Energetische Verwertung städtischen Laubs

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Dissertation

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Witzenhausen, 03.07.2017

Nodirjon Nurmatov

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Liste der veröffentlichten Artikel

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Abkürzungen

af	Ash free
AST	Ash softening temperature
CC	City centre
CV	coefficient of variation
CHP	Combined heat and power plant
$CO_{2äq}$	CO_2 Äquivalent
DIN	German institute for standardization
DM	Dry matter
GPS	Ganzpflanzensilage
HHV	Higher heating value
HW	Hand washed material
IFBB	Integrated generation of solid fuel and biogas from biomass
LHV	Lower heating value
l_N:	Normal litre
MF	Mass flow
MR	Main road
MW	Machine washed material
PAH	polycyclic aromatic hydrocarbons
PC	Press cake
PF	Press fluid
RA	Residential Area
RM	Raw material
ST	sweeping technique
s.e.:	Standard error
TM	Trockenmasse
UW	Unwashed material
VT	Vacuum technique

1. Einleitung

1.1 Entwicklung der Biogasbranche

Das durch die Ölkrisen in den 1970er Jahren und durch die verheerende Nuklearkatastrophe in Tschernobyl 1986 entstandene Stromeinspeisungsgesetz [1], sicherte die ersten Biogasanlagen mit festen Abnahmepreisen für Strom. Es war die Grundlage des Erneuerbare-Energien- Gesetzes (EEG) wodurch die Entwicklung aller Biogasanlagen mit dem Ziel der Erreichung der Energieunabhängigkeit auf der Basis Strom-Einspeisevergütung stark gefördert wurde. In den Jahren 2004, 2009, 2012, 2014 und 2017 wurde dieses Gesetz novelliert [2]. Der von Wetterbedingungen und Tagesablauf unabhängige Strom aus Biogas versprach Stabilität im Stromfluss, nachhaltige Bewirtschaftung und kostengünstige CO_2-Einsparung.

In der Anfangsphase 1992 existierten bundesweit 139 Biogasanlagen. Bis 2015 stieg die Anzahl der Biogasanlagen auf 8.861 mit 4.018 MW installierter elektrischer Leistung. Der Prognose nach sollten im Jahr 2016 etwa 43.000 Arbeitskräfte bei 9.009 Biogasanlagen 4.166 MW installierte elektrische Leistung erreicht haben [3]. Die Flächennutzung wuchs dementsprechend. 2015 wurden auf 1.393.000 ha landwirtschaftlichen Flächen Energiepflanzen für Biogas angebaut, davon 894.000 ha Mais (35% der gesamten Maisfläche) [4]. Betrachtet man den Einsatz von Nachwachsenden Rohstoffen in Biogasanlagen, so ist der Mais mit großem Abstand das am häufigsten eingesetzte Substrat (73% Massebezogen), gefolgt von Grassilage (12%), Getreide-Ganzpflanzensilage (GPS) (7%) und anderen Substraten (8%) [5].

Aus der Sicht des Natur-, Boden- und Klimaschutzes, sowie der Nahrungsmittelsicherheit und des Wohlstands der Bürger weist die Förderung der Bioenergie aus den landwirtschaftlichen Nutzflächen jedoch auch negative Auswirkungen auf. Bereits Mitte der 2000er Jahre, während die Biogasanlagen deutschlandweit expandierten, wurden die Folgen untersucht. Im Jahr 2007 stellte der Wissenschaftliche Beirat der Agrarpolitik (WBA) beim Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz fest, dass die Biokraftstoffe und das Biogas auf Maisbasis relativ hohe $CO_{2äq}$-Vermeidungskosten in einer Größenordnung von 150 bis weit über 300 €/t $CO_{2äq}$ aufwiesen, wobei Klimaschutz mit CO_2-Vermeidungskosten von unter 50 €/t $CO_{2äq}$ realisiert werden könnte [6]. Unbeabsichtigte, negative Folgen auf das Klima sind, dass Monokulturen wie Raps und Mais zum Zweck der CO_2-Vermeidung anstelle klimafreundlicherer Kulturen wie Grünland, Wälder und Mooren angebaut werden [7]. Die Kommission Landwirtschaft beim Umweltbundesamt (KLU) [8] bewertet den Anbau des Energiemaises mit ausgefallener Fruchtfolge in einem stark konzentrierten Raum als erhöhtes Gefahrenpotenzial für Böden und Gewässer durch Ausbreitung von Schädlingen, Erosion, Bodenverdichtung sowie Nährstoff- und Pflanzenschutzmittelauswaschung.

Die Auswirkung der boomenden Biogasanlagen auf landwirtschaftliche Erzeugnisse wie Milch ist wegen in der Region entstandener Konkurrenz um die Flächen sehr beachtenswert. Die vom

Grünlandumbruch und von der Umnutzung der Getreideflächen stark profitierende Biogaserzeugung schwächt die Rinderhaltung in der Konkurrenz um die Flächennutzung und beim Zugang zur Biomasse [8]. So haben sich die Pachtpreise zwischen 2007 und 2010 in ihrer Dynamik verstärkt. Innerhalb dieser Zeit ist die durchschnittliche Neupacht in den alten Bundesländern um 25% auf 348€/ha, in den neuen Bundesländern um 29% auf 166€/ha gestiegen. In dieser Konkurrenzsituation reagierten landwirtschaftliche Unternehmen mit Investitionen in die Tierhaltung, um das Volumen ihrer Wirtschaftsdünger (hauptsächlich Gülle) zu steigern und diese als Substrat in die Biogasanlage zu geben und die EEG-Vergütung für Gülle auszunutzen. Als Folge dieses Wettbewerbs kann die Eutrophierung des Bodens durch überschüssige Gärreste bezeichnet werden [9].

Die Biogasanlagen-Branche erlebte in ihrer 25jährigen Geschichte sowohl eine Hochkonjunktur als auch einen nachfolgend starken Rückgang. Das Bundesministerium für Wirtschaft und Energie schaffte mit der Novellierung des Gesetzes im Jahr 2014 [2] die Boni und weitere Vergütungen für die Biogasanlagenbranche ab. Das Ziel war es, bei gleichbleibendem Ausbau der Erneuerbaren Energien, den Durchbruch der Kostendynamik des EEG und die Begrenzung der Stromkosten für die Verbraucher zu erzielen. Mit dieser Novellierung wollte die Bundesregierung die Versorgungssicherheit durch ein besser organisiertes Strommarktsystem gewährleisten. Im Weiteren wurden die Regenerativen Energien über die Förderung der Kraft-Wärme-Kopplung und die Umsetzung der europäischen Energieeffizienz-Richtlinien [10] unterstützt. Der NaWaRo-, Gülle- und Gasaufbereitungsbonus wurde gestrichen. Die Wirtschaft sollte sich auf die Biogaserzeugung aus Abfall- und Reststoffen orientieren [2].

1.2 Verwertung städtischer biogener Rohstoffe

Während die Biogasanlagen auf Basis nachwachsender Rohstoffe (Mais, Weizen-GPS) seit dem Erlass des EEG-2000 in Anzahl und Größe wuchsen, blieb der Ausbau der Kapazitäten zur Verwertung von tierischen Nebenprodukten, pflanzlichen Rückständen und Abfällen hinter den Erwartungen zurück. Nach Angaben des Bundesministeriums für Wirtschaft und Energie lag der biogene Anteil des Abfalls am Bruttostromverbrauch im Jahr 2014 gerade bei 1.0 %. Bei der Stromerzeugung aus erneuerbaren Quellen machten sie nur 3.1 % aus. In der Wärmeproduktion von 155 TW/h lag der Anteil der Biomasse bei 88 % (136 TW/h) wobei der Betrag biogener Abfälle nur bei 7.5 % lag [11].

