareness towards environmental pollution, non-agricultural materials, like grass from roadside verges, may be all the more utilisable for energy recovery if appropriate pre-processing and combustion technologies are applied.

Chapter 3

Solid fuel generation from urban leaf litter in mixture with grass cuttings: chemical composition, energetic characteristics and impact of pre-processing

Abstract

Urban biomass from green areas is a potential resource for bioenergy recovery, which is widely unused. Different types of organic material (e.g. grass, leaf litter) usually occur in mixtures due to common collecting practice. Forty samples of grass, leaf litter (genera: *Acer*, *Quercus*, *Tilia*) and mixtures of both, containing one third grass or leaf litter, were investigated to evaluate the effect of the “integrated generation of solid fuel and biogas from biomass” technique on material and energy fluxes as well as relevant characteristics of resulting energy carriers. IFBB divides biomass into a fiber-rich press cake and a highly digestible press fluid by mashing with subsequent pressing. Ensiling of samples was successful with pH values ranging from 4.2 in grass to 4.8 in pure *Tilia* samples. Concentrations of most minerals with exception of Ca and Mg were higher in grass than in leaf litter silage. The IFBB treatment reduced the element concentration in the press cake independently from the substrate. Linear regression models revealed high influence of the initial concentration in silage on the concentration in the press cake. The lower heating value of the press cake was nearly constant ($19 \text{ MJ kg}^{-1} \text{ DM}_{\text{ash free}}$) independent from mixture. Methane yields from press fluid digestion ranged from 172 (mean of leaf litter samples) to 325 $\text{I}_N \text{ kg}^{-1} \text{ VS}$ (mixture of 33% leaf litter-66 % grass). For an evaluation of the economic and ecological potential, models of the spatial and temporal occurrence of these biomasses need to be established.

Introduction

Green areas in cities are a valuable contribution to human health and well-being (Chiesura 2004). Additionally, various ecosystem services are provided by parks, gardens and roadside greenings (e.g. Bolund & Hunhammar 1999; Larondelle & Haase 2013). However, the maintenance of green structures is an increasing challenge for municipalities, as it is a significant cost factor in times of small public budgets. Therefore, it seems attractive to utilize urban biomass for bioenergy recovery and, thereby, to reduce management costs through the revenues from energy provision. Additionally, energetic utilization of urban biomass could lead to reduced GHG emissions, enhanced biodiversity and an improved understanding of urban citizens for a

resource-efficient lifestyle, as they can contribute with their own garden wastes to the energy provision of the city.

In municipalities, grass cuttings, leaf litter and tree pruning occur as possible biomass for energy recovery (Springer 2012). Springer (2012) assessed a potential of 164 million t of biomass (DM) per year harvested from urban areas in the USA. In Germany, an amount of 4.6 million t green waste is collected annually (Kern *et al.* 2012). Current management practices are either to leave the biomass on the sites for decaying or to remove the biomass to landfills or composting, as well as waste incinerating plants (Springer 2012; Hogg *et al.* 2002). Widely used energy recovery technologies as fermentation or direct combustion in heating plants are usually not suitable for these biomasses, because grass cuttings tend to cause problems with floating and abrasion during wet fermentation (Prochnow *et al.* 2009b), while its high mineral content (especially chlorine and potassium) causes corrosion, slagging and emissions during combustion (Jenkins *et al.* 1998). Leaf litter provides only small methane yields during fermentation (Liew *et al.* 2012) and is contaminated with soil particles (Piepenschneider *et al.* 2015 a) possibly inducing abrasion and damage of combustion units and increases the risk of sedimentation in biogas reactors (Prochnow *et al.* 2009b). However, solid fuel quality of both, grass and leaf litter, may be improved by the IFBB procedure. The procedure aims at dividing ligno-cellulosic biomass into a fiber-rich press cake and a press fluid, which contains major shares of minerals and easy soluble carbohydrates. The biomass is mashed with warm water and subsequently dewatered mechanically (Wachendorf *et al.* 2009). During this pre-treatment, the mineral concentration (especially K and Cl) in the solid fraction is reduced significantly, enhancing the overall fuel quality. Similar effects were observed in senesced biomass of grassland swards, which were standing over winter (Gamble *et al.* 2015), as well as in cut material, which was treated with simulated rain (Tonn *et al.* 2011). However, common park management usually does not allow standing stocks over winter.

Further, biomass availability in urban environments is highly depending on seasons as leaf litter occurs during autumn, while major grass is cut from April to October but not in winter. In agriculture, unsteady availability of feedstock is usually tackled by ensiling. Ensiling of common agricultural products as grasses, corn or sorghum is well investigated (Buxton *et al.* 2003; McDonald *et al.* 1991; McEniry *et al.* 2014); however the perspectives of ensiling leaf litter are widely unknown. There have been some efforts to research possibilities of ensiling leaves as fodder mainly for goats or sheep. Khan *et al.* (2012) observed high silage quality in mixtures

of 75 % maize and 25% leaves from either *Syzygium cuminii* or *Mangifera indica* without any butyric acid odor and Tjandraatmadja (1993) added 33 % of *Leucaena leucocephala* or *Gliricidia sepium* to tropical grasses receiving silages with pH values <4.4. However, these tree species do not occur in common parks of Europe or North America and they are usually more or less evergreen. Therefore, ensiling in these studies was conducted with physiologically active leaves but not with leaf litter, whose chemical composition changes during leaf senescence (Bazot *et al.* 2013; Tyler 2005).

The general technical feasibility to process urban biomass with the IFBB technique was proven for specific input materials as grass cuttings from roadside verges (Piepenschneider *et al.* 2015 b) and leaf litter from urban park trees (Piepenschneider *et al.* 2015 a), as well as for a mixture of municipal and landscape conservation materials (Hensgen *et al.* 2011). Piepenschneider *et al.* (2015 b) put concerns about heavy metal contamination of grass from roadside green verges into perspective by showing that the concentration of various elements is in the range of agricultural grass and does therefore not hinder energetic utilization.

In practice, leaf litter and grass cuttings are often mixed together, either by collecting leaf litter with the last grass cut in autumn or by joint municipal disposal facilities. Therefore, it is important to understand possible interferences between these substrates during processing with the IFBB technique. To investigate several associated questions we chose a replacement experimental design, which cannot determine the quantitative influence of each component on a certain outcome, but allows some valid interpretation concerning interference (Jolliffe 2000).

In this study, we addressed the following questions: (i) is it possible to conserve leaf litter and leaf litter-grass mixtures as silage, (ii) what is the chemical composition of silage from pure urban grass and leaf litter samples, as well as from mixtures of both, (iii) what are the chemical and energetic characteristics of resulting press cakes and press fluids, (iv) does the mixing of leaf litter and grass cuttings influence the reduction of minerals during the IFBB process?

Chapter 3

Materials and methods

Biomass

Leaf litter was sampled in a park (“Bergpark Wilhelmshöhe”) within the city of Kassel in November 2013. Four batches of three different tree genera each were taken (*Acer*, *Quercus*, *Tilia*) from trees, whose distance was 100 m. Batches included minor leaf proportions of other genera, but shares of intended genera were as follows (in % DM \pm sd): *Acer* 90 \pm 4, *Quercus* 78 \pm 15 and *Tilia* 74 \pm 13.

Grass cutting material for the study was collected from the autumn cut of a common grassland sward and chopped to 5 cm on the day of ensiling. The biomass consisted to 69 % of dry matter of *Lolium perenne*. About 22 % of DM was *Trifolium pratense* and 9 % of DM were herbs or other grass species.

The experiment was based on a standard replacement series with constant total sample amount and varying proportions of individual components (Jolliffe 2000). Prior to ensiling grass and leaf litter were mixed from 0% leaf litter and 100 % grass to 100% leaf litter and 0 % grass with mixtures of 33 % leaf litter and 66 % grass, as well as 66 % leaf litter and 33 % grass, based on fresh matter. Thereby, a total of 40 silages were produced with four samples of pure grass and four samples of each mixture and leaf litter genus (24 samples) and four samples of each pure leaf litter batch (12 samples). Samples were ensiled in 60-l polyethylene barrels for 6 weeks minimum.

Pre-treatment by the IFBB procedure

The IFBB procedure was conducted as described in (Hensgen *et al.* 2012). Silage was mixed with water in a ratio 1:4 (FM based). The mixture was mashed for 15 min at 40°C under constant stirring and subsequently dewatered by a screw press (type AV, Anhydro Ltd.) with a pitch of 1:6 and a rotation speed of 6 revolutions per minute. The press fluid was immediately frozen at -20°C for subsequent digestion experiments.

Chemical analysis

Prior to ensiling, subsamples of single materials were taken for DM analysis. After ensiling, subsamples were taken for DM analysis, determination of organic acids and pH, as well as for analysis of element concentration, ash content and concentration of neutral detergent fibers (NDF). DM, element concentration, ash content and concentration of NDF were also determined in subsamples of the press cake after the pre-treatment with the IFBB procedure.

For DM analysis in all fractions, subsamples were dried at 105 °C for 48 h. For the determination of the ash content, a subsample was dried at 105°C and subsequently incinerated in a muffle oven at 550°C. Organic acids (acetic, propionic, iso butyric, butyric, iso valeric, valeric and caproic acid) were analyzed with gas chromatography with flame ionization detector (GC-FID) and the pH was tested in an aqueous solution. The amount of organic acids was used to correct the previously determined DM and ash content figures.

Element concentration was measured in subsamples, which were dried at 65°C and grinded with a cutting mill (SM 1, Retsch) with a 5 mm sieve followed by a sample mill (1093 Cyclotec, Foss) to pass a 1 mm sieve. Concentrations of C, H and N were determined by an elemental analyzer (Vario MAX CHN Elementar Analysensysteme GmbH) using 150 mg of dried material. Concentrations of Al, Ca, Cl, K, Mg, P, S and Si were determined with inductively coupled plasma optical emission spectrometry (ICP-OES) and concentrations of Na with inductively coupled plasma mass spectrometry (ICP-MS).

For determination of NDF concentration, half of the samples (both silage and press cake) were analyzed with a fiber analyzer (ANKOM A220). A subsample of about 0.5 g was sealed in a filter bag and boiled with neutral detergent solution and alpha-amylase without use of Na₂SO₃, as this regularly leads to loss of lignin (Soest *et al.* 1991) and thereby to an underestimation of NDF. Filter bags were subsequently rinsed three times with alpha-amylase solution for 5 min and then with acetone for 3 to 5 min. After drying, NDF concentration was calculated as

$$NDF [\% DM] = \frac{(m_3 - (m_1 * C)) * 100}{m_2 * DM}$$

where m_1 is mass of empty filter bag, m_2 is mass of sample, m_3 is mass of organic matter after boiling and incineration and C is the “blank-bag correction” factor. The determined NDF concentration in 40 of a total of 80 samples were used for near-infrared calibration of NDF concentrations. A near-infrared spectroscope (XDS Rapid Content Analyser; FOSS NIRSystems Inc.) was used, and NDF values for the 80 samples were predicted after cross-validation ($R^2 = 91.4$, RSC = 3.3; RSC defined as the ratio of standard deviation and standard error of cross validation).

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Heating value

The higher heating value was calculated based on C, H and N concentrations using the formula of the following (Friedl *et al.* 2005):

$$HHV \left[\frac{kJ}{kg DM} \right] = 3.55 C^2 - 232 C - 2230 H + 51.2 C * H + 131 N + 20,600$$

Lower heating value (LHV) was calculated from the higher heating value (HHV) taking the enthalpy of water vaporization into account:

$$LHV \left[\frac{kJ}{kg DM} \right] = HHV - \left(8.937 * \frac{H \% DM}{100} \right) * 2.2$$

Digestion experiments with press liquids

For measuring methane yields from the press fluid, we followed the methodology and experimental setup of Bühle *et al.* (2012b) and Zerr (2006) taking the German standard (Verein Deutscher Ingenieure 2006) into account. Three replicates of 4 kg press fluid mixed with 8 kg inoculum were digested in gas-proof polyethylene containers at mesophilic temperature (37±1°C). Digestion of pure inoculum served as a control and allowed identifying the proportion of methane originating from press fluid and inoculum. Fermentation time was 14 days, as the daily biogas production is below 1 % of total biogas production at this time. At days 1, 2, 3, 4, 7, 9, 11 and 14 of digestion, amount of biogas and methane concentration in the biogas was analyzed with a wet drum gas meter (Ritter TG5) and a gas analyzer (GS IRM100), respectively. Current air pressure and temperature were recorded to calculate the methane yield under normalized conditions (273.15 K, 1013.25 hPa). Methane yields (l_N, litres normalised to normalised to 273.15 K and 1013.25 hPa) were referred to volatile solids in order to present the feedstock-specific methane yield (Prochnow *et al.* 2009b). These were determined by incineration of a subsample of press fluid at 550°C in a muffle furnace after drying at 105°C in a drying oven. To compensate partly for the loss of highly volatile organics during drying, we added the amount of organic acids, for which we assumed a mass flow into the press fluid similar to water, as they are highly water soluble. The chemical oxygen demand was measured with a cell test (LCK 514, Hach-Lange).

Statistical analysis

Statistical analysis as well as generation of figures was conducted with the software R (R Core Team 2013). Samples were insofar independent as they were stored and processed in single

batches after mixing. However, single replacement series were established by mixing grass from one sward with a distinct leaf litter batch (three genera in four independent repetitions each). Thus, the requirements of multiplicity and independence (Casler *et al.* 2015) were fulfilled by single batches taken in the field but no longer within and among each repetition series. Thereby, the naturally occurring variance was reduced. However, the aim of this study was not to show the variance of parameters in biomass but to focus on possible interactions of biomasses during processing, which might influence the quality of the solid fuel. To avoid that natural variance masks these interactions it was necessary to reduce it to a minimum level. For statistical analysis, we therefore renounced the comparison among levels of leaf litter share (trends are visible from tables) and focused on linear regression analysis to predict the element concentration in the press cake from the element concentration in the silage. Models were visually checked for homoscedasticity and normal distribution of residuals. Few occurring outliers were removed from the analysis if Cook's distance was >0.5 . For linear regression analysis the car package was used taking single samples (40 results for each factor) into account (Fox & Weisberg 2011).