Laut Biogas-Atlas 2014-2015 [12] wurde die erste Bioabfallvergärungsanlage im Jahr 1989 in Betrieb genommen und Anfang der 1990er Jahre technisch deutlich erweitert. In den Jahren zwischen 1998 und 2005 wurden 1 bis 5 Anlagen pro Jahr installiert. Ab dem Jahr 2006 stabilisierte sich die Entwicklung und es wurden 8 bis 10 Bioabfallvergärungsanlagen pro Jahr in Betrieb genommen. 2014 wurden in Deutschland 104 Biogut- und Grüngutvergärungsanlagen (ohne Speiserestfermenter) registriert. Diese Anlagen unterteilen sich in drei Verfahrenskategorien: - Boxen- bzw. Garagen, Pfropfenstrom und typische Nassvergärung. Die Zahl der Boxenanlagen liegt bei 31 und macht 30 %

aller Anlagen aus. Dasselbe gilt auch für Pfropfenstromanlagen (31 Anlagen, 30 % aller Anlagen). Die Nassvergärung ist stärker verbreitet und wird in 42 Anlagen (40 % aller Anlagen) betrieben. Obwohl die Zahl der Boxen-, und Pfropfenstromanlagen geringer ist im Vergleich zu den Nassvergärungsanlagen, werden in beiden Anlagentypen dennoch höhere Anteile an Bio- und Grüngut (jeweils mehr als 95 %) eingesetzt, während in Nassfermentern nur etwa 20 % Biogut und Grüngut und etwa 80 % Gewerbeabfälle und Speisereste eingeführt werden [12]. Aus diesen 104 Anlagen erzeugen 92 Anlagen Strom und nur 12 Anlagen speisen Gas ins Netz ein.

Die Europäische Union strebt an, 20 % ihres Stroms im Jahr 2020 aus erneuerbaren Quellen zu produzieren und ruft alle Mitgliedsstaaten dazu auf, neben den nachwachsenden Rohstoffen auch andere vorhandene Potenziale wie landwirtschaftliche Reststoffe und urbane biogene Abfälle zu fördern [13]. Der nationale Plan des Bundesministeriums für Wirtschaft und Energie ist, den Anteil an Erneuerbaren Energien in der Stromerzeugung von derzeit rund 33 % auf 40-45 % im Jahr 2025, auf 55-60 % im Jahr 2035 und mindestens auf 80 % bis zum Jahr 2050 zu steigern. Dabei soll der Bioabfall den größten Biomassenanteil ausmachen (EEG-Novellierung in 2017) [2].

Die Bedeutung des städtischen biogenen Abfallstoffs in Erneuerbaren Energien zu erhöhen, ist nicht nur ökologisch sinnvoll, sondern auch ökonomisch kostengünstig. Die erste Regelung für Abfall und seine sinnvolle Wiederverwertung waren unter den Richtlinien 1999/31/EG über Abfalldeponien koordiniert [14]. Hierbei wurde von den Mitgliedsländern gefordert, die Deponierung grundsätzlich zu kontrollieren, im besten Fall den Abfall zu vermeiden, wiederzuverwerten und energetisch zu nutzen. Mit dem Erlass der Abfallrahmenrichtlinie (2008/98/EC) [15] schrieb die europäische Union vor, dass die Mitglieder die vorhandenen Ressourcen im Abfall nach einer fünfstufigen Hierarchie wieder stofflich oder energetisch nutzen sollten. Diese Aufforderung wurde mit BioAbfV [16] in Kombination mit BiomasseV [17] verstärkt, und zwar mit dem Zweck, biogene Rohstoffe aus dem Abfall separat zu erfassen und energetisch zu nutzen. Auf nationaler Ebene wird in Deutschland die Festbrennstoffproduktion aus biologisch abbaubaren Reststoffen nach Kriterien des Kreislaufwirtschaftsgesetzes [18] und [2] Erneuerbaren Energien Gesetz, unter Berücksichtigung des Wasserhaushaltgesetzes und Bundesbodenschutzgesetzes, sowie Gesetz zur Sicherstellung der Biogasanlagen und Luftreinhaltung geregelt.

1.3 Städtisches Laub als Energieträger, Verfahren und Potenzial

Im Sinne oben genannter Richtlinien und Gesetze, weckt der Laubabfall [19] neben dem urbanen Gras [20] und Grünschnittmaterialien [21] das Interesse, ihn energetisch zu verwerten. Unter den städtischen Biomassen hat das Laub einen besonderen Charakter. Es ist ein Material, welches in Gärten von privaten Haushalten oder auf kommunalen Flächen anfällt und von anderen Biomassen separat erfasst werden kann. Während sich die Kommunen von Mitte Frühling bis Mitte Herbst intensiv mit Grünschnitt und Rasenschnitt beschäftigen, kann der Laubfall von Oktober bis Dezember die höchste Einsatzkapazität örtlicher Reinigungsdienste in Anspruch nehmen. Bisher wurde dieses Material aufgrund seines hohen Ligningehaltes als für eine Kompostierung geeignet eingestuft [22, 23]. Der hohe Ligningehalt ist auch der Grund, warum dieses Material einen sehr geringen Biogasertrag aufweist. Dieser ist mit 15-25 m^3/t FM und einem CH_4-Gehalt von 55 % deutlich geringer als der von Mais oder Grassilage (Mais 210 Nm^3/t FM, Grassilage 180 Nm^3/t FM) [24]. Auch Liew et al. [25] berichten, dass Laub eine geringe Biogasausbeute aufweist (55.4 l_N/Kg FM). Wenn das Laub aber durch IFBB-Verfahren (Integrierte Festbrennstoff und Biogasproduktion aus Biomasse) verarbeitet wird, kann der Biogasertrag bezogen auf die organische Trockenmasse im Presssaft nur bis 172 l_N/Kg erhöht werden [26]. Obwohl das Laub für die Biogasgewinnung wenig Bedeutung hat, ist es bedingt durch den hohen Ligningehalt für die Festbrennstofferzeugung interessant [27, 28, 29]. Qualitätsuntersuchungen des Brennwertes ergaben, dass der Presskuchen des Laubes dieses Materials etwa 19.0 MJ/Kg TM aufweist [19, 20].

Die veröffentlichten Daten zur jährlichen Laubmenge der Reinigungsdienste der Städte ermöglicht eine grobe Vorstellung hinsichtlich des Potenzials dieses Materials. Auf Nachfrage bei lokalen und regionalen Behörden in 50 Klein- und Großstädten nach dem jährlichen Laubvorkommen, konnte festgestellt werden, dass in den Großstädten München und Hamburg das jährlich anfallende Laub zwischen 10.000 und 15.000 t betragen kann, was je nach Qualität in einem Heizkraftwerk verbrannt, oder auf einer Kompostanlage verarbeitet wird. Die über den Garten- und Landschaftsbau und die Stadtreinigungsdienste gesammelte Laubmenge kann in einer Großstadt wie Berlin auf bis zu 96.000 t ansteigen [24]. Städte wie Köln, Frankfurt, Stuttgart, Dortmund, Essen, Leipzig, Bremen und Kassel weisen nach Angaben der jeweiligen Stadtreinigungsdienste jährlich etwa 4.000 bis 6.000 t Laub auf In Düsseldorf, Dresden, Hannover, Nürnberg, Münster und Karlsruhe werden etwa 1.000 bis 2.000 t diese Art von Biomasse pro Jahr beseitigt. Städte mit weniger als 100.000 Einwohnern erfassen diesen Abfall nicht getrennt, dort ist er in den Erfassungsmengen von Grünschnitt enthalten. Die Menge an Laub in den kleineren Städten und Kommunen scheint für eine zusätzliche Infrastruktur für Laubbeseitigung (Lauberntemaschinen, Laubtransport, Lager und Verarbeitungsanlage) nicht ausreichend zu sein. Jedoch lässt die Menge dieses Materials Kommunen bzw. öffentlich-rechtliche Entsorgungsträger Verwertungsmaßnahmen ergreifen. So kann das Laub auch nach Angaben einzelner Städtischer Reinigungsdienste zur Beseitigung mit hohen Kosten in Verbrennungsanlagen geliefert werden [24, 30].

Bei der Verwertung des Laubes ist allerdings darauf zu achten, in welcher Form es vor Ort vorhanden ist. Das Laub, welches über Saugmaschinen von den Straßen, Grünstreifen entlang der Straßen und aus den Haushalten über Laubsäcke mit Sorgfalt gesammelt wird, enthält theoretisch lediglich geringe Störstoffanteile und kann als biologisch abbaubare Garten- und Parkabfälle (ASN 200201, AVV) [31] eingestuft werden. Daher reicht bei der Verarbeitung eine optische Kontrolle und einfache Sortierung aus. Das Laub kommt im Herbst auch im Kehricht mit anderen Siedlungsabfällen (ASN, Kapitel 20, AVV) [31] gemischt vor. Aus technischer Sicht ist es möglich, den Laubanteil aus dem gesamten Straßenkehricht (ASN 200303, AVV) [31] zu entnehmen, dies wird aber vermutlich wegen des kostenintensiven Verfahrens nicht durchgeführt. Martin et al. [32] berichtet, dass das Kehrichtlaub durch Glas, Metall, Plastik, Steine und andere Störstoffe belastet sein kann, aber der Verschmutzungsgrad des Sauglaubs ist unbekannt.

Die Brennstoffeigenschaften des Laubes werden unter anderem durch den Aschegehalt beeinflusst. Je geringer der Aschegehalt desto höher der Brennwert. Die schädlichen Inhaltstoffe (Schwermetalle, Mineralstoffe) dürfen gesetzliche Grenzwerte nicht überstreiten. In Abhängigkeit der Nutzung des Brennstoffs aus biologisch abbaubaren Materialien, können die Qualitätsstandards strenger oder lockerer sein. Findet die Verfeuerung des Festbrennstoffs in den privaten Haushalten (Kamin, Ofen und automatisierte Feuerungsanlagen) statt, müssen erhöhte Emmissionsstandards erfüllt werden [33]. Ist der Brennstoff dagegen im industriellen Bereich im Einsatz, kann eine höhere Konzentration an Schadstoffen geduldet werden [34]. Die Richt- und Grenzwerte der Mineralstoffe (Ca, Cl, K, Mg, N, Na, P, S) und Schwermetalle (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) des festen Brennstoffs aus Biomasse sind in wissenschaftlichen Artikeln und Normen festgelegt [35, 36, 37]. Neben den Mineralstoffen und Spurenelementen werden der K_2O/CaO-Index (Schlacke-Bildungsrisiko-Index) [38] und der 2S/Cl-Index (Korrosion-Bildungsrisiko-Index) in der Qualitätsbestimmung berücksichtigt [39].

1.4 Ziele der Arbeit

Das städtische Laub stellt in Großstädten ein Nutzungspotenzial dar. Wenn dieses Material in eine Form (Pellet, Brikett) gepresst wird, lässt es sich leicht lagern, transportieren und sowohl industriell, als auch privat im Haushalt verwenden. Wenn die örtlich-rechtlichen Entsorgungsträger anstreben, die in ihrer Einsatzregion anfallenden biologisch abbaubaren Reststoffe möglichst vollständig energetisch zu verwerten, kann Laub eine Energielücke füllen. Da dieses Material aufgrund politischen Desinteresses im besten Fall kompostiert und im schlimmsten auf einem Sammelplatz offen gelagert wurde, wird das Material bislang nicht als potenzieller Energieträger wahrgenommen. Nicht nur das, sondern auch die Störstoffbelastung, die während der Ernte zustande kommt, sorgte dafür, dass diese Biomasse bisher unberücksichtigt blieb. Jedoch stellt die Biogaskrise die Energiewirtschaft vor die Herausforderung, die biologisch abbaubaren Reststoffe vollständig zu nutzen, weshalb das Laubmaterial wegen seines hohen Vorkommens in deutschen Großstädten eine Bedeutung für die Energieerzeuger haben könnte.

Übergeordnetes Ziel dieser Arbeit war, den Verschmutzungsgrad des Laubs zu bestimmen und seine Tauglichkeit als Festbrennstoff zu untersuchen. Um diese Parameter zu bestimmen wurden folgende Tests mit Stadtlaub durchgeführt:

1. Wirkung des typischen IFBB-Verfahrens (Integrierte Festbrennstoff und Biogasproduktion aus Biomasse) (Konditionierung bei 40°C für 15 Minuten und mechanische Entwässerung) und des Waschens (bei 10-12°C für 5 Minuten) auf die Aschegehaltreduktion: Hierbei wurde städtisches Laub, welche aus drei Stadtteilen stammt und mit zwei Sammelverfahren geerntet wurde, vor dem Waschen (Ausgangsmaterial), nach dem Waschen (gewaschenes Laub) und nach dem Pressen (Presskuchen) auf ihren Aschegehalt untersucht.

2. Mineralstoffinhalte des Materials und Effekt des Waschens: Alle Materialien (Ausgangsmaterial, gewaschenes Material und Presskuchen) wurden auf ihre Mineralstoffgehalte (Ca, Cl, K, Mg, Na, P, S) untersucht.

3. Spurenelemente und Polyzyklische Aromatische Kohlenstoffe des städtischen Laubs: Spurenelemente (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) und PAK (16 Stoffe) wurden in allen Materialien untersucht. Die Ergebnisse dieser Untersuchung umfassen auch den Einfluss der Waschanlage auf die Reduktion der Schwermetalle.

4. Bestimmung der Energiegehalte der Materialien, der Ascheschmelztemperatur und der Schlackebildungsindizes: Diese Kennzahlen wurden über die CHNO-Gehalte des Materials ermittelt.

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2. Chemical Properties and Ash Slagging Characteristics of Solid Fuel from Urban Leaf Litter

2.1 Abstract

Urban leaf litter occurs in significant, yet unknown, quantities and is regularly disposed of or composted. Instead, it could be widely used as a regional resource for solid fuel production. Samples of five tree genera (*Acer, Aesculus, Fagus, Tilia, Quercus*) were taken after leaf abscission and analyzed for elemental composition (C, H, N, S, Ca, Cl, Cu, K, Mg, Mn, Na, P, Zn) and ash slagging behavior. Ash content was generally high (13.8 % dry matter) due to soil adherence. Mashing and subsequent mechanical separation significantly reduced concentrations of Cl, K and S in the resulting press cake, resulting in concentrations of 0.01, 0.36 and 0.07 % dry matter respectively (mass flow into press cake: 25.6, 51.54 and 73.83 %, respectively). Average lower heating value of the press cake was 19.22 MJ kg^{-1} dry matter (ash free). Processing elevated the mean ash softening temperature from 1233 °C for raw materials to 1245 °C for press cakes. However, processing did not alter ash content, which indicates that additional washing is necessary for a further increase in fuel quality.

2.2 Introduction

Trees are an essential element of cityscapes as they offer environmental services and enhance the attractiveness of cities [1]. However, they are also an increasing burden to city administrations, which have to dispose of the autumn foliage. The disposal is not only cost-intensive but also an organizational challenge, as the EU legislation considers urban foliage to be waste once it is collected and, therefore, the waste hierarchy shall be applied, which defines actions to be taken in descending order of priority: prevention, preparing for re-use, recycling, other recovery, disposal. For bio-waste, composting (as recycling) and digestion (as other recovery), are particularly considered to be suitable (Directive 2008/98/EC, Articles 4, 22). However, it is further stated that it might be justified for biodegradable waste to depart from the waste management hierarchy in specific cases ‘‘as the environmental balance of the various options available for the management of this waste depends on a number of local factors’’ [2]. On the one hand, one essential local factor might be the increasing demand for renewable energy (e.g. solid fuels). On the other hand, the global warming potential of compost production from organic waste is significantly higher than the global warming potential attributed to its incineration [3]. Also, specific urban biomasses (e.g. leaf litter) are difficult to handle with the conventional anaerobic digestion technique due to low methane yields [4] and abrasion during wet fermentation, which can occur because of soil adhesion [5]. Alternatively, combustion of urban biomass may be suitable, as thermal treatment of waste is considered to be a reasonable part of an integrated waste management system when life-cycle thinking is considered [6].