Results and discussion

DM of untreated material and silage

DM content of grass was 14.9 ± 0.9 %, while the DM content (\pm sd, in %) of leaf litter was 26.8 ± 2.6 for *Acer*, 28.8 ± 1.6 for *Quercus* and 23.7 ± 2.4 for *Tilia*. After ensiling, the mean DM content of all samples (mixed and pure) was 21.9 ± 4.1 % with a minimum value of 14.1 % in grass silage and a maximum value of 31.9 % in pure *Quercus* leaf litter silage.

pH and organic acids in silages

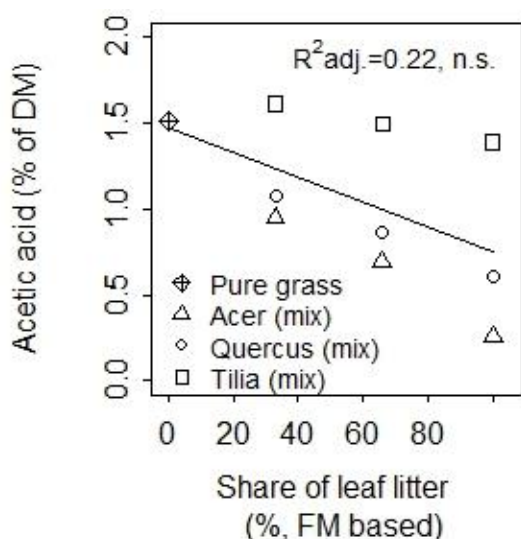
Lowest pH values were measured for pure grass silages with a mean of 4.2 ± 0.0 and highest values were detected for pure *Tilia* with a mean of 4.8 ± 0.5 (Table 5). Cherney & Cherney (2003) suggested a pH value <4.2 for low DM silage and a pH value <5.2 for high DM silage as guiding value for a proper fermentation process. pH values detected in this study, rising with increasing DM content, were in accordance with these guiding values. Mixing leaves of *Syzygium cuminii* or *Mangifera indica* with maize or grass resulted in pH values of silage between 4.6 and 4.9 with 25, 50 and 75 % contributions of leaves (Khan *et al.* 2012) and pH values <4.5 were detected in mixtures of grass and 33 % leaves of *Leucana laucocephala* or *Glidricidia sepium* (Tjandraatmadja 1993).

Table 5. Mean pH values with standard deviations for leaf litter-grass-mixtures after ensiling for 6 weeks minimum. Mixtures were produced based on mass shares of FM (fresh matter).

Genus	Mean pH \pm Sd at varying shares of leaf litter (FM based)			
	0 %	33 %	66 %	100 %
<i>Acer</i>	4.2 \pm 0.0	4.2 \pm 0.1	4.5 \pm 0.6	4.3 \pm 0.2
<i>Quercus</i>	4.2 \pm 0.0	4.2 \pm 0.1	4.4 \pm 0.3	4.7 \pm 0.3
<i>Tilia</i>	4.2 \pm 0.0	4.5 \pm 0.3	4.5 \pm 0.3	4.8 \pm 0.5

0 % leaf litter is equivalent to 100 % grass

In 65 % of the samples the concentration of butyric acid in the DM was below 0.1 %, indicating a successful ensiling process in low DM silage (Cherney & Cherney 2003). However, 13 % of samples, which were mainly derived from pure *Quercus* and *Tilia* leaf litter, had a butyric acid concentration between 0.5 and 2 % of DM. For silage with rather high DM content a guiding limiting value of 0.5 % DM was suggested (Cherney & Cherney 2003), which was exceeded by those samples. However, for a poorly fermented silage significant higher values of >2.5 % DM are given in literature (McDonald *et al.* 1991). Increased concentrations of butyric acid may occur due to a lack of or an inefficient utilization of fermentable carbohydrates, whereby acidification is slow and clostridia may ferment the already formed lactic or acetic acids into butyric acid (Pahlow *et al.* 2003). However, for *Tilia* samples the concentration of acetic acids remained stable independently from leave proportion (Figure 4), while for *Acer* and *Quercus*

**Figure 4.** Concentration of acetic acid (% of DM) of silage from leaf litter (*Acer*, *Quercus*, *Tilia*) in mixture with grass. Solid line indicates linear regression based on all 40 underlying samples.

mixtures the acetic acid concentrations decreased significantly according to Pearson's product moment correlation ($p=0.01$ for both correlations) with decreasing grass share. Thus, highest acetic acid concentrations in the DM were measured in pure grass samples with a mean value of 1.5 ± 0.2 %, which is rather low considering an acetic acid concentration of 2 to 5 % in well-preserved silage (McDonald *et al.* 1991). The question, if this is due to a lactic acid based fermentation or if this is rather an indicator of an overall reduced production of acids with increasing leaf litter share, has to remain open, as lactic acid concentrations were not determined. In summary, ensiling of pure tree leaf

litter seems to be possible in terms of achieving anaerobic stability, as long as the existing guidelines given for fodder production are carefully obeyed.

Chemical composition of silage

NDF concentration in grass silage (35.2 % of DM) was rather low but within the range of values detected in silage from *L. perenne* (42.6 % of DM) and *T. repens* (30.0 % of DM) at first cutting date (McEniry *et al.* 2014). Element concentrations in ensiled grass were mostly in line with findings of previous studies. Ca, Mg and K concentrations (1.40, 0.25, 2.66 % of DM, respectively, Table 6) were similar to levels detected by Hopkins *et al.* (1994) in fresh material from a sown sward of *L. perenne* and *T. repens* at the fourth cut (mean values of years 2-4: 1.12, 0.25, 2.60 % of DM, respectively), also when taking a slight DM loss (e. g. 4 % measured by the reference McGechan 1990) during ensiling into account. N concentration in grass (2.36 % of DM, on average) was close to concentrations of 2.5 % found in silage from *L. perenne* cut in May (McEniry *et al.* 2012).

Table 6. Chemical composition of leaf litter-grass-mixtures after ensiling for 6 weeks minimum. Standard deviations refer to the variability among tree genera and are therefore not applicable for pure grass samples.

Parameter	Mean value (% DM) \pm Sd at varying shares of leaf litter (FM based)			
	0 %	33 %	66 %	100 %
C	33.41	37.33 \pm 0.98	40.21 \pm 1.41	42.49 \pm 1.73
H	4.69	4.93 \pm 0.06	5.17 \pm 0.11	5.37 \pm 0.12
N	2.36	1.60 \pm 0.12	1.21 \pm 0.18	0.89 \pm 0.13
NDF	35.18	39.18 \pm 3.63	44.32 \pm 4.49	51.85 \pm 5.90
Ash	31.37	25.95 \pm 1.69	19.88 \pm 2.18	15.95 \pm 3.32
Al	0.97	0.81 \pm 0.02	0.49 \pm 0.01	0.31 \pm 0.04
Ca	1.40	2.11 \pm 0.59	2.29 \pm 0.67	2.61 \pm 0.90
Cl	1.16	0.57 \pm 0.05	0.41 \pm 0.04	0.16 \pm 0.06
K	2.66	1.91 \pm 0.18	1.24 \pm 0.05	0.70 \pm 0.27
Mg	0.25	0.36 \pm 0.06	0.37 \pm 0.07	0.47 \pm 0.07
N	2.36	1.60 \pm 0.12	1.21 \pm 0.18	0.89 \pm 0.13
Na	0.33	0.18 \pm 0.01	0.12 \pm 0.01	0.07 \pm 0.01
P	0.30	0.23 \pm 0.02	0.18 \pm 0.01	0.15 \pm 0.05
S	0.18	0.14 \pm 0.02	0.11 \pm 0.03	0.10 \pm 0.02
Si	5.98	4.90 \pm 0.26	4.46 \pm 0.75	3.09 \pm 0.54

NDF, neutral detergent fiber; 0 % leaf litter is equivalent to 100 % grass

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Concentrations of P (0.3 % of DM) and S (0.18 % of DM) were close to or in the range of literature values (0.37 % of DM Hokins *et al.* 1994, 0.32 % of DM Piepenschneider *et al.* 2015 b and 0.37 % of DM Hopkins *et al.* 1994, 0.06 of % DM McEniry *et al.* 2012, respectively). In contrast, Na and Cl concentrations were rather high (0.33 % of DM and 1.16 % of DM, respectively) compared to values found in fresh ryegrass-clover mixture (Na: 0.17 % of DM, Hopkins *et al.* 1994) and in silage from perennial ryegrass (Cl: 0.43 % of DM, McEniry *et al.* 2012) or in silage from roadside verges with high *L. perenne* share (Na: 0.01 % of DM, Cl: 0.51 % of DM, Piepenschneider *et al.* 2015 b). Similarly, concentrations of Al and Si were higher than expected with 0.97 and 5.98 % of DM, respectively, in comparison with previously detected concentrations in the mentioned material from roadside verges (Al: 0.03 % of DM, Si: 1.07 % of DM, Piepenschneider *et al.* 2015 b). However, this deviation is explainable by the high ash content of 31.37 % of DM, which indicates a significant amount of soil adherence to the leaf litter collected. Silicon is the second frequent element in soil (after oxygen) and aluminum the most frequent metal (Scheffer *et al.* 2010). An ash content of about 10 % of DM can be regularly assumed for such material (McEniry *et al.* 2012; Piepenschneider *et al.* 2015 a, b).

Only concentrations of C, H, Ca, Mg and NDF were higher in the collected leaf litter (42.49, 5.37, 2.61, 0.47 and 51.85 % of DM, respectively) than in grass. However, C and H concentrations were low in grass, as well as in leaf litter in comparison to previous studies involving leaf litter (Piepenschneider *et al.* 2015 a) and a variety of 18 European grassland sites (Bühle *et al.* 2014). For Ca and Mg, the values found for leaf litter exceeded literature values (Tyler 2005). However, during leaf senescence both elements tend to increase in concentration (Tyler 2005; Lin & Wang 2001) depending on several abiotic factors as soil fertility, leaf nutrient status or summer temperature (Hagen-Thorn *et al.* 2006). NDF concentrations of fresh leaves were found to be extremely variable with 9.6 % of DM for leaves of *Sesbania sesban* (Bonsi *et al.* 1995), 29.8 and 31.1 % of DM for leaves of *Prunus persica* and *Prunus domestica*, respectively, (Salem *et al.* 2013), 40.6 % of DM for olive leaves (Molina-Alcaide & Yáñez-Ruiz 2008) and 66.1 % of DM for leaves of *Quercus incana* (Sharma *et al.* 2008). A high NDF concentration indicates a reduced degradability of biomass during fermentation as degradation of hemi-cellulose and lignin are reported to be challenging (Prochnow *et al.* 2009b), whereas fibers are favorable in combustion as lignin in particular increases the heating value (Lewandowski & Kicherer 1997).

Concentrations of Cl, K, N, Na and P were lower in leaf litter than in grass but in a range, which was also observed in previous studies on leaf litter (Heckman & Kluchinski 1996; Piepenschneider *et al.* 2015 a). Further, ash contents were similar to values detected in the above-mentioned studies and the authors assume that these high values were caused by contamination through soil adherence. The actual ash content of leaf litter is assumed to be well below 10 % (Piepenschneider *et al.* 2015 a) without any soil adherence. Si concentrations of 1.1 % of DM and Al concentrations of 0.07 % of DM have been measured in freshly fallen leaf litter of *Fagus sylvatica* (Joergensen *et al.* 2009), which are lower than concentrations identified in this study (Si: 3.09 ± 0.54 , Al: 0.31 ± 0.04 % of DM). Like for the grass samples, the elevated concentrations are probably due to soil adherence, as indicated by the high ash content. Mixtures of grass and leaf litter showed intermediate concentrations for all elements, as well as for ash and NDF. Values were continuously increasing (Ca, Mg, NDF) or decreasing (Al, Cl, K, N, Na, P, S, Si, ash) according to the share of both components in the mixtures.

Characteristics of IFBB products press cake and press fluid

In the press cake concentrations of C were increasing with increasing share of leaf litter (Table 7). Thus, highest C concentrations with a mean value of 50.5 ± 1.8 % of $DM_{\text{ash free}}$ were detected in the samples from pure leaf litter. This is in accordance with results of Piepenschneider *et al.* (2015 a), which revealed mean C concentrations of 50.8 % of $DM_{\text{ash free}}$ in the press cake of urban leaf litter from five tree genera (*Acer*, *Aesculus*, *Fagus*, *Quercus*, *Tilia*). H and N concentrations in the press cake from pure leaf litter in this study (6.4 and 1.0 % of $DM_{\text{ash free}}$ respectively) were also similar (6.34 and 0.96 % of $DM_{\text{ash free}}$, respectively, Piepenschneider *et al.* 2015 a). In comparison to the composition of the press cake from leaf litter, C concentrations in press cake of pure grass samples were lower (48.6 % of $DM_{\text{ash free}}$), while N concentrations were higher (2.6 % of $DM_{\text{ash free}}$). However, the lower heating values of press cakes (18.6 to 18.9 $\text{MJ kg}^{-1} DM_{\text{ash free}}$) were very similar for the mixtures. Referring to DM including ash, the lower heating value was higher in pure leaf litter because the ash content was lower. However, the lower ash content was partly caused by lower soil adherence and thus, cannot be further interpreted. Beside the heating value, the K_2O/CaO index is an important quality parameter for solid fuels, as it indicates the level of risk for ash slagging (Steenari *et al.* 2009). For press cake from pure grass the K_2O/CaO index accounted for 0.6, which was higher than in press cake produced from semi-natural grassland (0.5), however low in comparison to untreated grass silage (1.5, Bühle *et al.* 2014). The index values decreased with increasing share of leaf

litter, which indicates a lower risk of slagging. Press cake from pure leaf litter had an K_2O/CaO index of 0.1 in accordance with previous research, which detected an index of 0.15 in press cake from leaf litter of a variety of different tree genera and a corresponding ash softening temperature of well above 1200 °C (Piepenschneider *et al.* 2015 a).