Leaf litter is usually collected by municipalities for composting, burial or direct incineration [7]. Alternatively, the leaf litter waste stream could be redirected to convert leaf litter into a high-quality solid fuel. In contrast to incineration in a commercial waste treatment plant, which needs to be paid to accept waste, this would offer two main advantages to municipalities: leaf litter is converted from waste into a product, which could be sold and thereby possibly balance the costs for leaf litter removal; and autonomous energy is provided for local demand. The fuel could be burned in decentralized biomass boilers, in buildings, which might not be connected to district heating. This would require that the fuel characteristics of leaf litter are close to those of commonly used fuels, for which wood is used as reference in this study.

Due to comparatively high fiber content (e.g. lignin 23.1 % dry matter (DM) [4]), leaves are considered suitable for combustion, but research is limited. There are some studies focusing on leaf residues from logging or agricultural activities. Zamorano et al. [8] have investigated characteristics of pellets produced from leaf litter of olive trees and found higher ash and nitrogen concentrations (12.34 % DM, 1.09 % DM, respectively) than in lopping residues of almond trees, black poplars or holm oaks, and a higher heating value (HHV) of 18.58 MJ kg^{-1} DM. In fresh *Eucalyptus gunnii* leaves a higher heating value of 17.6 MJ kg^{-1} DM was found [9].

Heckman and Kluchinski [10] studied the chemical composition of urban leaf litter to evaluate its applicability to farm land. They highlighted the influence of the collecting technique on the elemental composition of leaves, as higher concentrations of Al were found in machinery-collected material. They considered higher concentrations of Al to be an indicator for contamination with urban soil, which can be a source of heavy metals (esp. Pb and Cd), and also a severe abrasive of machinery. Additionally, the elemental composition of biomass is highly variable depending on species, type of plant tissue, stage of growth and growing conditions [11]. In particular, alkali and alkaline earth metals, in combination with silica and chlorine, cause detrimental effects during combustion [11]. For example, Cl and S may cause corrosion and K lowers the ash melting temperature [11, 12]. Additionally, high S concentrations ([0.2 % DM) lead to elevated SO_x emissions and NO_x emissions regularly increase with fuel N content [12]. High Cl concentrations may cause the formation of potentially toxic polychlorinated dibenzo-p-dioxins (PCCD) and polychlorinated dibenzofurans (PCDF) [12].

Wood is usually used as a biomass reference with optimum combustion properties. Studies comparing fuel properties from municipal leaf litter with wood are lacking, but deeper insight into the element composition of leaf litter is given by forest science literature or studies on municipal leaf litter for purposes other than energy recovery. Leaves contain higher concentrations of several minerals, which are detrimental to combustion, than wood [10, 13, 14]. For further evaluation of the suitability of a certain biomass for combustion, the quotient of certain elements is crucial as it affects the ash melting behavior. In literature, there exists a variety of indices to estimate the slagging tendencies of solid fuels [15]. We used the quotient of K_2O and CaO, as a high ratio was shown to be strongly associated with low ash melting points [16].

To reduce the mineral concentration in the fuel and, thus, to diminish the risk of corrosion, slagging and harmful emissions, the integrated generation of solid fuel and biogas from biomass (IFBB) technique was suggested [17]. Its core procedure is the mashing (mixing with warm water) and subsequent mechanical dehydration of biomass. Thereby, a fiber-rich press cake and a press fluid are produced, in which the press fluid contains the main proportion of minerals. The feasibility of the technique is well investigated for grass of different origins including seminatural material and mixtures of semi-natural with urban biomass (e.g. lawn cut [15, 18]). Whether the IFBB technique might also be able to improve the quality of a solid fuel derived from leaf litter is unclear.

Some companies reserved legal rights for machinery configurations to produce pellets from leaf litter (e g. [19]) and some municipalities started burning leaf litter in non-waste incinerators [20] without any scientific evidence of its comprehensive suitability. Therefore, it is essential that a comprehensive study on characteristics relevant for combustion of leaf litter in biomass boilers is conducted to provide necessary information on the politically promoted utilization of municipal residues for energy recovery.

This paper aims to (1) assess the elemental composition of leaf litter from common urban park tree genera, (2) to determine the heating value of urban leaf litter, (3) to evaluate the ash melting temperature of ash from urban leaf litter and (4) to clarify the influence of the IFBB technique on the concentration of elements, the heating value and the ash melting behavior of urban leaf litter.

2.3 Material and Methods

2.3.1 Sampling and Processing

Samples from five different genera (*Acer, Aesculus, Fagus, Tilia, Quercus*) were taken in autumn 2012 from a park (‘‘Bergpark Wilhelmshöhe’’) within the city of Kassel, which is located in the state of Hesse (Germany). The park has an outreach of 240 ha and was constructed between 1696 and 1866. For each genus, three leaf litter samples of about 10 kg were collected beneath randomly selected trees. Shortly after sampling (2 days maximum) the leaf litter was processed applying the IFBB technique (Fig. 2.1 [17, 18]). Therefore, biomass was mashed with a leaf litter-tap water ratio of 1–4 (based on fresh weight) for 15 min at 40°C. Afterwards, solid and liquid fractions were separated by a screw press (type AV, Anhydro Ltd) with a volume reduction in the ratio of 6:1 and a speed of 6 rotations per minute using a sieve with 1.5 mm hole size. The resulting press cake was dried and pressed into a solid fuel. For element and dry matter analysis, before and after the IFBB process, samples from parent material and press cake were dried at 65°C for chemical analysis, and another set of samples at 105°C for 48 h for dry matter determination. The resulting press fluid is not considered

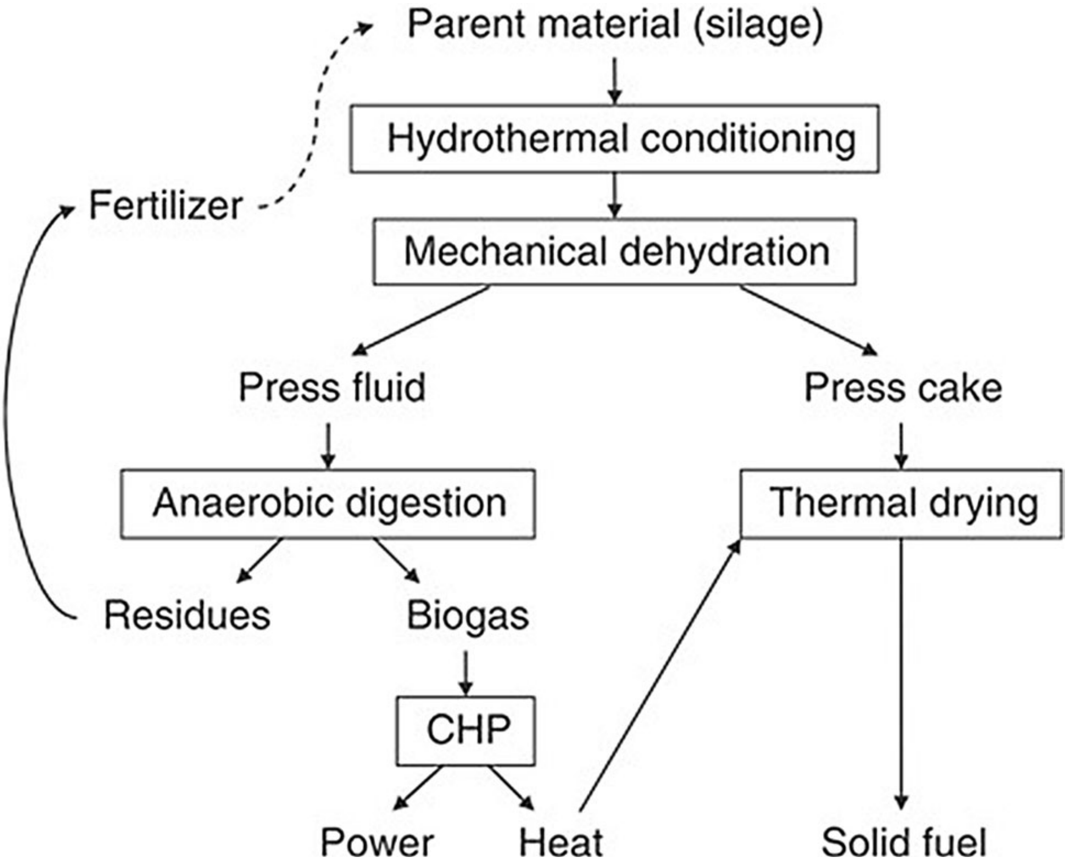

Fig. 2.1 *Flow chart of the integrated generation of solid fuel and biogas from biomass technique (taken from Wachendorf et al. [17]). CHP abbreviates combined heat and power plant.*

in this study as the recoverable energy from the fluid is < 20 % of the energy recoverable from the silage in case of direct combustion [21].

2.3.2 Elemental Composition

Samples of both raw material and press cake were grinded with a cutting mill (SM 1, Retsch) to pass through a 5 mm sieve and subsequently to 1 mm size with a sample mill (1093 Cyclotec, Foss). The concentrations of C, H and N were measured with an elemental analyzer (Vario MAX CHN Elementar Analysensysteme GmbH). Concentrations of Ca, Cl, Cu, K, Mg, Mn, Na, P, S and Zn were analyzed with X-ray fluorescence spectroscopy. Ash content was determined by incineration of a subsample dried at 105°C in a muffle furnace at 550 °C.

2.3.3 Mass Flow

Mass flows (MF) of elements from the raw material into the press cake were calculated according to the formula:

$$MF = \frac{mass_{presscake} \times DM_{presscake} \times concentration\ of\ X_{presscake}\ DM}{mass_{rawmaterial} \times DM_{rawmaterial} \times concentration\ of\ X_{rawmaterial}\ DM} \times 100$$

where X is the measured element.

2.3.4 Heating Value

The higher heating value (HHV) was calculated from C, H and N according to the formula [22]:

$$HHV\left[\frac{MJ}{kgDM}\right] = 3.55C^2 - 232C - 2230H - 51.2C \times H + 131N + 20.600$$

From the HHV the lower heating value (LHV) was calculated taking the enthalpy of water vaporisation into account:

$$LHV\left[\frac{MJ}{kgDM}\right] = HHV - \left(8.937 \times \frac{H\%DM}{100}\right) \times 2.2$$

2.3.5 Ash Melting Behavior and Slagging Indices

For determining the ash melting behavior, subsamples of 100 g were incinerated in a muffle furnace at 550°C. Subsequently, the material was annealed for 1 h at 700°C for full incineration. Cylindrical test pieces of 3 mm diameter and 3 mm height were taken from the ash produced, then pressed and investigated with a hot stage microscope (Hesse Instruments EM-201) according to the German institute for standardization (DIN 51730). Pictures taken with a CCD-Camera were analyzed by image analysis software to determine the ash melting temperatures: softening, spherical, hemispherical and flowing. During the ash melting trial the temperature within the microscope was increased by 10 K/min and a picture was taken every minute. If the software was unable to identify the form of the cylinder, temperatures were determined visually, based on the pictures. Frequently, spherical and hemispherical temperatures could not be clearly differentiated neither automatically nor visually. Therefore, in this paper only the softening and flowing temperatures are presented, which could be clearly identified in all cases.

The slagging index K/Ca was calculated as the ratio K_2O/CaO, according to Bühle et al. [15], based on the corresponding element concentrations in the fuel.

2.3.6 Statistics

Differences between raw material and press cake, considering element concentrations, ash softening and ash flowing temperatures, and heating values were detected by Kruskal–Wallis test applying R [23] without differentiation in genera, as data were not normally distributed. For testing differences between genera Kruskal–Wallis test was used with the post hoc function ‘‘kruscalmc’’ [24]. Linear regression analysis was conducted to determine the relationship of element concentrations in the raw material and in the press cake. Multiple linear regression analysis was used to determine the influence of elements on the ash melting behavior. To detect multicollinearity the variance inflation factor was used.

2.4 Result and Discussion

2.4.1 Elemental Composition of the Raw Material

Major (Ca, Cl, K, Mg, N, Na, P, S) and minor (Cu, Mn, Zn) elements were detected in the biomass. Many element concentrations in the leaf litter were at an intermediate level compared to wood and herbaceous material (Table 2.1). K concentrations in the raw material were rather high (0.62 % DM on average) compared to literature values from leaf litter. Nevertheless, they fell below the high concentrations of herbaceous material (about 75 % lower). Concentrations of S (0.08 % DM) and P (0.14 % DM) in the raw material were below concentrations which were found in herbaceous material and which could, in case of S, be detrimental to combustion processes or cause relevant quantities of SO_x emissions [12]. Concentrations of N (0.83 % DM) and Na (0.03 % DM) in the raw material fell below concentrations known from herbaceous material. However, concentrations of S, P, N and Na did not reach wood-like levels and N concentrations exceeded the guiding value for unproblematic combustions (<0.6 % DM) [12]. Cl concentration in leaf litter was close to the concentration in wood, while for Ca, Mg and trace elements, concentrations exceeded the corresponding values for herbaceous material. Ca (2.17 %) and Mg (0.3 % DM) concentrations in the raw material were higher than concentrations found in former studies on leaf litter, herbaceous material or wood. Cu, Mn and Zn concentrations fell in or below the range of concentrations that have been found for leaf litter of an unmanaged forest.

In autumn, macromolecules are degraded before leaves fall and minerals are partly re-translocated into the bark during the process of leaf senescence [25, 26]. Tyler [14] found decreasing K, Mg, Na, P and S concentrations from July to November, whereas those of Ca increased. This might explain the higher Ca concentrations and reduced N, Na, P and S concentrations in leaf litter compared to herbaceous material. Increasing Ca concentrations were also observed by Lin and Wang [27] for three mangrove species. Contrary to the finding of Tyler [14] for beech leaves; Cl, Na and Mg concentrations were also increased. Investigations on tree species in Lithuania found decreased amounts of N, K, P and S per unit leaf area in senesced leaves, though Ca and Mg contents did not change, with the exception of Ash (*Fraxinus excelsior*) leaves [25]. Thus, some variance in element concentration in leaf litter has to be expected dependent on species, but also on various other factors, e.g. soil fertility [25].

Concentrations of various elements varied among genera in the present study (Table 2.2). *Tilia* tended to contain comparatively high concentrations of Ca, Cl, Mg, N, S and Mn (deviation from mean in %: +24, +50, +42, +24, +34, +80, respectively), and for *Acer*, high levels of Cl, K and P (deviation from mean in %: +86, +80, +31, respectively) were detected. In contrast, concentrations of most elements were close to average values for *Aesculus*, *Fagus* and *Quercus*. In cities a multitude of tree species are planted, however, few species are regularly chosen for street trees with *Tilia* and *Quercus* among the most popular ones [28]. Only detailed investigations on leaf litter samples from municipal cleaning services will clarify the actual composition of the material, which might, inter alia, depend on locality (e.g. park, street, garden) and time of sampling (beginning of autumn, end of autumn).

2.4.2 Effect of IFBB Procedure on Solid Fuel Characteristics

Applying the IFBB procedure reduced the concentration of Cl in the biomass, resulting in a concentration of 0.01 % DM in the press cake, which is close to concentrations known from coniferous wood (Table 2.1). Likewise, the comparatively low concentrations of P and S were further and significantly diminished. The mean concentrations of K and Mg were also reduced significantly with a relative reduction of 42 and 10 %, respectively. However, concentrations of other elements were not reduced significantly. The concentration of Ca, for example, stayed at a relatively high level, which exceeds even the concentration in herbaceous material. As Ca is known to increase the ash melting temperature its continuance in the press cake is favorable [12]. Less favorable is the relatively high mass flow of N into the press cake resulting in a mean N concentration of 0.8 % DM, which still exceeds the guiding value for an unproblematic combustion (<0.6 % DM) [12]. However, advanced boiler technique can solve this problem by adapted partial pressure of O_2 (air staging) and temperature adjustment [29]. Minor elements were not influenced by the IFBB treatment; concentrations were already within ranges, which do not give rise for concern. Mn concentrations were considerably below those found for litter of an unmanaged forest (Table 2.1) and Cu and Zn concentrations fell below the limiting value of a DIN specifying non-woody pellets for non-industrial use (limiting values for Cu 20 mg kg^{-1} DM, for Zn 100 mg kg^{-1} DM [30]). Element concentrations in the PC could be reliably predicted by linear regression from the corresponding concentrations in the raw material (Table 2.1). Regressions were significant throughout and R^2 adj. was at least 0.8 in general. Lower R^2 adj. values were only calculated for Cu, with 0.71, and Cl, with 0.42. The relatively low R2 adj. for Cl might be caused by the strong tendency of Cl to leach into the press fluid.