Press fluids derived from grass samples had a DM concentration of 1.3 % of FM with a tendency to decrease to 1 % of FM with increasing leaf litter share (Table 7). The chemical oxygen demand (COD) follows this pattern in general (14.5 in press fluid from pure grass to 10.8 g l⁻¹ in press fluid from pure leaf litter), though highest concentrations were detected in the press fluid of the mixture with 33 % leaf litter (15.0 g l⁻¹). This pattern is also valid for methane yield derived from press fluids, which was highest in press fluid of the 33 % leaf litter - 66 % grass mixture with a value of 325±24 l_N kg⁻¹ VS. However, the concentration of volatile solids was lowest in this mixture (64.5 % of DM). Possibly, leaf litter provides a more structured matrix, which allows minerals to rinse out during dewatering more easily than through a highly compacted mass of grass biomass, and thereby may alter the relative share of volatile solids.

Table 7. Characteristics of press cake and press fluid. Standard deviations refer to the variability among tree genera and are therefore not applicable for pure grass samples.

Parameter	Mean value ± Sd at varying shares of leaf litter (FM based))			
	0 %	33 %	66 %	100 %
Press cake				
C (% of DM _{ash free})	48.6	50.0±1.5	50.4±1.6	50.5±1.8
H (% of DM _{ash free})	6.7	6.5±0.1	6.4±0.1	6.4±0.1
N (% of DM _{ash free})	2.6	1.6±0.1	1.3±0.1	1.0±0.1
Ash (% of DM)	20	16±2.8	13±3.2	11±3.4
LHV (MJ kg ⁻¹ DM)	14.9	15.9±0.5	16.4±0.6	16.8±0.7
LHV (MJ kg ⁻¹ DM _{ash free})	18.6	18.8±0.1	18.9±0.2	18.9±0.2
K ₂ O/CaO Index	0.6	0.3±0.1	0.2±0.1	0.1±0.1
Press fluid				
DM (% of FM)	1.3	1.2±0.1	1.1±0.1	1.0±0.1
COD (g l ⁻¹)	14.5	15.0±2.2	11.9±1.6	10.8±1.6
VS (% of DM)	66.8	64.5±2.9	65.8±5.6	71.5±1.4
Methane yield (l _N kg ⁻¹ VS)	271	325±30	259±50	172±57

COD, chemical oxygen demand; DM, dry matter; FM, fresh matter; LHV, lower heating value; VS, volatile solids; 0 % leaf litter is equivalent to 100 % grass

However, also the quality of volatile solids seems to be influenced by the mixing ratio, as indicated by highest COD and methane yield at this mixture level. The exact underlying mechanisms cannot be clarified in this study. In particular, the applied method for determining volatile solids does not comprise all compounds as some are already lost during drying. Although we corrected the figures for organic acids, we do not know the amount of lost alcohols. However, methane yield data seem to be valid, as the mean coefficient of variation of laboratory repetitions was small with 0.1 for both, the whole data set and the given mixture. Additionally, repetitions were treated independently, being digested in different subunits, while the same standardized inoculum was used for all repetitions.

Impact of IFBB procedure on element concentrations

The concentration of investigated elements in the press cake was generally highly depending on their concentration in the silage (Figure 5). However, the slope and intercept were variable possibly due to different tendencies to dissolve in water from plant material. For example, the concentrations of Cl and K are known to leach into the press fluid very easily (Hensgen *et al.* 2011) leading to a small increase in concentration in the press cake even when the concentration in the silage increased substantially. This resulted in a relative reduction of Cl and K concentration in the press cake of 94 % for Cl and of 69 % for K compared to the concentrations in the silage. In contrast, the regression models predicting Ca and Mg concentrations in the press cake in dependency on their concentrations in the silage showed a parallel shift from the intersecting line indicating a certain amount of soluble ions. However, parts of the Ca and Mg ions seem to be fixed to fibrous molecules and are therefore not available for dissolving. For Ca it is known, that it can be found dissolved in the vacuole and as structural element in cell membrane and cell wall. Magnesium also occurs in the vacuole, as well as in chloroplasts and functions as stabilizer of nucleic acid configuration (Maathuis 2009). Ions from the vacuole are potentially higher leachable as they are already dissolved. Remarkably, the amount of Ca and Mg ions removed stayed constant, while total concentration increased. The slope of the regression model predicting Al concentrations in the press cake indicated also a certain amount of fixed ions, however, the relative amount of soluble ions was highly proportional to the total concentrations. Similarly, the relative reduction of Na and P concentrations increased by up to 68 %, each, with increasing initial concentration.

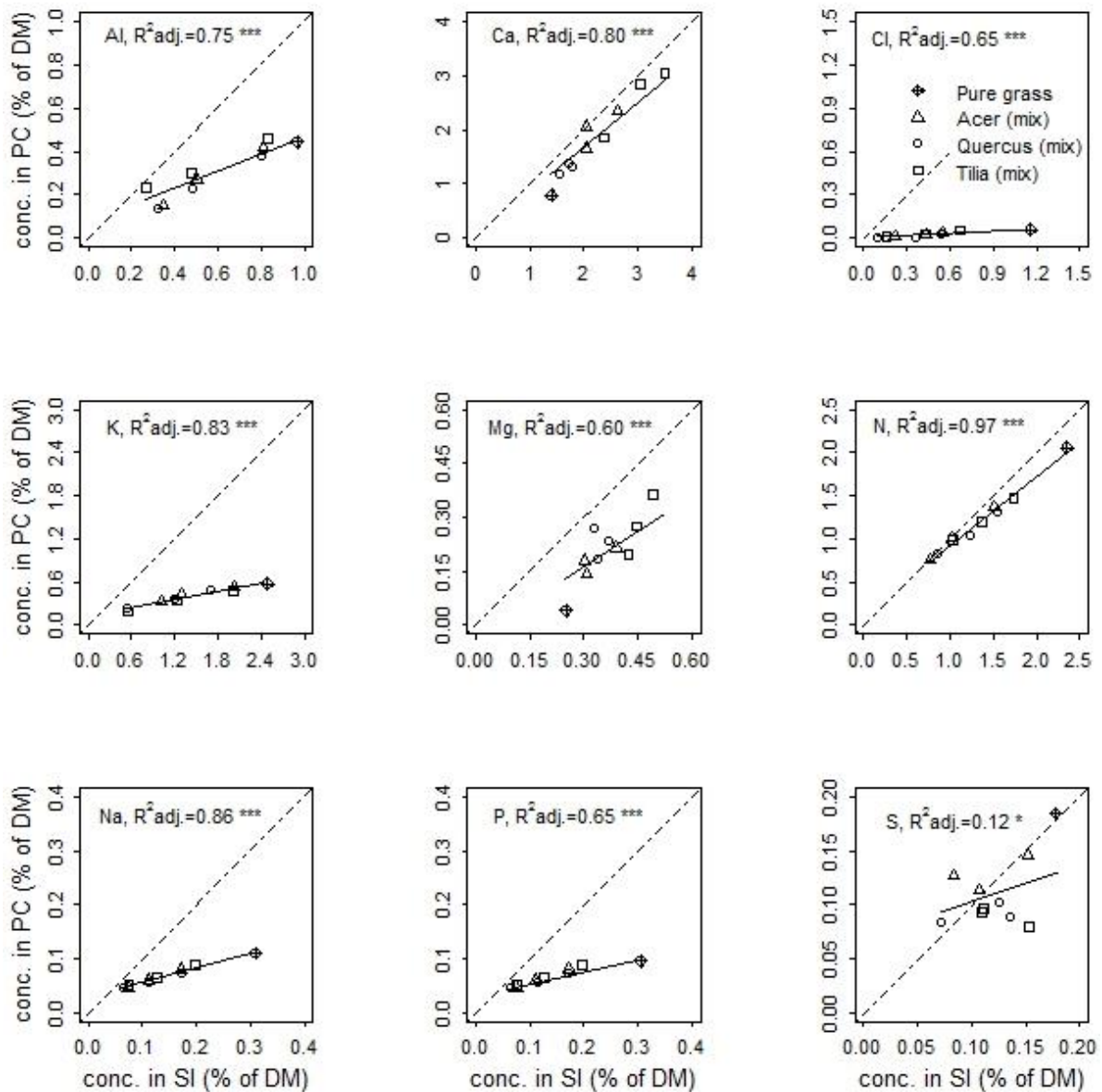


Figure 5. Concentrations of elements in the press cake (PC) depending on concentrations of elements in the silage (SI). Solid line indicates linear regression model based on all 40 underlying samples. *** indicate significance of linear regression model with $p < 0.001$, * significance of < 0.05 .

However, the relative reduction did not reach levels of K and Cl, but was in accordance with previous findings, which detected a relative reduction of Na concentration of 66 % and of P concentrations of 74 % (Piepenschneider *et al.* 2015) in grass from roadside verges applying the IFBB technique. Piepenschneider *et al.* (2015) found a relative reduction of 29 % for N, which is higher than in this study with a maximum relative reduction of 15 %. Rather small mass flows of N into the press fluid have also been reported by Hensgen *et al.* (2011), who

mentioned that in mature leaf tissue most N is strongly bound in structural or insoluble proteins (Mattson 1980).

Noteworthy, all samples, including pure grass and leaf litter, as well as mixtures, were the basis for the highly valid linear regression models explaining the element concentration in the press cake by the element concentration in the silage. Thus, the material itself played a minor role in determining the quality of the press cake. This supports the target of the IFBB system to flexibly use different urban biomass types for energy recovery.

Energy flux

The main share of energy contained in the silage (calculated from the heating value based on C, H and N concentrations) was transferred into the press cake with a range from 67 to 89 % of energy contained in silage from pure grass and pure leaf litter samples, respectively (Figure 6). With increasing energy flux into the press cake, the energy originating from biogas decreases continuously from pure grass to pure leaf litter samples. This is probably due to the decreasing mass flow of dry matter into the press fluid and the lower methane potential of leaf litter-rich samples. High energy fluxes into the press cake have been calculated by Böhle *et al.* (2012a), who detected a net energy transfer into the press cake of about 80%. Losses of energy are most likely caused by undegraded substrate leaving the process in digestates, leading to values of less than 100% for the accumulated energy derived from press cake and biogas. Standard deviations between tree genera were very low, indicating that effects of genera are of minor importance.

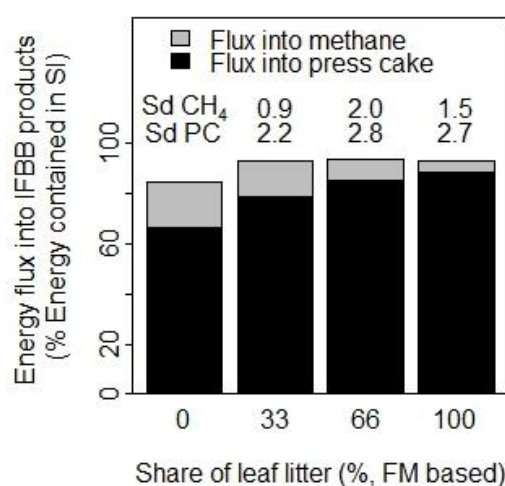


Figure 6. Energy flux into press cake (PC) and press fluid (PF) as proportion of energy contained in silage (SI). Standard deviations (Sd) refer to the variability among tree genera and are therefore not applicable for pure grass samples.

Chapter 3

Conclusions

Grass and leaf litter biomass occurs in urban environments. A main challenge for utilizing these biomasses is their temporal irregular occurrence. However, ensiling for storage of pure grass and leaf litter, as well as of mixtures, is possible with a higher quality in grass samples or mixtures than in pure leaf litter samples. For energy recovery by combustion the concentration of minerals in the fuel is crucial. Mineral (for example K or Cl) concentration usually decreased with an increasing share of leaf litter. Though, concentrations of Ca and Mg, which have structure functions in plants, increased with increasing share of leaf litter. The IFBB procedure reduced the concentration of elements (Al, Ca, Cl, K, Mg, N, Na, P, S, Si) in the press cake, and concentrations in the press cake were highly depending on their concentration in the silage, except for S. Thus, no interactions between fractions concerning the element concentration in the press cake were detected, which underpins the high potential of the IFBB technique to treat different biomasses. However, highest methane potential, as well as COD was measured in mixtures of 66 % grass and 33 % leaf litter. Possibly, there are some interactions between substrates, which concern the mass flow of carbohydrates and might issue from the combination of structure (from leaf litter) and sugars (from grass). The press cake as main product comprised major parts of the energy originally contained in the silage and the lower heating value of ash-free biomass was not influenced by mixing of grass and leaf litter, but was constantly close to the lower heating value of wood. Therefore, bioenergy recovery from municipal biomasses with the IFBB technique is not only possible for pure materials but also for mixtures, as frequently occurring in urban maintenance practices. To evaluate the economic and ecological potential of the technique in cities, quantitative models of temporal and spatial biomass occurrence need to be developed.

Chapter 4

Grass from urban roadside verges for energy recovery by anaerobic digestion or combustion after pre-processing

Abstract

Grass from urban roadside verges is a potential, though widely unused, resource for bioenergy recovery. Two possible bioenergy recovery techniques were tested, i.e. i) direct anaerobic digestion of the whole parent material and ii) the “integrated generation of solid fuel and biogas from biomass” procedure, which divides biomass into a press fluid and a press cake by mashing and mechanical dewatering. Biomass yield, chemical composition and canopy height of biomass, contribution of functional groups, fermentation characteristics of silage and press fluids, as well as characteristics of the produced solid fuel was investigated, applying a 4-cut management for anaerobic digestion, a 2-cut management for IFBB and an 8 times mulching as a reference. Mean annual biomass yield (2013 and 2014) was 3.24, 3.33 and 5.68 t dry matter ha⁻¹ for the mulching, 4-cut management and 2-cut management, respectively. Yields were higher in 2014 due to more favourable weather conditions. Fibre concentration was higher in material of the 2-cut management than in the 4-cut management, however, methane yield of the corresponding silages was the same. Highest methane yield was gained from press fluids with 292 l_N kg⁻¹ volatile solids. The press cake had a lower heating value of 16 MJ kg⁻¹ dry matter and a K₂O/CaO index of 0.51-0.88. Gross energy output was 26.4 GJ ha⁻¹ for anaerobic digestion and 84.4 GJ ha⁻¹ for IFBB. Thus, an altered roadside verge management with reduced cutting frequency might allow a significant energy recovery and improved ecosystem services, i.e. increased biodiversity.