Despite partly significant differences in element concentrations between raw material and press cake, mass flows of minerals into the press cake were higher than those detected in former studies on grass [18]. Smallest mass flows (Table 2.2) were found for Cl (25.62 ± 9.39 %) and K (51.54 ± 9.79 %) in accordance with Hensgen et al. [18], who observed mass flows of 1 % of Cl and 19 % of K. However, as mass flows of minerals into the press cake were comparatively high, the mass flow of dry matter was likewise (86.02 ± 9.19 %). Thus, a high proportion of fibers could be transferred into the solid fuel.

In summary, it must be clearly stated, that the IFBB procedure does not have the same overarching mineral elutriation effect in treating leaf litter compared to studies on grassland biomass (e.g. [18]). However, it substantially reduces two of the most detrimental elements (Cl and K) resulting in an improved quality of press cake for combustion.

Table 2.1 *Mean concentrations of Ca, Cl, K, Mg, N, Na, P, S, Cu, Mn and Zn in raw material (RM) and press cake (PC) as well as combustion relevant data of municipal leaf litter of five tree genera in comparison to literature values.*

	Mean		Linear regr. Model conc$_{RM}$ versus conc$_{PC}$		Literature values				
	RM	PC	R^2 adj. If sig.	Slope	Leaf litter of unman. forest [a]	Municipal leaf litter (mach. coll.)[b]	Municipal leaf litter (hand coll.)[b]	Coniferous wood[c]	Herbaceous material[c]
Ca (%)	2.17	2.13	0.95	0.81	0.87	1.64	1.80	0.09	0.35
Cl (%)	0.05	0.01***	0.42	0.19	-	0.13	0.28	0.01	0.75
K (%)	0.62	0.36**	0.92	0.42	0.25	0.38	0.48	0.04	1.50
Mg (%)	0.30	0.27*	0.95	0.88	0.12	0.24	0.25	0.02	0.17
N (%)	0.83	0.80	0.96	0.84	-	1.00	0.78	0.10	1.30
Na (%)	0.03	0.03	0.80	0.70	0.01	0.01	0.01	0.002	0.10
P (%)	0.14	0.11**	0.88	0.70	0.07	0.11	0.11	0.006	0.30
S (%)	0.08	0.07*	0.93	0.87	0.08	9.20	0.12	0.02	0.19
Cu (mg kg^{-1})	6.80	7.45	0.71	1.10	6.30	550.00	5.00	2.00	5.00
Mn (mg kg^{-1})	151.94	136.53	0.98	0.90	1850.00	81.00	820.00	-	-
Zn (mg kg^{-1})	28.65	26.97	0.98	1.01	36.00	23.83	56.00	10.00	25.00
Ash (%)	13.80	12.06	n.d.	n.d.	5.28	-	-	0.30	7.00
LHV (MJ kg $^{-1}$)	16.12	16.49						18.8[d]	17.5[e]
Ash softwning temperature (°C)	1233.00	1245						1426[d]	1100[e]
Index K2O/CaO	0.25	0.15**							

Results of linear regression (concentration of each element in RM versus concentration in PC) are presented. All values refer to DM if not otherwise indicated
n.d. not determined, LHV lower heating value
*Levels of significance: * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$*
[a] [14]; [b] [10]; [c] [12], if data were given ash free, the concentrations including ash were calculated and are presented in this table; [d] [33]; [e] [21]

Table 2.2 *Mean concentration of Ca, Cl, K, Mg, N, Na, P, S, Cu, Mn, Zn and ash in % DM, as well as DM in % fresh matter in the raw material (RM) and the press cake (PC) of municipal leaf litter of five tree genera and mass flows into press cake in % of content in the raw material ± standard deviation.*

	Acer		Aesculus		Fagus		Quercus		Tilia		Mass flow into PC
	RM	PC	RM	PC	RM	PC	RM	PC	RM	PC	
Ca (%)	2.06	2.21	3.06	2.76	1.68	1.65	1.37	1.42	2.68	2.62	85.51 ± 10.47
Cl (%)	0.09	0.01	0.03	0.01	0.02	0.01	0.03	0.01	0.07	0.03	25.62 ± 9.39
K (%)	1.12	0.56	0.62	0.35	0.33	0.19	0.47	0.33	0.58	0.37	51.54 ± 9.79
Mg (%)	0.28	0.24	0.28	0.25	0.28	0.26	0.24	0.20	0.43	0.38	75.62 ± 8.90
N (%)	0.76	0.72	0.78	0.76	0.71	0.66	0.80	0.79	1.12	1.07	82.77 ± 9.82
Na (%)	0.04	0.03	0.03	0.03	0.01	0.01	0.03	0.02	0.05	0.05	77.62 ± 18.15
P (%)	0.19	0.14	0.12	0.10	0.10	0.08	0.15	0.10	0.16	0.13	64.85 ± 8.01
S (%)	0.09	0.07	0.08	0.07	0.06	0.05	0.07	0.06	0.11	0.10	73.83 ± 9.89
Cu (mg kg^{-1})	7.17	6.90	7.53	8.70	5.83	6.33	8.67	9.97	4.80	5.33	93.57 ± 10.66
Mn (mg kg^{-1})	128.00	116.00	87.20	74.30	81.17	73.70	190.67	172.33	272.67	246.33	77.65 ± 11.67
Zn (mg kg^{-1})	26.63	24.17	18.60	16.50	24.90	23.83	39.33	37.50	33.77	32.83	80.65 ± 10.22
DM (% FM)	33.62	40.66	26.04	39.32	26.95	45.43	31.32	42.91	30.09	31.77	86.02 ± 9.19
Ash (%)	19.04	19.02	14.60	12.70	6.70	6.70	9.40	6.70	18.90	15.00	76.77 ± 17.01

2.4.3 Ash Content

Mean ash content was 13.8 % DM in the raw material and 12.06 % DM in the press cake (Table 2.1). This is considerably more than in wood (<1 % DM) or even in herbaceous material (about 7 % DM [12]). However, the mass of oxides calculated from inorganics measured in the raw material is about 4.7 % DM. Adding an approximate value of 2.35 % DM for SiO_2 (1.1 % Si in beech leaf litter DM [13]), we can assume an actual ash content of leaf litter of about 7.05 % DM. This is higher than reported by Tyler [14] and Jörgensen et al. [13], who found 5.28 % DM and 3.63 % DM in beech leaf litter, respectively. However, Jörgensen et al. [13] detected a Ca concentration of 0.6 % DM, which is much lower than values measured in this study. Thus, assuming a comparatively high ash content of about 7.05 % DM from inorganic elements, another 6.75 % DM have to be of other origin. It is very likely that these 6.75 % DM arise from soil adherence as already found by Heckman and Kluchinski [10]. This might also explain the large differences in ash content between tree genera found in our study (Table 2.2). Taking comparatively ‘‘clean’’ samples of leaf litter from *Fagus* (ash content: 6.7 % DM) was possible, as an underlying layer of the previous year’s leaf litter avoided soil contamination of the sampled material, whereas leaf litter of *Acer* was sampled from bare soil surface (ash content: 19.4 % DM). Soil particles are not beneficial in the combustion process but cause high abrasion of the machinery and increase the maintenance effort. Additionally, Si is an abundant element in soils and lowers the ash melting temperature, thus disturbing the combustion process [12, 31]. Therefore, a cleaning step to separate soil particles from the biomass will be essential to make this resource usable. This applies in particular to leaf litter collected by municipal machinery [10].

2.4.4 Higher and Lower Heating Value

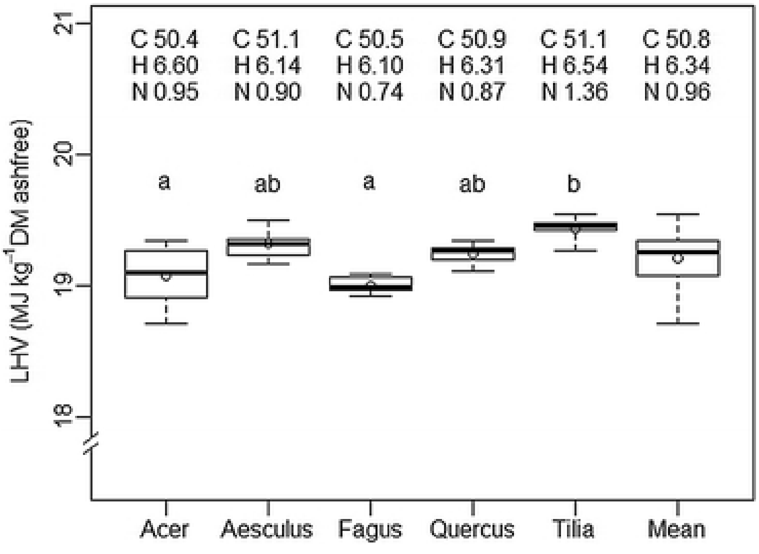

Fig. 2.2 *Concentrations of carbon$_{af}$, hydrogen$_{af}$ and nitrogen$_{af}$, as well as lower heating value$_{af}$ (LHV$_{af}$) in municipal leaf litter of five genera referring to DM ash free (af). LHVs$_{af}$ for raw material and press cake are not separated as they did not differ significantly. Different letters indicate significant differences between genera. Whiskers indicate minimum and maximum values. Circles represent means.*

Both the higher (HHV) and the lower heating value (LHV) of press cake exceeded the corresponding value in the raw material by approximately 0.4 MJ kg^{-1} DM, resulting in a mean LHV of 16.49 MJ kg^{-1} DM and HHV of 17.57 MJ kg^{-1} DM. As the heating value depends on the ash content and the ash content of collected leaf litter in turn highly depends on soil adherence, heating values are additionally presented for ash free (af) DM to allow comparisons among species and to give an outlook of the potential energy content of cleaned leaf litter (Fig. 2.2). Differences in heating value between raw material and press cake (0.1 MJ kg^{-1} DM$_{af}$) were not significant both for LHV$_{af}$ and HHV$_{af}$, therefore, only mean values over species are given. LHV$_{af}$ ranged between 18.71 and 19.55 MJ kg^{-1} DM$_{af}$ with an overall mean value of 19.22 MJ kg^{-1} DM$_{af}$. Highest LHV$_{af}$ were found for *Aesculus* (19.31 MJ kg^{-1} DM$_{af}$) and *Tilia* (19.44 MJ kg^{-1} DM$_{af}$) with a significant difference between *Tilia* and *Acer* (19.07 MJ kg^{-1} DM$_{af}$) and *Fagus* (19 MJ kg^{-1} DM$_{af}$). The high levels of LHVs$_{af}$ for *Aesculus* and *Tilia* corresponded with the C$_{af}$ concentrations (51.1 % DM$_{af}$), which were highest in these two species. Both species are commonly used as medical plants because of relatively high concentrations of compounds (e.g. essential oils, triterpene saponins [32]), which are rich in C and, thus, may lead to elevated C$_{af}$ concentrations. Furthermore, for *Tilia*, an outstanding high N$_{af}$ value was detected (significantly higher than N$_{af}$ concentrations in *Fagus* and *Quercus*). Therefore, LHV of leaf litter is potentially close to that of coniferous wood (18.8 MJ kg^{-1} DM [33]), provided an appropriate cleaning step is applied.

2.4.5 Ash Melting Temperature

The mean ash softening temperature was 1233 °C in the raw material and 1245 °C in the press cake and was thereby between the ash softening temperatures of herbaceous material (1100 °C, Table 2.1 [21]) and coniferous wood (1426 °C [33]). Neither the softening nor the flowing temperature differed significantly between raw material and press cake. However, some variation between tree genera could be observed, with *Aesculus* and *Fagus* having higher ash softening temperatures (1256 and 1268 °C, respectively) than the other genera (lowest at 1218 °C of *Tilia* leaf litter ash, Fig. 2.3). Differences were not significant, though the K_2O/CaO-Index was smallest for these two genera (*Aesculus*: 0.14, *Fagus*: 0.13, although not significantly different from *Tilia* with

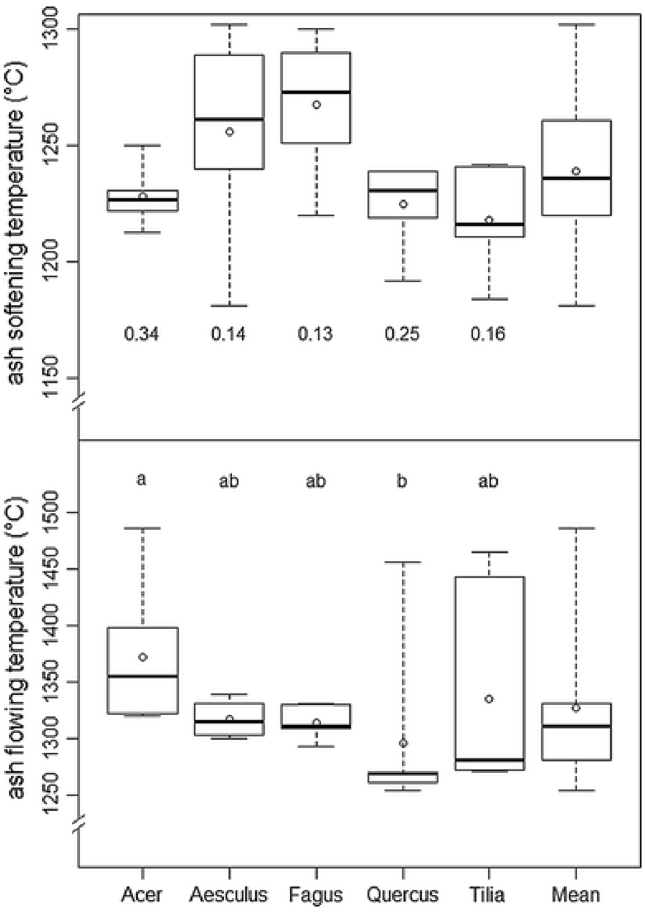

Figure 2.3 *Ash softening (top figure) and ash flowing temperatures (bottom figure) of municipal leaf litter from five tree genera. Data for raw material and press cake are not separated as they did not differ significantly. Different letters indicate significant differences between genera and are only displayed if significant differences were found. Whiskers indicate minimum and maximum values. Circles represent means. Numbers give values for* K_2O*/CaO-Index*

0.16). The ratio of K to Ca in the sample was shown to be a reliable predictor for the risk of slagging [34]. Due to the high Ca concentrations in leaf litter the index is considerably lower than that found for grass (IFBB treated and untreated [15]), indicating elevated ash softening temperatures.

The figures indicate that the intra-genera variance is high in general. Maximum value for ash flowing temperature was found for Acer with 1486 °C. The mean value for Acer was 1372 °C, which was significantly higher than the mean value of *Quercus* (1297 °C). It should also be noted that the temperature range of the ash softening temperature, 1181–1302 °C, is considerably smaller than the range of the ash flowing temperature (1254–1486 °C).

A linear regression model with elemental composition explaining the ash melting behavior could not be determined due to high multicollinearity. Additionally, the variance in ash softening and flowing temperatures might be predominantly explainable by the soil content, as the share of Si highly influences the ash melting behavior [31] and might mask the effect of other minerals. Nevertheless, the K_2O/CaO-Index could be decreased significantly and thereby the risk of slagging may be reduced (Table 2.1).