Introduction

Grass from roadside verges within cities is usually not used, but cut and left in place to decay (mulching). Greening and subsequent maintenance of roadside verges is conducted by municipalities for public interest, as green areas enhance the well-being of inhabitants and reduce the negative effects of sealed surfaces, e.g. heating-up during summer (Bolund & Hunhammar 1999; Kottmeier *et al.* 2007). However, maintenance of green roadside verges is cost-intensive and can barely be borne by public authorities (Lottner & Kruis 2002). Utilisation of the biomass in bioenergy recovery could reduce or even neutralise these costs by revenues from energy provision. Additionally, biomass from roadside verges is categorised as waste and thereby

contributes to the municipal waste fraction, which accounts for 7-10 % of the total waste generated in the European Union (European Commission 2014b). The European Commission defined nine priority objectives in their 7th Environment Action Programme. The 2nd objective is “to turn the Union into a resource efficient, green and competitive low-carbon economy” with a special focus on turning waste into a resource (European Commission 2014c). Thus, bioenergy recovery from roadside greening might not only contribute to the local energy provision and unburden public coffers, but also help to achieve the EU-wide environmental and economic aims.

Common energy recovery practices, which are used to process herbaceous material are i) anaerobic digestion and ii) direct combustion. Anaerobic digestion of grass from roadside verges is possible in general (Delafield 2006), however, in wet mono-digestion, technical problems such as blocking and floating are known from the utilisation of agricultural grass silage (Thamsiroj & Murphy 2010). Alternatively, co-digestion of grass from roadside verges or public green areas with manure or sewage sludge has been investigated (Moor *et al.* 2013; Hidaka *et al.* 2013). Both studies showed the general technical suitability of co-digestion, but the grass feedstock was not further described in terms of maturity. Stage of vegetation, which is affected by cutting frequency, is known to consistently influence the specific methane yield, which is mainly due to varying crude fibre concentrations (Prochnow *et al.* 2009b). Higher stage of maturity and the corresponding higher fibre concentrations generally lead to decreased feedstock-specific methane yields (Prochnow *et al.* 2009b). Thus, a cutting frequency which allows biomass harvest at an early maturity stage is favourable for anaerobic digestion.

Direct combustion of grass from roadside verges is difficult in general, as herbaceous material contains high mineral concentrations, which can be detrimental to the combustion process. For example, Cl, S and K are mainly responsible for corrosion mechanisms and may enhance melting of ashes and slagging of the furnace (Oberberger *et al.* 2006). Therefore, a mineral content as low as possible is favourable, which naturally occurs in mature grassland vegetation (Buxton & O’Kiely 2003). To minimise negative effects of minerals in combustion, it is appropriate to pre-treat the biomass by washing with subsequent mechanical dewatering to thereby leach major amounts of occurring minerals. One possibility to conduct leaching is the IFBB process, which separates biomass into a fibre-rich press cake and a press fluid that contains major parts of the minerals and highly soluble carbohydrates (Wachendorf *et al.* 2009). The IFBB technique has been well investigated, including different biomasses (semi-natural

grassland, Hensgen *et al.* 2012, green cut from nature conservation and households, Hensgen *et al.* 2011, leaf litter (Piepenschneider *et al.* 2015) and grass from urban roadside verges Piepenschneider *et al.* 2015). The procedure proved to consistently separate the fibres from the majority of minerals and highly soluble carbohydrates. Various research confirmed the possibility to leach minerals from herbaceous biomass technically (King *et al.* 2012) or by natural processes, i.e. through rainfall on cut material (Tonn *et al.* 2011) or by delaying the harvest into early next spring with the biomass being uncut during winter (Gamble *et al.* 2015). Nevertheless, these more natural options are not suitable for urban environments due to road safety and cityscape reasons. Additionally, the leachate cannot be used, which may contain considerable amounts of fermentable substances, and would be lost for energy provision.

Therefore, technical opportunities to recover grass from roadside verges for energetic purposes are existing. Yet, to date it is unclear, if the recovery is economically feasible. To evaluate this question, it is crucial to get an idea of the amount of harvestable biomass and the corresponding outcome of utilisable energy, i.e. electricity and heat. Research concerning urban grass focused on lawns and recommended low-maintenance species, fertiliser application, pest regulation and irrigation procedures (Hubbell *et al.* 1997; Walker *et al.* 2007; Saeedi Pooya *et al.* 2013; Bijoor *et al.* 2014; Dobbs & Potter 2014). Beard & Green (1994) reviewed the functional, recreational and aesthetic components of turf grass. However, few authors assessed the quantity of lawn biomass to subject it to energetic utilisation (Springer 2012). Research concerning the biomass from roadside verges is scarce. For Germany, a theoretical biomass potential of more than 1 million t fresh matter has been estimated taking grass from roadsides (including all types of roads) and an annual yield of 8-13 t FM ha⁻¹ (depending on management intensity) into account (Kretzschmar & Thrän 2009; Rommeiss 2006). However, this estimation is based on questioning responsible public entities in the state of Baden-Württemberg, who themselves have only scarce data on biomass, as mulching is the most common management option. On Welsh non-urban roads a biomass yield of 2.5-3.3 t DM ha⁻¹ a⁻¹ was assessed using up-scaled mowing equipment and considering a mowing frequency of 1-2 harvests per year (Delafield 2006). Although the above-mentioned studies are originating from different European regions and are based on a very practical rather than on a scientific approach, the results obtained are pretty close. Nevertheless, a sound scientific investigation on grass from roadside verges, its yield and chemical composition, is necessary to pave the way for sustainable energetic recovery of this material.

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Therefore, in this study we focused on grass harvested with different cutting frequencies to (i) determine the biomass yield from urban roadside verges, (ii) define the material in terms of fibre concentration, (iii) measure the methane potential of produced silage and of press fluid, (iv) evaluate the heating value of the produced solid fuel and (v) compare the energy recovery options in terms of gross energy yield.

Material and methods

Investigation sites and sampling of biomass

Grass was collected from roadside verges within the city of Kassel, which has about 200,000 inhabitants and an area of 107 km² (Tremlová *et al.* 2013). 10 investigation sites of 120 m² each were established next to roads with a traffic load of between 1,500 and 35,500 cars per working day and with a mean distance of 9.4 m to the closest road (Figure 1). Vegetation cover was dominated by *Agrostis stolonifera*, *Festuca rubra* and *Lolium perenne* (Piepenschneider *et al.* 2015 b). Each of the 10 sites was equally divided into three plots of 40 m² to establish three management regimes: 8 times mulching as reference, according to the currently conducted procedure; 4 harvests; and 2 harvests. Cuts were carried out at three week intervals for mulching, six week intervals for the 4-cut management, and at 12 week intervals for the 2-cut management, starting in calendar weeks 18, 21 and 27 in 2013 and 14, 17 and 23 in 2014, respectively. Due to unusually high productivity in 2014, an additional harvest was taken in all management regimes in calendar week 47. Height of biomass (height of tallest plant) was measured with a folding ruler at the time of harvest. Contribution of functional groups (graminoids, legumes, forbs) to total dry matter was assessed visually in accordance with Davies *et al.* (1993). High quality of estimation was ensured by calibrating with randomly sampled material, which was fractionated and dried in the laboratory. Samples for yield assessment were taken in triplicates at 5 cm height with scissors from a quarter of a square meter each. Fresh matter yield was determined immediately after cutting. To determine dry matter content, samples were dried at 105°C in a drying oven. Samples for fibre and elemental analysis were cut at 5 cm height with scissors from the remaining area taking at least 10 random grasps and dried at 65°C. Subsequently, the area was mowed with a flail mower (AS Motor 570 SM). On the mulching sub-areas the biomass remained, while on the 2- and 4-cut sub-areas the biomass was raked and ensiled for six weeks minimum in 30 l polyethylene barrels or 2.7 l tubes. Silage could only be produced in the first half of 2013 due to low levels of biomass in the second half of the year.

Processing of biomass

After opening the barrels or tubes, subsamples were taken for dry matter analysis by drying at 105°C in a drying oven. Additionally, 2 kg of each silage were frozen at -20°C for subsequent digestion experiments. Remaining silage from the 2-cut management was processed by applying the IFBB procedure. Silage was mixed with warm (40°C) water in the ratio 1:4 (fresh matter based) and stirred for 15 min at constant temperature. Subsequently, the mixture was divided into a press cake and a press fluid using a screw press (type AV, Anhydro Ltd.) with a pitch of 1:6 and a rotation speed of 6 revolutions per min. Press fluid was immediately put into a freezer at -20°C for digestion experiments. Press cake was dried at 65°C for element analysis and a subsample was dried at 105°C in a drying oven for determination of DM.

Digestion experiments

Digestion experiments were conducted following the experimental set-up of Zerr (2006), taking the German standard (Verein Deutscher Ingenieure 2006) into account. Frozen substrates (silage and press fluid) were thawed for 60 h at room temperature (~ 20°C). 400 g of silage was chopped by hand to approximately 5 cm in length and mixed with 8 kg of inoculum and 3.6 kg of water. 4 kg of press fluid were mixed with 8 kg of inoculum. Digestion of silage took place in two replicates for 35 days, digestion of press fluids in three replicates for 14 days using gas-proof polyethylene containers at mesophilic temperature (37±1°C) and 15 min stirring every hour. Pure inoculum was digested separately to subtract the methane yield of the inoculum from the total amount of methane produced in mixtures and thereby calculate the actual yield from the sample. Biogas was collected in gas-proof bags and volume was measured with a wet drum gas meter (Ritter TG5) at digestion days 1, 2, 3, 4, 7, 9, 11 and 14 for press fluids and additionally on days 16, 18, 21, 24, 28, 31 and 35 for silages. After these periods the daily biogas production was below 1 % of total biogas production at this time. Methane concentration in biogas was analysed with a gas analyser (GS IRM100). Methane yield was standardised to normalised conditions (273.15 K, 1013.25 hPa) and referred to volatile solids. These were determined by drying a sub-sample at 105°C in a drying oven and subsequent incineration in a muffle furnace at 550°C. Mass loss was taken as volatile solids. As parts of the volatile solids are lost during drying due to high volatility (Porter & Murray 2001), the total amount of volatile solids in silage was corrected applying the formula (Weißbach & Kuhla 1995)

$$VS_{corrected} [\%] = 2.08 + 0.975 * VS_{uncorrected} [\%]$$

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To correct the amount of volatile solids in press fluid, we assumed that the fraction of highly volatile substances calculated as above from the corresponding silages has the same mass flow as water into the press fluid because most of them are highly water soluble (e. g. short fatty acids, alcohols).

Chemical analysis

Samples for fibre (raw material) and elemental analysis (raw material and press cake) were grinded with a cutting mill (SM 1, Retsch) to pass a 5 mm sieve and subsequently with a sample mill (1093 Cyclotec, Foss) to 1 mm.

Fibre concentrations (NDF - neutral detergent fibre, ADF - acid detergent fibre, ADL - acid detergent lignin) were predicted on the basis of near-infrared spectroscopy (XDS Rapid Content Analyser; Foss NIR Systems Inc.) after cross validation (NDF: $R^2 = 0.95$, RSC=4.4; ADF: $R^2 = 0.87$, RSC=2.8; ADL: $R^2 = 0.79$, RSC=2.2; RSC defined as the ratio of standard deviation and standard error of cross validation) with calibrations from semi-natural grassland and additional samples from the actual study (17 % of total number of samples). These samples were analysed for NDF, ADF and ADL with a fibre analyser (ANKOM A220). Therefore, subsamples of about 0.5 g were sealed in a filter bag. For NDF determination, filter bags were subsequently boiled with neutral detergent solution and alpha-amylase. We renounced the use of Na_2SO_3 , which regularly leads to an underestimation of NDF due to the loss of lignin (Soest & Wine 1967). For ADF determination, filter bags were boiled with acid detergent solution and water and subsequently rinsed with acetone and dried at 105°C. ADL analysis was conducted from ADF bags by adding H_2SO_4 solution, subsequent washing with water and addition of NaOH solution. Filter bags were then washed with hot water, again rinsed with acetone and dried at 105°C. Filter bags were incinerated in a muffle furnace at 550°C and NDF, ADF and ADL concentrations were calculated as

$$\text{Fibre type [\% of DM]} = \frac{(m_3 - (m_1 * C)) * 100}{m_2 * DM}$$

where m_1 is mass of empty filter bag, m_2 is mass of sample, m_3 is mass of organic matter after boiling and incineration and C is the “blank-bag correction” factor.

C, H and N concentrations in the press cake were determined with an elemental analyser (Vario Max CHN Elementar Analysensysteme) in 150 mg of dried material. From these the higher heating value (HHV) was calculated as (Friedl *et al.* 2005)

$$HHV \left[\frac{kJ}{kg DM} \right] = 3.55 C^2 - 232 C - 2230 H + 51.2 C * H + 131 N + 20,600$$

Lower heating value (LHV) was calculated from the higher heating value using the formula:

$$LHV \left[\frac{kJ}{kg DM} \right] = HHV - \left(8.937 * \frac{H \% DM}{100} \right) * 2.2$$

where 8.937 is the mass share of hydrogen in water molecule and 2.2 is the enthalpy of water of vaporisation.

Sampling and processing of soil

Soil samples were taken in 2013 at 0 to 30 cm depth at six points of each site, dried at room temperature and sieved to pass a 2 mm sieve. For each site, a mixed sample was analysed for soil texture, nutrient concentration and pH. Soil texture was determined after carbonate destruction by sieving sand and clay fractions. N concentration was measured with an elemental analyser (Vario Max CHN Elementar Analysensysteme) in 150 mg of dried material. K concentrations were determined in 1 g of dried soil by inductively coupled plasma-optical emission spectrometry after *aqua regia* digestion. P concentrations were measured after reaction with *aqua regia* and Scheel solution I and II by absorbance at 700nm using a Jenway 6400 spectrophotometer. pH was determined in CaCl₂ with a pH meter (WTW inoLab pH 720 with Schott Instruments BlueLine electrode 14 pH).

Climate Data

Monthly data on mean temperature and total precipitation in Kassel in 2013 and for the period 2003-2012, were available from the German meteorological service, who operated a weather station in Kassel prior to, and including, 2013. One missing value for total precipitation in July 2013 was added from a nearby weather station (city of Gießen, about 100 km distance, Deutscher Wetterdienst 2014). In 2014, data were not available; therefore, we acquired them from a private meteorological service (WetterKontor GmbH 2015).

Statistical analysis

Figures were generated with R software (R Core Team 2013). The R software was also used to detect differences in fibre concentration, yield, height and contribution of functional groups between or among managements applying either Wilcoxon's rank-sum test for differences between two independent groups or Kruskal-Wallis test for differences among more than two independent groups with the post-hoc function "kruscalmc" (Giraudoux 2014). Both tests are

non-parametric, as normal distribution of residuals was usually not given. Managements were connected by sites, as every management was conducted on each site. Therefore, the overall variance in site parameters applies to each management system equally. Differences between managements might thereby become more distinct, and significant differences should be interpreted against this background.

To identify differences in yield and fibre concentration between and among single harvests the mixed model procedure MIXED was conducted applying SAS 9.2 with the harvest treated as nested effect within sites as repeated measures factor. Covariance parameters were estimated by a likelihood-based method (restricted maximum likelihood) referring to a first-order autoregressive model (AR (1)), which is commonly used for repeated measurements with equally spaced observations (Littell *et al.* 2006). Least-square means were adjusted with the studentised maximum modulus method to account for multiple tests and used to detect fixed effects among harvests taking the covariance structure into account. Denominator degrees of freedom were estimated according to Satterthwaite approximation.

Results and discussion

Soil parameters and climate conditions

Soil texture indicated mainly silty loam, one site with loam and one site with silty clay loam (Table 8) according to FAO definition (Food and Agriculture Organization of the United Nations 2006). pH values ranged from 5.82 to 7.50 with a mean value of 6.86. K concentrations (mean 2.97 g kg⁻¹ DM) in soils were for all sites higher than target concentrations for agricultural purpose (Baumgärtel *et al.* 1999). In contrast, P concentrations (mean 0.08 g kg⁻¹ DM) were very low (Kerschberger *et al.* 1997).

Table 8. Soil parameters of 10 investigation sites within the city of Kassel. Concentrations refer to DM.

	Mean	Sd	Min	Max
Soil texture (%)				
Sand	31	11	12	47
Clay	21	6	13	35
Silt	48	14	28	71
Nutrient concentration				
N (%)	0.16	0.04	0.11	0.26
P (g kg ⁻¹)	0.08	0.02	0.06	0.10
K (g kg ⁻¹)	2.97	0.88	1.79	4.83
pH	6.86	0.64	5.82	7.50

N concentration in soils ranged from 0.11 to 0.26 % of DM. Similar results were found in residential soils with a concentration of about 0.2 % of DM in 0-10 cm depth with a decreasing concentration with increasing depth (Raciti *et al.* 2011).

The mean temperature in Kassel for March to October in the years 2003-2012 was 13.6°C (Table 9). The mean temperature for 2013 (12.6°C) was below this value, while the mean temperature for the same period in 2014 (13.4°C) was very similar. Mean of total rainfall for March to October in the years 2003-2012 was 396.7 mm. In 2013 the total rainfall in this period was 359.2 mm with exceptionally low rainfall during June, July and August, while mean temperatures were higher than average in July and August. Thus, the climate was dryer than usual. In contrast, a rather humid climate was observed in 2014 with higher than average rainfalls in nearly all months, and double or nearly double rainfall in July and August. Noteworthy also was the temperature in October 2014, which was, at 11.6°C higher than the average value of October 2003-2012 (9.2°C).

Table 9. Temperature (°C) and rainfall (mm) in the city of Kassel in the vegetation period of the investigation years 2013 and 2014, as well as average mean temperature and sum of precipitation in the period of 2003-2012.

	Temperature (°C)			Rainfall (mm)		
	Average 2003-2012	2013	2014	Average 2003-2012	2013	2014
March	5.1	0.1	7.2	47.5	32.8	9.1
April	10.0	8.6	10.9	30.1	38.4	28.9
May	13.5	11.8	12.0	69.8	124.1	94.2
June	16.5	16.0	15.0	68.6	32.1	78.0
July	18.3	19.6	18.8	71.1	30.5	125.5
August	17.7	18.4	15.1	62.0	33.9	127.1
September	14.1	13.5	14.6	47.7	67.4	65.9
October	9.2	10.6	11.6	44.1	98.6	73.1
Overall average/sum	13.6	12.6	13.4	396.7	359.2	528.7

Yield

Mean total annual yields of 2013 and 2014 were highest in the 2-cut management (5.68 ± 3.90 t DM ha⁻¹) with lower quantities in the 4-cut management (3.33 ± 1.82 t DM ha⁻¹) and the mulching management (3.24 ± 2.46 t DM ha⁻¹, Table 10). Although yields did not differ significantly among management options, total yield of urban grass tended to increase with decreasing cutting frequency. In order to produce high yields for bioenergy recovery a reduced cutting

frequency therefore seems favourable. Yields were in a range known from semi-natural grassland with, e.g. 4.1 t DM ha⁻¹ in meadow foxtail vegetation, 5.1 t DM ha⁻¹ in purple moor grass vegetation or 5.4 t DM ha⁻¹ in acute sedge vegetation (Herrmann *et al.* 2014). For weekly mowing, Walker *et al.* (2007) measured low mean yields for unfertilised lawns of *Poa pratensis* (1.9 t DM ha⁻¹) and *Festuca arundinacea* (2.2 t DM ha⁻¹).

Higher yields with lower cutting intensity have also been observed for single years, however, yields in 2014 were higher with an increase of 37, 44 and 82 % in comparison to the yield of 2013 for the 2-cut management, 4-cut management and the mulching management, respectively. The higher yields in 2014 were probably due to favourable weather conditions with exceptionally high rainfall in summer followed by a warm October, which allowed an additional harvest in all management regimes. Similarly, Springer (2012) observed a *Cynodon dactylon* biomass production of 3.5 t DM ha⁻¹ in lawns, which were cut 12 times during the growing season, in a year with average precipitation, and of 4.4 t DM ha⁻¹ in a year with high rainfall. Walker *et al.* (2007) measured a mean yield of 1.4 t DM ha⁻¹ with weekly cuts during the growing season (April to November) of two years for unfertilised *Lolium perenne* cultivars sown one year previously. Yield in the first year was about 30% higher than in the second, which the authors (Walker *et al.* 2007) attributed to the higher rainfall in 2014.

Table 10. Annual yield in t DM ha⁻¹ in 2013 and 2014, as well as height of biomass (cm), share of functional groups (% of DM) and mean fibre concentrations (% of DM) in 2013 given for 2-cut, 4-cut and mulching management. Letters indicate significant differences if existing.

	2-cut	4-cut	mulching
2013	4.79±3.82	2.73±1.64	2.3±1.55
2014	6.57±3.99	3.94±1.86	4.19±2.89
Mean yield	5.68±3.90	3.33±1.82	3.24±2.46
Height	57±29 ^a	32±15 ^b	23±11 ^c
Graminoids	69±18	61±19	58±20
Legumes	8±17	13±13	14±15
Forbs	23±12	25±12	29±19
NDF	55.72±6.15 ^a	51.52±3.51 ^b	nd
ADF	32.44±3.06 ^a	30.05±2.08 ^b	nd
ADL	5.06±1.17 ^a	4.45±1.26 ^b	nd

ADF, acid detergent fibre; ADL, acid detergent lignin; NDF, neutral detergent fibre; nd, not determined

Reduced cutting frequency might lead to an altered species composition with potentially higher biodiversity and enhanced flowering aspect. Firstly, this may have ecological advantages. Smith *et al.* (2015) found higher insect numbers in lawns of forbs native to the sites (UK; e.g. *Achillea millefolium*, *Bellis perennis*, *Pilosella officinarum*, *Potentilla reptans*, *Prunella vulgaris*, *Ranunculus repens*) than in grass-dominated lawns (>60 %). Secondly, the cityscape may change to more colourful, semi-natural grassland-like roadside verges (Tikka *et al.* 2000), which are usually valued as beautiful by inhabitants. It remains uncertain however, to what extent the change in species composition would lead to a change in yield.

Mean yield among harvests differed, partly statistically significantly, between the first and the second half of the vegetative period, with higher values in the first half (Figure 7). Concerning the 4-cut management and the mulching regime, growth declined in July and August in both experimental years to equal levels (3rd harvest in the 4-cut management and the 5th and 6th harvest in the mulching management). While growth remained low in 2013, it recovered in 2014. As for the 2-cut management yield of the 1st harvest was double that of the 2nd harvest, with a more distinct difference in the dry year of 2013. Low grass growth at the end of June or beginning of July is known as “mid-summer depression”, which has been described since early research on grass growth (Alberda 1957). It is probably caused by a variety of climatic influences and corresponding physiological reactions of plants. High growth temperatures reduced the leaf/stem ratio in herbage (Buxton & O’Kiely 2003), which might lower the overall sward density.

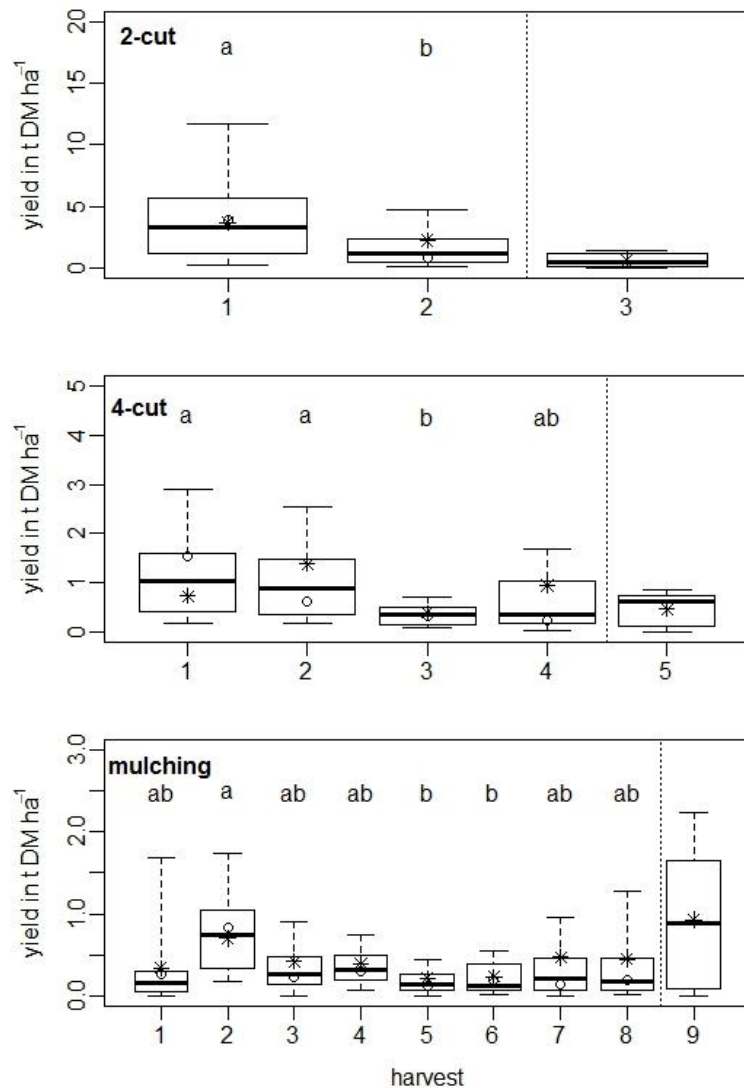


Figure 7. Yields of single harvests and cutting regimes. Letters indicate significant differences of mean yields (2013 and 2014) between or among harvests considering 10 sites per cut. Circle: mean yield in 2013, star: mean yield in 2014. In 2014 an additional harvest was necessary due to unusual high productivity (additional cut is not included in statistics).

Height and functional groups

Traffic safety is the overarching objective of roadside maintenance. Therefore, the height of vegetation is crucial as it influences the sight of road users, which might be particularly relevant at junctions. In a survey on different Welsh road types with a 2-cut management of roadside verges, vegetation height was usually between 20 and 60 cm with a maximum height of 100 cm (Delafield 2006). The maximum height measured in our study was 130 cm, however this was one single grass stem. Mean height of biomass was considerably lower with values of

57±29 cm in the 2-cut management, 32±15 cm in the 4-cut management and 23±11 cm in the mulching management (Table 10). As data were measured in the rather dry year 2013, there is reason for concern that in 2014 maximum heights increased, but actual canopy height was not measured in 2014. However, biomass yield and biomass height were highly correlated (Pearson's r : 0.96 ; present data, calculation not shown in detail) across sites. Therefore, maximum heights would be expected during the main growth period, which was, for both years, the first half of the year, with similar yields for the highest yielding 2-cut management across both years (Figure 7). For that reason, significantly increased heights in 2014 are unlikely.

Contributions of functional groups to the biomass DM did not differ significantly among management options, as standard deviation among sites was high (Table 10). Mean contribution and standard deviation of graminoids was 69±18, 61±19 and 58±20% of DM with increasing management intensity, while contribution of legumes was 8±17, 13±13 and 14±15% of DM for 2-cut, 4-cut and mulching management, respectively. Forbs contributed the remaining quantity with about 20 to 30% of DM. For the 2-cut management, this composition was close to values found for lowland hay meadows (NATURA 2000 habitat type 6510) with about 65% of DM contributed by graminoids, 8% contributed by legumes and 27% contributed by forbs (Andruschkewitsch *et al.* 2014).

Fibre concentration

Mean concentration of fibre fractions was significantly higher in material harvested in a 2-cut management (NDF 55.7, ADF 32.4, ADL 5.1% of DM, respectively) than in material cut in a 4-cut management (NDF 51.5, ADF 30.1, ADL 4.5% of DM, respectively, Table 10). Fibre concentration is highly dependant on the stage of maturity at harvesting date (Buxton & O'Kiely 2003). In perennial ryegrass (*Lolium perenne*) harvested in mid May, the NDF, ADF and ADL concentrations were 49.6, 26.9, 1.4% of DM, respectively (McEniry *et al.* 2012), while concentrations in biomass harvested at the beginning of June were higher with 60.9, 36.6 and 2.8% of DM, respectively. Concentrations detected in our study were therefore at an intermediate level, although ADL concentrations were higher (Figure 8).

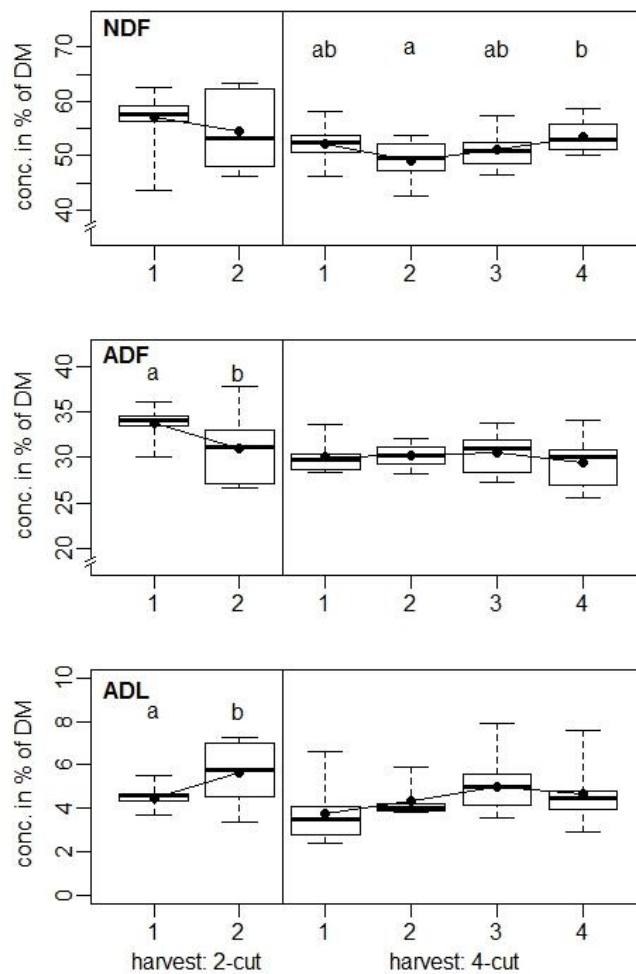


Figure 8. Fibre concentrations (ADF, acid detergent fibre; ADL, acid detergent lignin; NDF, neutral detergent fibre) in material from single harvests of 2-cut and 4-cut management in 2013. Letters indicate significant differences in fibre concentration among harvests.

Within the 2-cut management system NDF concentrations did not change between 1st and 2nd harvest, while ADF concentrations significantly decreased and, in contrast, ADL concentrations increased significantly up to a mean value of 5.6% DM (Figure 8). Within the 4-cut management system ADF and ADL concentrations did not differ among harvests, but NDF concentrations varied significantly between the 2nd (49.1% of DM) and 4th harvest (53.6% of DM). Compared to subsequent seasons, high radiation during long days in spring together with low dark respiration losses of plants during night, are known to result in low fibre concentrations and high concentrations of soluble sugars, which alters the share of fibrous structures in total herbage (Buxton & O'Kiely 2003). However, this effect is not pronounced in our data.

Fermentation characteristics

Samples from all 10 investigation sites were taken at the 1st harvest of the 2-cut management and the 2nd harvest of the 4-cut management to produce silage. At the other dates, biomass was too low for silage production at some sites (Table 11 shows number of sites, which could be harvested). VS concentration in silage of the 2-cut and the 4-cut management, as well as in press fluids from silage of the 2-cut management equally levelled at 93 to 94 % of DM. Only VS concentration in the 1st harvest of the 4-cut management was higher with 96 % of DM. In comparison, volatile solid concentrations of 90-93 % DM were detected for a variety of grass species at different maturity stages (McEniry & O’Kiely 2013). However, in that study volatile organics like volatile fatty acids and alcohols were neglected in VS determination, which might lead to a slight underestimation (Weißbach & Kuhla 1995) and might explain the difference.

Table 11. Sample number and mean concentration of volatile solids in silages and press fluids, as well as mean methane concentration in biogas and mean methane yield with Sd.

	Silage		Silage		Press fluid	
	2-cut management		4-cut management		2-cut management	
	1 st	2 nd	1 st	2 nd	1 st	2 nd
Sample number	10	6	8	10	10	4
VS (% of DM)	93.9±2.1	93.5±2.2	96.4±3.5	93.4±2.3	93.9±2.9	93.3±4.0
Methane conc. in biogas (%)	56±5	54±4	51±7	58±2	60±3	60±4
Methane yield (l _N kg ⁻¹ VS)	221±28	211±37	222±42	241±30	292±33	245±20

Methane concentration was lowest in biogas from silage of the 4-cut management in the 1st harvest (54% of biogas), while in biogas from press fluid highest methane concentrations were detected (60% of biogas). Similarly, methane yields from silage of the 2nd harvest in the 2-cut management were lowest (211 l_N kg⁻¹ VS), while press fluids produced highest yields (292 and 245 l_N kg⁻¹ VS for fluids from 1st and 2nd harvest of 2-cut management, respectively). Methane yields of silage from the 1st and 2nd harvest of 4-cut management accounted for 222 and 241 l_N kg⁻¹ VS, respectively. For perennial ryegrass, McEniry & O’Kiely (2013) detected methane yields of 263 l_N kg⁻¹ VS, when harvested mid of May and of 246 l_N kg⁻¹ VS, when harvested at the beginning of June. This corresponds well with our data when considering a slight overestimation due to differences in VS determination, as discussed above.

Chapter 4

In our study, methane yields did not differ significantly between cutting regimes. . In contrast, a wide range in methane yield (104-365 $\text{I}_N \text{ kg}^{-1} \text{ VS}$) was observed for silages produced from *Alopecuretum pratensis* with 1st cuts taken between May and February of the following year from semi-natural grasslands, with highest methane yields from biomass cut in May [47]. Further, McEniry & O’Kiely (2013) found a marked influence of harvesting date on the methane yield from *Lolium perenne*, which was positively correlated with total solids digestibility and negatively correlated with NDF concentration. Crude fibre concentration was also a significant predictor for methane yield when processing biomass from semi-natural grasslands (Herrmann *et al.* 2014). In accordance, higher methane yields from grass of the 4-cut management than from grass of the 2-cut management have been detected in our study (though not statistically significant), as NDF concentrations were higher in material from the 2-cut management. Additionally, the lower NDF concentration in the 2nd compared to the 1st harvest of the 4-cut management, might have led to elevated methane yields, although the difference was not statistically significant. For the 2-cut management, methane yields from silage, as well as from press fluid tended to decrease from 1st to 2nd harvest. While NDF concentrations did not change, the ADL concentration increased, which might be the reason for reduced digestibility. In digestion experiments with lawn clippings a specific methane production of 402.5 $\text{I}_N \text{ kg}^{-1} \text{ VS}$ was measured (Yu *et al.* 2014), which is considerably higher than values detected in our study, even if an overestimation of values due to different VS determination is taken into account. Although the stage of maturity was not described in the study of Yu (2014), “lawn clippings” are probably conducted at a high frequency, resulting in a low maturity of material. Therefore, the well-known relationship between specific methane production and stage of maturity seems to be valid for both agricultural and urban grass cuttings.

Characteristics of press cake

Concentrations of C, H and N were approximately 44, 6 and 1 % of DM, respectively (Table 12). For H and N, these results are similar to concentrations measured in press cakes from semi-natural grassland, however C concentrations of semi-natural grassland were higher (49% of DM, Böhle *et al.* 2014), which might be due to higher ADL concentrations in the latter study. Lignin has a higher carbon concentration than cellulose or hemicellulose (Blosen & Lohmann 2003).

Table 12. Press cake characteristics; differences were not tested for statistical significance due to unequal number of samples and because of the non randomised samples at 2nd cut (samples could only be taken at sites with high growth). Literature data on coniferous wood are given for comparison.

	Press cake 2 cut management		Coniferous wood ¹
	1 st cut	2 nd cut	
Sample number	10	5	-
C (% of DM)	43.49±0.59	43.98±1.22	51
H (% of DM)	5.99±0.09	6.07±0.16	6.3
N (% of DM)	1.03±0.15	1.44±0.25	0.1
HHV (MJ kg ⁻¹ DM)	17.34±0.23	17.60±0.47	20.3
LHV (MJ kg ⁻¹ DM)	16.16±0.21	16.41±0.44	19.1
Ash (% of DM)	6.89±1.44	7.56±2.15	0.3
K ₂ O/CaO	0.88±0.23	0.51±0.12	-

¹ Data for C, H, N and ash taken from [11]

The calculated HHV was 17-18 MJ kg⁻¹ DM and the LHV about 16 MJ kg⁻¹ DM, which is 1-2 MJ kg⁻¹ DM less than found for a wide range of semi-natural grasslands (Bühle *et al.* 2012a) and about 3 MJ kg⁻¹ DM less than for coniferous wood (LHV 19.1 MJ kg⁻¹ DM; calculated from data given in Obernberger *et al.* 2006). Again, this difference may partly be due to lower C concentrations in our urban material. Ash contents ranged from about 7 to 8% of DM in press cakes produced from 1st and 2nd harvest of the 2-cut management. This is slightly higher than the values reported for press cakes from semi-natural grassland (6% of DM, Bühle *et al.* 2012a), although considerably lower than ash contents measured in press cakes from mixtures of landscape conservation material and urban green waste (13-21% of DM, Hensgen *et al.* 2011). Considering the ash content of the press cake, external factors might be more important than the mineral concentration of the parent material itself, as soil contamination of silage depends on the harvesting technique and on soil type (Cherney & Cherney 2003). The proportion of K to Ca in the fuel has been found important for the melting process of ash from biomass combustion, with lower index values indicating a reduced risk of slagging (Öhman *et al.* 2000; Steenari *et al.* 2009). The K₂O/CaO index was 0.88 and 0.51 in the 1st and 2nd harvest of the 2-cut management. Bühle *et al.* (2014) found an index of 0.5 in press cakes from semi-natural grassland, and 1.5 in the corresponding silages. Therefore, the index of the press cake from silage of the 1st harvest from roadside verges is comparably high. This might be due to elevated K concentrations in silage caused by extraordinary dry weather conditions (Piepenschneider

et al. 2015 b). Furthermore, increased K concentrations may also be due to drought stress, as was found for various *Trifolium* species (Iannucci *et al.* 2002).

Energy provision

In order to recover material from roadside verges for bioenergy production one of the main decision factors for maintenance will be the primary energy balance. From our data, a rough estimation of the potential gross energy output from the recovery techniques is possible. The energy content in methane produced from material of 1 ha roadside verge managed with 4 cuts and processed with common biogas technology is 26.0 GJ (Table 13). This is in accordance with Delafield (2006), whose data allow assuming a gross energy potential (lower heating value) of 26.4 GJ ha⁻¹ roadside verge, although a lower cutting frequency (1-2 cuts) was conducted in her practical trial. From a calculation based on a practical trial in Denmark with 2 cuts, a gross energy potential of about 20 GJ ha⁻¹ roadside verge can be expected (Meyer *et al.* 2014). In contrast, the energy content in methane produced from press fluid of material from 1 ha roadside verge managed with 2 cuts and processed with common biogas technology is 10.3 GJ, as only about 20% of the energy contained in the initial parent material goes into the press fluid. However, about 80% of the dry matter contained in silage goes into the press cake (Hensgen *et al.* 2012), which corresponds to an energy content of 74.1 GJ ha⁻¹ harvested.

Table 13. Gross energy recovery per hectare: IFBB and common anaerobic digestion in comparison. Calculations for recovery with IFBB are based on data of the 2-cut management and for recovery by anaerobic digestion on data of the 4-cut management.

	IFBB	Anaerobic digestion
Share press fluid (%)	20.00	-
Energy content in produced Methane (GJ ha ⁻¹)	10.3	26.4
Share press cake (%)	80.00	-
Energy content in press cake (GJ ha ⁻¹)	74.1	-
Sum (GJ ha ⁻¹)	84.4	26.4

Therefore, a total energy amount of 84.4 GJ ha⁻¹ could be recovered by the IFBB procedure. Considerable differences in gross energy potential between whole crop anaerobic digestion and the IFBB procedure have also been observed in a study on the energy efficiency of processing biomass from semi-natural grassland by dry fermentation versus the IFBB system (Bühle *et al.* 2012a).

The much lower conversion efficiency of dry fermentation was due to the high amounts of digestate residues, which still contained about 50% of energy of the parent material, whereas with the IFBB technique an efficiency of about 50% was determined. When including the amount of energy input to the calculations, the energy balance was distinctly better for the IFBB procedure than for dry fermentation in terms of non-renewable primary energy saving potential (Bühle *et al.* 2012a).

Comprehensive life-cycle analysis and economic analysis have to be conducted for the various management options. All energy input has to be taken into account when shifting from mulching, which only requires energy for mowing, to harvesting and processing urban grassland with completely altered energy requirements for harvest, transporting and processing. In a theoretical approach for Denmark, a net energy gain of 3.8-4.6 GJ ha⁻¹ was estimated when evaluating the utilisation of grass from roadside verges in farm scale biogas plants (calculated from data given in Meyer *et al.*; 2014). For urban environments, the complex logistic situation due to small-scaled structures have to be considered in future assessments of economic and ecological balances.

Conclusions

Grass from roadside verges is comparable to semi-natural grassland in terms of yield, fibre concentration and usability in bioenergy conversion techniques. Increasing yields were detected with decreasing management intensity resulting in 5.7 t DM ha⁻¹ in the 2-cut management and 3.2 t DM ha⁻¹ in the mulching management. As biomass height averaged 57 cm applying low cutting frequency (2-cut management), traffic safety might at the most be of concern at junctions, yet associated sward maturity might offer the opportunity of flowering, which may enhance ecosystem services. Methane yield from silage did not differ between management options (2-cut and 4-cut management), although the fibre concentration increased with lower cutting frequency. However, methane yield from press fluid was higher than from silages. The derived press cake had a LHV of 16 MJ kg⁻¹ DM. Processing the biomass from the 2-cut management with the IFBB procedure results in a gross energy output three times higher than anaerobic digestion of material from the 4-cut management. Whether this difference is still detectable when taking the input energy into account has yet to be evaluated. Life-cycle analysis and economic studies will be necessary to identify the optimum management option.

Chapter 5

Synthesis

General discussion

The suitability of the energetic conversion of urban biomass into biogas or solid fuel was examined focussing on a variety of perspectives, which were mainly technical. Crucial points of implementation were discussed on all levels of sustainability: economic, social and ecological.

Technical

Within this thesis, I presented data, which indicate that the exploitation of urban biomass with biogas technology as well as with IFBB technique is possible, though with different gross efficiencies, and in the case of biogas technology, without taking leaf litter into account. As the chemical composition of urban grass did not differ significantly from agricultural grass, no additional challenges are expected. The main advantage of the IFBB technique is its broad application potential including not only grass but also leaf litter. Additionally, hedge clippings were shown to be a suitable resource (Hensgen *et al.* 2011).

Within the municipal waste disposal system, the separation of organic waste from other fractions by the originators is well established in Germany (Hogg *et al.* 2002). The separate collection, which is already established and to which inhabitants are used, can be seen as the first step towards an utilisation of the material.

The energy recovery of urban biomass with the IFBB technique involves the advantage that the produced solid fuel is easily transportable and storable and thereby, flexibly usable in times of energy demand. This flexibility is usually not available with biogas technology. However, concepts of demand-driven biogas supply were recently developed, offering in general two options: biogas storing and flexible biogas production, while combinations of both are possible, too (Hahn *et al.* 2014b). Following Hahn *et al.* (2014b), “flexible biogas production focus on influencing the anaerobic digestion [...] process to adapt the biogas production to the biogas demand”. This could, on the one hand, be managed by variable substrate feeding, potentially in connection with disintegration techniques. The adapted feeding management in terms of substrate types and feeding frequency pose high expertise demands on the operator, in particular concerning the knowledge of fermentation dynamics of the different substrates. On the other hand, an adaption of the biogas plant configuration focussing on flexible biogas

generation is possible. This could be managed by “generating a liquid substrate with a high content of easy digestible organic matter, which is fed in variable amounts into fixed bed digesters to increase the biogas production within a short time” (Hahn *et al.* 2014b). The IFBB press fluid could be one possibility for such a liquid substrate. As presented, the IFBB press fluid results in higher specific methane yields (by tendency) within 14 days than the corresponding grass silage in 35 days. However, no large-scale commercial plant is running with an adapted configuration (Hahn *et al.* 2014b).

In general, critical factors for bioenergy implementation are rather non-technical (McCormick & Kaberger 2007), but economic and social: scale effects, competition in bioenergy sector, competition with other business, integration, national policy, as well as local policy and opinion (Roos *et al.* 1999).

Economic

Scale effects (as mentioned in the above paragraph) include large production series, as well as joint standards or availability of specialists (Roos *et al.* 1999). Taking the quantity of 4.4 million t (FM) green waste into account, which is already collected by municipalities (Funda *et al.* 2009) and assuming that three quarters of this amount would be available for bioenergy recovery and each plant would need about 30 000 t of material, a number of about 100 IFBB plants could be realised in Germany. Therefore, the potential is low in comparison to about 8 000 existing biogas plants (Agentur für Erneuerbare Energien e.V. 2015). As another comparison: only about 1 000 sewage water treatment plants (out of 10 000 plants in Germany) are equipped with digestion towers, even though the utilisation of sewage sludge in fermentation is seen as an economic and energy efficient method of sewage sludge treatment (Fraunhofer-Institut für Grenzflächen- und Bioverfahrenstechnik IGB accessed 2015). These numbers clearly show that the implementation of the IFBB technique in urban environments is hampered by scale effects – for manufacturers and consultants the market is small; for operators little experience exists and few specialists are available. This problem might be solvable on a European level, if a strong network of IFBB actors is established, who would offer the necessary support and structures.

Competition with other businesses is negligible so far as urban biomass is widely unused and municipalities are strongly interested in bioenergy utilisation (Funda *et al.* 2009), although

competition might occur within the bioenergy sector regarding feedstocks such as wood pellets and wood chips. The IFBB solid fuel will have to compete with these feedstocks in price, quality and purchasing opportunities. As the quality of the IFBB solid fuel is slightly lower than the quality of wood chips (LHV of beech wood chips: 15.3 MJ kg^{-1} with 15% water content (Hartmann 2009) means an additional energy concentration of about 10 % in comparison to the press cake generated from grass of roadside verges) a reduced price has to be taken into account when creating economic scenarios. However, in municipalities (green) waste disposal and energy provision is mostly held by public authorities. The tasks are regularly fulfilled by in-house companies, which act highly independently, but within a framework given by a joint public holder. Thereby, a strong cooperation between raw material provider and solid fuel customers can be established without major efforts, thus creating a competitive advantage. With such a cooperation an integration of an IFBB procedure in other municipal activities, as well as the exploitation of synergies is possible. It will be a political decision, which is dependent on national, but also on local policy.

Public subsidies might enhance the implementation of new technologies, which face the risk of market innovation as investors cannot reliably foresee, if their investment will provide a return. This is in particular valid for technologies, which are competitive only at medium- or long-term (Sachverständigenrat für Umweltfragen 2007).

For semi-natural grasslands, Blumenstein *et al.* (2012) presented an economic evaluation of different management and utilisation opportunities including mulching, composting, dry fermentation and IFBB stand-alone (no connection with a biogas or sewage water treatment plant) or IFBB add-on (connection with a biogas or sewage water treatment plant). The utilisation of the material applying an IFBB add-on plant showed a clear potential for profitability. In comparison to the other opportunities, the system revealed highest total annuity. Main influencing parameters were the price, which could be assumed for solid fuel sale, and its rate of increase. The annuity was calculated as positive assuming a farm field distance below 15 km (Blumenstein *et al.* 2012). While neither the material nor the plant configuration differs significantly between rural and urban environments, the logistics in municipalities are considerably more complex as green areas are fragmented and dispersed. However, urban green areas are regularly mulched or mown already, green waste is collected and leaf litter is taken from roads. Thus, it has to be discussed, which costs actually have to be attributed to a potential energetic utilisation. Thinking from the plant operators' point of view, it would be possible

to pay revenues for the material, which is delivered to the plant without taking the actual harvesting and transporting costs into account. For the public disposing entities, this could lead at least to a reduction of costs as they regularly pay for the disposal at present. Thereby, disposal fees taken from the public could be minimised as already happened in Munich, where organic waste is treated with biogas technology (Funda *et al.* 2009).

When focussing on the profitability of a biogas or sewage water treatment plant with a connected IFBB plant, the application of the IFBB press fluid in flexible biogas production becomes relevant. The press fluid showed lowest additional flexibility costs at thermal biogas capacities of 2650 kW and 3710 kW, when 72 h of flexibility (weekend) are required (Hahn *et al.* 2014a). Thus, the operator of a fermentation unit would benefit from an IFBB system not only as additional income possibility but also as a source of a cost-efficient substrate that allows a flexible power generation and thereby, the potential receipt of additional incentives (Deutscher Bundestag 2014).

Social

National policy could contribute to the establishment of IFBB plants with funding, as well as with lobbying. Though, as the IFBB solution is a relatively special development in comparison to biogas technology, for example, the probability of national support is expected to be rather low. Local politicians, instead, can promote the IFBB system in their local urban environment with its specific challenges. They can envision more easily, how an IFBB procedure could be implemented and how it could support political aims on all discussed levels: ecological, economic and social. However, local politicians are highly dependent on public opinion. Therefore, the first step of any IFBB implementation in urban environments is the full and proactive involvement of the citizens.

An important advantage regarding the utilisation of urban green waste residues is the fact that there is barely competition with food, feed, fibre or fuel production at present, as the material is widely disposed in landfills or burnt in incineration plants (Hogg *et al.* 2002). However, this is a snapshot of the current situation, which might change in future. Hoogwijk *et al.* (2003) defined in a meta-analysis 6 crucial factors for future global biomass availability for energy: the future food demand, the food production systems, productivity of energy crops and forests, usage of bio-materials, availability of degraded land and competing land uses. This list makes clear that the future biomass amounts available for energy recovery are not

only determined by national agriculture, waste and nature conservation politics but are also dependent on national and world-wide needs and trends in human diet, and the development of recycling of materials into high value products. As for urban green waste, on the one hand the material use (e.g. as composite material, Feldmann & Bledzki 2014) could become a competing utilisation opportunity, particularly as the European waste hierarchy prefers recycling instead of energy recovery (The European Parliament and the Council of the European Union 2008). However, synergies and cascading utilisation could be possible if the energy industry would be able to incinerate composite material in adapted boilers. Additionally, specialised technique is necessary to extract fibres from the biomass and residues as short carbohydrates and proteins might be suitable for biogas technology. On the other hand, urban horticulture is expanding. While urban horticulture regularly contributes to food security in developing countries, it has a rather recreational and educational meaning within developed countries (Eigenbrod & Gruda 2015; Specht *et al.* 2014). Some studies indicate that a certain self-reliance concerning fresh vegetable and fruit would be possible within cities (up to 100 % in Cleveland, Grewal & Grewal 2012; Mok *et al.* 2014). However, within the same studies concerns are expressed, that gardening on major open spaces might not be wanted by inhabitants (Grewal & Grewal 2012) and that there is little research on the question of whether self-reliance is necessary or feasible (Mok *et al.* 2014). Schnell (2013) stated that for the majority of community-supported agriculture members “local” is not a spatial concept but “an important part of direct experience and sensory input in shaping their experience of place”. Therefore, urban horticulture might occupy open space to a certain extent, though inhabitants might insist on park areas for various emotional reasons (Chiesura 2004) as parks are part of a cities’ identity, too (e.g. Bergpark Wilhelmshöhe in Kassel, Central Park in New York City). Further, major parts of the material investigated in this study are not directly affected by urban horticulture as leaf litter, for example, is not part of human diet, neither from common urban tree species nor from fruit trees.

Reduced cutting frequency (2- or 4- cut management, instead of 8 times mulching) led to significantly taller swards, which changed the cityscape. Additional visual change resulted from the opportunity of forbs with erected stems to flower (e.g. *Leucanthemum vulgare*; Figure 9). Although blooming grassland might enhance the recreational value of urban green areas, inhabitants might not be satisfied with the altered appearance. Green area (in particular park) management should therefore include participation of inhabitants (Chiesura 2004). Also, some urban structures (e.g. sports field, memorials) are not suitable for tall vegetation.



Figure 9 Flowering *Leucanthemum vulgare* at a roadside verge within the city of Kassel managed with 2 cuts.

Ecological

Climate protection is one of the main present environmental challenges (Lal Pandey 2014). Renewable energies shall therefore save at least as much CO₂ equivalences (CO₂-equ.) as they emit. The calculation of a CO₂ balance evaluating the recovery of urban biomass for energetic purpose would be part of an overarching life-cycle analysis, which was not yet conducted. A main challenge of such an analysis is the choice of boundaries. Usually, the “system should be modelled in such a manner that inputs and outputs at its boundary are elementary flows” (European Committee for Standardization 2006). Therefore, the system should comprise the acquisition of raw materials, as well as the transportation of raw materials, products and residuals (European Committee for Standardization 2006). With regard to the system of energy generation from urban biomass, these instructions would mean that the harvest, as well as all following logistics, would have to be modelled and evaluated in order to set up a complete LCA. As mentioned above, urban green areas are already managed, partly by mowing, and green waste (leaf litter from roads, private garden residues) is collected at present. Therefore, the amount of emission, which have to be attributed to the potential energetic recovery of these biomasses, is not necessarily determined by a mere “output” calculation, but might refer to the additional quantities caused by the system change. It is not yet clarified if there would be additional emissions as, for green areas at least, a comparison of frequent mulching with lenient mowing has yet to take place.

Bühle *et al.* (2012a) calculated in their LCA with a field-plant distance of 5 km focussing on the energetic utilisation of semi-natural grass. For establishing ecological balances of the utilisation of semi-natural grass in fermentation, they assumed an annual yield of 3.8 t DM ha⁻¹ with a specific methane potential of 213 l_N kg⁻¹ VS. As presented above, an annual yield of 3.3 t DM ha⁻¹ with a methane potential of 231 l_N kg⁻¹ VS (mean of first and second cut) can be expected from grass of urban roadside verges in a 4-cut management. Therefore, the study of Bühle *et al.* (2012a) might allow a rough prospect of the CO_{2-equ} saving potential, which can be expected from the recovery of grass from roadside verges in fermentation: annually 1.35 t CO_{2-equ} ha⁻¹. However, in comparison to the study of Bühle *et al.* (2012a) treating urban grass areas in a 2-cut management with subsequent IFBB procedure would lead to higher annual biomass yields (5.68 t ha⁻¹) though with less specific methane potential from the press fluid (about 100 l_N kg⁻¹ VS less) and reduced LHV of the press cake (about 1.5 MJ kg⁻¹ DM less). Therefore, a direct comparison with the results of Bühle *et al.* (2012a) to assess the potential CO_{2-equ} savings of an IFBB system becomes increasingly inaccurate. Whether the potential CO_{2-equ} savings (3.65 t CO_{2-equ} ha⁻¹ annually, Bühle *et al.* 2012a) presented for an IFBB add-on plant (with external heat source) are also achievable in an urban environment, has therefore to remain open.

Next to climate protection, renewable energy techniques are supposed to contribute to the long-term energy supply (Deutscher Bundestag 2014). As presented, the application of the IFBB technique can recover higher gross energy quantities from grass of roadside verges than applying biogas technology. Assuming a conversion efficiency of about 50 % (Bühle *et al.* 2012a) an approximate primary energy saving potential of 42.2 GJ ha⁻¹ can be expected, yet under the precondition that harvest and transport is not included in the calculation following the argumentation above. For transport, this assumption seems possible, as Bühle *et al.* (2012a) presented a negligible influence of farm-field distance in a sensitivity analysis provided with their LCA. Which influence has to be expected by the complex harvesting procedures have to remain open. However, not considering energy input for harvest, as well as for transport and knowing that the city of Kassel, as example for a German city, has an area of 284 ha roadside green verges (Department for Environment and Gardens of the city of Kassel 2013), a thermal energy amount of approximately 12 TJ could be provided annually by applying the IFBB technique. This would be enough energy for 330 households with 100 m² and a thermal energy consumption of 100 kWh m⁻² per year. If Kassel's 200,000 inhabitants lived

with two persons per household (in accordance with the German mean, Statistisches Bundesamt 2015b), the energy provision from roadside verges would therefore meet the thermal energy demand of about 0.3 % of inhabitants. This figure makes clear that recovering grass from urban roadside verges will not extensively supply the inhabitants with energy. However, the figure is improvable, when not only grass from roadside verges, but also other urban biomass fractions are taken into account: leaf litter, hedge clippings, material from private gardens and parks, which might be managed by different entities.

In a study from Berlin, an approximate amount of 100 kg leaf litter per urban tree was calculated (Ingenieurconsulting Umwelt und Bau 2011). Assuming that this number holds true for other cities, the 62 000 trees in Kassel (Department for Environment and Gardens of the city of Kassel 2013) would account for an additional biomass of 6 200 t FM per year. As this material is known to have potentially high ash contents (Heckman & Kluchinski 1996), future research will show if, and under which circumstances, leaf litter will contribute to urban energy provision.

Though the share of inhabitants, whose thermal energy demand could be satisfied by utilising urban biomass recovery techniques, seems low, the exploitation of the unused potential would contribute to the sustainable management of cities' green waste. Next to an, albeit small, contribution to the energy provision, GHG savings as a result of fossil primary energy substitution are possible as discussed. Further GHG savings might arise from reduced "wild composting" in the landscape and composting in small heaps, which is in particular popular in Germany (and Austria) in comparison to other EU member states (Hogg *et al.* 2002). Involvement of inhabitants could motivate them to contribute to their own energy supply with their garden waste.

Utilising the urban grass biomass for energy generation would allow a reduced cutting frequency in comparison to the currently widely applied mulching treatment, which requires low cutting intervals of 1-3 weeks in the vegetation season to gain an easy degradable material. In contrast, for the IFBB procedure a high fibre content as a result of low cutting frequency is favourable, as it leads to a higher solid fuel quality. As for biogas technology, material of low maturity leads to higher biogas yields, but harvesting needs to be possible, both in technical, as well as in economic terms. Therefore, a 4-cut management might be suitable. A reduced cutting frequency might lead to higher biodiversity (Zechmeister *et al.* 2003) as, on the one

hand forbs can flower and produce seeds and on the other hand, plants, which are adapted to extensive management due to their physiological characteristics, could establish (Louault *et al.* 2005). In addition to potentially enhanced plant biodiversity, fauna biodiversity could be improved (Batáry *et al.* 2012; Smith *et al.* 2015).

However, enhanced biodiversity might reduce the biomass yield because of the changing species composition. A reduced yield after management change might also result from decreased amounts of nutrients, which are not returned to the soil through decomposition, as before, but are carried along with residues (ash e.g. for cement production; digestate e.g. as agricultural fertiliser depending on the national legal requirements). Whether a decreased yield would occur is questionable, however, as the observed figures are already in the range of low-yield extensively managed grasslands (Herrmann *et al.* 2014; Melts *et al.* 2014).

In summary, urban areas provide the outstanding opportunity to use synergetic effects of economic, social and ecological political aims. This concerns, amongst others, renewable energy generation, reduced GHG emissions, fossil primary energy savings, decreased fees for green waste management and enhanced biodiversity. Further support for adaptation of green area management to the multiple political requirements of municipalities, might arise from the envisaged amendment of the waste directive (2008/98/EC) and the landfill of waste directive (1999/31/EC). The proposal contains the demand to not accept biodegradable waste by 2025 in landfills for non-hazardous waste (European Commission 2014b). Therefore, utilisation opportunities need to be developed.

Conclusions

This thesis presents data on the energetic potential of urban green waste. Based on a field experiment in the city of Kassel and subsequent laboratory investigations utilising grass from roadside verges and grass-leaf litter mixtures, I conclude:

- (i) The concentrations of 16 elements (Ca, Cl, K, Mg, N, Na, P, S, Al, Cd, Cr, Cu, Mn, Pb, Si, Zn) measured in grass from roadside verges at different maturity stages were in general similar to concentrations, which were reported for conservation or agricultural grassland in literature. Only Ca, N and P concentrations exceeded literature values possibly due to weather and soil conditions. In mixtures, the concentration of minerals (Al, Cl, K, N, Na, P, S, Si) decreased with increasing share of leaf litter. However, concentrations of Ca and Mg, which have structural functions in plants, increased. NDF, ADF and ADL concentrations differed significantly between maturity stages of grass from roadside verges. While NDF and ADF concentrations were within the range of literature data, ADL concentrations were rather high (5.06 % of DM and 4.45 % of DM in the 2-cut and 4-cut management, respectively). In grass-leaf litter mixtures, the NDF concentration increased with increasing share of leaf litter.
- (ii) The IFBB procedure reduced the concentrations of all observed elements in grass from roadside verges, but Al and Mn, whose concentrations were not influenced, as well as Cu and Cr, whose concentrations increased significantly possibly due to steel abrasion during processing. Mixtures revealed that, mineral concentrations (Al, Ca, Cl, K, Mg, N, Na, P, not S) in the press cake were highly depending on their concentration in the raw material and no interactions between materials were observed.
- (iii) In the press cake generated from grass of roadside verges, as well as from mixtures the concentration of particularly harmful elements for combustion (Cl, S, N) were below the German standard for non-woody solid fuels (DIN EN 14961-6:2012). The major part of energy contained in the raw material (mixtures of grass and leaf litter) flew into the press cake resulting in a lower heating value of about 15 MJ kg⁻¹ DM to 17 MJ kg⁻¹ DM. The difference resulted from the ash content, which was high in biomass used for mixtures possibly due to soil contamination as result of harvesting methods compared to grass from roadside verges, whose ash content

was <10 % in accordance with DIN EN 14961-6:2012. A washing step to reduce the ash fraction in soil-contaminated biomass has to be considered. The lower heating value of the press cake from grass of roadside verges was about 16 MJ kg⁻¹ DM. Specific methane yields of press fluid from grass of roadside verges were 292 l_N kg⁻¹ VS and 245 l_N kg⁻¹ VS in the first and second cut, respectively. The specific methane yield of press fluids produced from grass-leaf litter mixtures ranged from 172 to 325 l_N kg⁻¹ VS with highest yields in the mixtures with 33 % leaf litter and lowest yields in press fluid from pure leaf litter. DM concentration decreased with increasing leaf litter share and concentration of VS was lowest in the mixtures with 33 % leaf litter and highest in press fluid from pure leaf litter. Potential interactions between substrates concerning the mass flow of carbohydrates and minerals might issue from the combination of structure (from leaf litter) and sugars (from grass).

- (iv) Mean biomass yield of grass from roadside verges was 5.68 t DM ha⁻¹ in the 2-cut management, 3.33 t DM ha⁻¹ in the 4-cut management and 3.24 t DM ha⁻¹ in the mulching management. The mean specific methane yield ranged from 211 l_N kg⁻¹ VS to 241 l_N kg⁻¹ VS in the second cuts of the 2-cut and 4-cut managements, respectively.
- (v) A gross energy yield of 84.4 GJ ha⁻¹ was assessed applying IFBB technique and 26.4 GJ ha⁻¹ applying anaerobic digestion on grass from roadside verges. Harvest, transport and residue management was not considered in the calculation. Future investigations including these aspects will allow a comprehensive evaluation of the conversion techniques on ecological, economic and social levels.

Chapter 6

Summary

Urban biomass from green areas is a potential resource for bioenergy, which is widely unused. Municipalities maintain green areas, though the material is either left in place to decay, disposed or burnt in incineration plants, which is cost-intensive but do not involve any revenues for the public authority. Instead, the material could be used in bioenergy recovery. Two possible bioenergy recovery techniques were investigated utilising herbaceous material from urban roadside verges i) direct anaerobic digestion (4 cuts per year) and ii) the “integrated generation of solid fuel and biogas from biomass” (IFBB) technique, which divides biomass into a press fluid and a press cake by mashing and mechanical dewatering (2 cuts per year). As reference, the current management (8 times mulching) was conducted though without recovering opportunity. Additionally, the suitability of mixtures of grass and leaf litter for the IFBB technique was investigated. Mean annual biomass yield was 3.24, 3.33 and 5.68 t dry matter ha⁻¹ for the mulching, 4-cut management and 2-cut management, respectively. Even though the fibre concentration was higher in material of the 2-cut management than in material of the 4-cut management, specific methane yields did not differ significantly. The lower heating value of the press cake produced from grass of roadside verges was about 16 MJ kg⁻¹ DM, while the press cake from the grass-leaf litter mixture had a lower heating value ranging from 15 to 17 MJ kg⁻¹ DM dependent on the ash content. The ash content in mixtures was higher than the limiting value of the DIN EN 14961-6:2012 (defining non-woody solid fuels) due to soil adherence possibly caused by harvesting methods; however the ash content of grass from roadside verges was below the limit. The element concentration (Ca, Cl, K, Mg, N, Na, P, S, Al, Cd, Cr, Cu, Mn, Pb, Si, Zn) of the material was in general similar to agricultural or conservation grassland. In mixtures, element concentrations (Al, Cl, K, N, Na, P, S, Si) decreased with increasing leaf-litter share, but concentrations of Ca and Mg, as well as of neutral detergent fibre increased. The IFBB technique reduced the concentrations of Cl, K and N reliably, which are particularly detrimental in combustion. Besides the potentially high ash content, no technical reason was detected during the investigations, which would hamper the energetic recovery of the tested urban material. However, economic, social and ecological implications of an implementation have to be taken into account. A simple consideration based on the current knowledge give rise to the expectation that bioenergy recovery of urban material could be sustainable at all levels.

Chapter 7

Zusammenfassung

Städtische Biomassen der Grünflächen bilden eine potentielle, bisher weitgehend ungenutzte Ressource für Bioenergie. Kommunen pflegen die Grünflächen, lassen das Material aber verrotten oder führen es Deponien oder Müllverbrennungsanlagen zu. Diese Praxis ist kostenintensiv ohne für die Verwaltungen finanziellen Ausgleich bereitzustellen. Stattdessen könnte das Material energetisch verwertet werden. Zwei mögliche Techniken, um Bioenergie zu gewinnen, wurden mit krautigem Material des städtischen Straßenbegleitgrüns untersucht i) direkte anaerobe Fermentation (4 Schnitte im Jahr) und ii) „Integrierte Festbrennstoff- und Biogasproduktion aus Biomasse“ (IFBB), die Biomasse durch Maischen und mechanisches Entwässern in einen Presssaft und einen Presskuchen trennt (2 Schnitte im Jahr). Als Referenz wurde die aktuelle Pflege ohne Verwertungsoption mitgeführt (8faches Mulchen). Zusätzlich wurde die Eignung von Gras-Laub-Mischungen im IFBB-Verfahren untersucht. Der mittlere Biomassertrag war 3.24, 3.33 und 5.68 t Trockenmasse ha⁻¹ jeweils für die Pflegeintensitäten Mulchen, 4-Schnitt- und 2-Schnittnutzung. Obwohl die Faserkonzentration in der Biomasse der 2-Schnittnutzung höher war als im Material der 4-Schnittnutzung, unterschieden sich die Methanausbeuten nicht signifikant. Der Presskuchen aus dem krautigen Material des Straßenbegleitgrüns hatte einen Heizwert von 16 MJ kg⁻¹ Trockenmasse, während der Heizwert des Presskuchens der Gras-Laub-Mischung in Abhängigkeit vom Aschegehalt zwischen 15 und 17 MJ kg⁻¹ Trockenmasse lag. Der Aschegehalt der Mischungen war höher als der Grenzwert nach DIN EN 14961-6:2012 (für nicht-holzige Brennstoffe), was auf erhöhte Bodenhaftung auf Grund der Erntemethoden zurückzuführen sein könnte. Der Aschegehalt des krautigen Materials vom Straßenrand hielt die Norm jedoch ein. Die Elementkonzentration (Ca, Cl, K, Mg, N, Na, P, S, Al, Cd, Cr, Cu, Mn, Pb, Si, Zn) im krautigen Material war generell ähnlich zu Landwirtschafts- oder Naturschutzgrünland. In den Mischungen nahm die Elementkonzentration (Al, Cl, K, N, Na, P, S, Si) mit zunehmendem Laubanteil ab. Die Konzentration von Ca, Mg und der Neutral-Detergenz-Fasern stieg hingegen an. Die IFBB-Technik reduzierte die Konzentrationen der in der Verbrennung besonders schädlichen Elemente Cl, K und N zuverlässig. Außer den potentiell hohen Aschegehalten, wurde während der Untersuchungen kein technischer Grund entdeckt, der einer energetischen Verwertung des getesteten urbanen Materials entgegenstehen würde. Ökonomische, soziale und ökologische Auswirkungen einer Umsetzung müssen

beachtet werden. Eine oberflächliche Betrachtung auf Basis des bisherigen Wissens lässt hoffen, dass eine bioenergetische Verwertung städtischen Materials auf allen Ebenen nachhaltig sein könnte.

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List of other publications

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Piepenschneider M, Nurmatov N, Bühle L, Hensgen F, Wachendorf M (2015) Chemical properties and ash slagging characteristics of solid fuels from urban leaf litter. *Waste and Biomass Valorization*, online first, doi 10.1007/s12649-015-9457-1.

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