2.5 Focus of Further Research

The study showed that the IFBB treatment considerably improved the fuel quality in terms of Cl and K concentrations. However, this effect cannot be considered relevant if the overall ash content remains at a high level. For this reason, an additional washing step to decrease the ash content that is most likely caused by soil adherence is required. In other words, the effect of IFBB can only be exploited in concurrence with soil removal. This is particularly relevant to an economical point of view, as the price of the wood chip market is only reachable if the ash content is further reduced to produce a similar fuel quality. In summary, the development of a soil separation apparatus is crucial for the economically viable application of urban leaf litter in energy recovery.

To evaluate the potential contribution of urban leaf litter to meet energy requirements it would be necessary to determine the amount of available material. However, municipalities frequently do not record the amount of leaf litter, which occurs during autumn in their administrative districts. In many cases it is even not known how many trees are growing on the cities' areas, which might serve as a bridge to calculate the amount of leaf litter. Pauleit et al. [28] tried to close this knowledge gap by an extensive cross-European study using a questionnaire, which was completed by city administrations. It revealed that in most cities 50–80 street trees occur per 1000 inhabitants. However, due to the lack of information in city administrations it was not possible to ensure a consistent methodology. This inconsistency between urban forest inventories was also reported by Keller and Konijnendijk [35], who additionally found that the six interviewed cities focused on street trees and barely included park or private trees in their inventories. Thus, the actual number remains unclear.

However, there were surveys commissioned by single European municipalities to assess the amount of leaf litter or number of trees. In Berlin, for example, 17,000 t of leaf litter (fresh matter) per year can be expected [36]. In England 590 plots of 4 ha in 147 towns, including London, were chosen to get an overview on the urban tree population [37]. The report revealed that about 50 % of plots had 10–50 trees or shrubs per ha. Low-density residential areas provided the highest tree/shrub densities, which was not influenced by town size. Only 12 % of trees were actually growing alongside streets. The main deciduous species detected were *Crataegus spp*., *Acer pseudoplatanus, Betula pendula* and *Fraxinus excelsior.* Strohbach and Hasse [38] chose a remote sensing approach to determine the carbon storage capacity of urban trees in the city of Leipzig. The canopy cover was about 19 % of the city area. The authors sounded a note of caution to transfer values to other cities, which might differ in urban characteristics, e.g. population size or structure of urban forest. Therefore, future research should not only focus on technical advances in leaf litter treatment but also on developing a reliable method for assessing the urban leaf litter potential.

2.6 Conclusion

The elemental composition of urban leaf litter supports its utilization in combustion, as high Ca levels increase the ash softening temperature and Cl concentrations are close to those of wood. Concentrations of the detrimental elements K and S were lower than in herbaceous material and could be further reduced by the IFBB procedure. The heating value of leaf litter is potentially close to the heating value of wood, though this could not be confirmed due to high soil adherence. To eliminate problems caused by soil particles a washing step is essential to further improve characteristics of this promising material.

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3. High Quality Solid Fuel Production from Leaf Litter of Urban Street Trees

3.1 Abstract

Leaf litter is a growing concern for cities. Due to adherent dirt such biomass is rarely utilized nowadays but may constitute a renewable energy source for communities or private households. Leaf litter from main roads, residential areas and city centres collected by the vacuum technique or the sweeper technique was sampled and analysed for ash content and chemical composition. Ash content of leaf litter collected by the sweeping technique was higher (21.6%–40.1% dry matter, DM) than in material collected by the vacuum technique (12.0%–21.7% DM). Leaf litter from residential areas had the highest contamination (21.7%–40.1% DM), followed by main roads (20.8%–26.2% DM) and city centres (12.0%–21.6% DM). Ash content was reduced by up to 60% with a washing treatment and reached values comparable to those achieved by multiple manual rinsing, which was conducted as a reference treatment. The chemical composition of washed leaf litter could be further improved by mechanical dehydration treatment due to a reduction in harmful elements for combustion such as K, Cl, Mg and S. Heating value of leaf litter increased and the risk of corrosion and ash melting during combustion were reduced.

3.2 Introduction

Trees are an increasing burden to city administrations, which have to dispose the autumn foliage. The disposal is not only cost-intensive but also an organisational challenge, as the EU legislation considers urban leaf litter to be waste once it is collected. Therefore, the waste hierarchy shall be applied, which defines actions to be taken in descending order of priority: prevention, preparing for re-use, recycling, other recovery, and disposal. Leaf litter is usually collected by municipalities for composting, burial or direct incineration [1]. Evidence of leaf litter use for energy production is scarce, as methane yields are low with conventional anaerobic digestion techniques [2], and abrasion during wet fermentation may occur because of soil adhesion [3]. Though combustion of leaf litter may be an efficient conversion process, ash concentration is a known problem, whether it is natural or caused by contamination due to collection, transport or storage. While leaf litter collected in urban parks showed average ash concentration of 13.8% dry matter (DM) [4] and 17.5% DM [5], values can be as high as 34.8% DM when collected from street and pavement surfaces in practice [6]. Removal of ash after combustion is costly and the various ash fractions (bottom ash, cyclone fly-ash and filter fly ash constituting 60% 90%, 10%–35% and 2%–10%, respectively, according to Van Loo and Koppejan [7]) need to be deposited or processed because of their content of hazardous elements (e.g., heavy metals, organic contaminants). Furthermore, ash slagging may cause damage in boilers [8] and increasing ash concentrations reduce the gross calorific value of biomass [9]. According to German standards, ash concentrations in fuels may not exceed certain limiting values, i.e., 1.0%–3.0% for wood chips, 1.5%–

7.0% for wood pellets [10] and 4.0%–10.0% DM for pellets made from non-woody biomass to prevent impairment of combustion systems and the environment [11]. In addition to ash problems, several elements incorporated in non-woody biomass have severe negative effects if applied in the combustion process. It is mainly the higher proportions of potassium and magnesium in non-woody biomass that lead to problems of ash melting at lower temperatures, slagging and fouling, whereas the higher proportions of nitrogen and sulphur can lead to higher emissions (NO_x, SO_2), and the higher proportions of chlorine, sulphur and potassium lead to corrosion [12]. In addition, the relatively high ash concentration reduces the heating value of leaf litter.

Redirection of the present leaf litter waste stream to convert leaf litter into a high-quality solid fuel would be an appealing alternative. In contrast to incineration in a commercial waste treatment plant, which needs to be paid to accept waste, this would offer two main advantages to municipalities: leaf litter is converted from waste into a product, which could be sold and thereby reduce the costs for leaf litter removal; and autonomous energy is provided for local demand. The fuel could be burned in decentralised biomass boilers, e.g., in buildings, which might not be connected to district heating. This would require that the fuel characteristics of leaf litter are close to those of commonly used solid fuels and that they comply with the limiting values of the German regulations [11]. To reduce the mineral concentration in the fuel and to diminish the risk of corrosion and slagging, the IFBB (Integrated Generation of Solid Fuel and Biogas from Biomass) technique was suggested [13]. Its core procedure is mixing of biomass with warm water and subsequent mechanical dehydration. Thereby, a fibre-rich press cake and a press fluid are produced, the press fluid containing the main proportion of minerals. The feasibility of the technique is well investigated for grass of different origins including semi-natural material [14] and mixtures of semi-natural with urban biomass (e.g., lawn cut; [15]). First investigations with leaf litter showed that the effect of IFBB treatment on ash reduction was not as large as for grass material [4], so the authors considered introducing a washing step prior to dehydration to eliminate problems caused by soil particles adhering to leaf litter.

This paper aims to determine the effects of (i) provenience (main road, residential area, city centre); (ii) collecting techniques (road sweeper, vacuum device); (iii) washing (machine washing, manual washing) and (iv) mechanical dehydration on the ash and mineral concentration and the solid fuel quality in leaf litter, which was collected by the cleansing department of the city of Kassel through one full leaf litter fall period.

3.3 Material and Methods

3.3.1 Collection of Leaf Litter

Collection of leaf litter was conducted in collaboration with the cleansing department of the city of Kassel. The city of Kassel is located in the middle of Germany and has about 200,000 inhabitants and an area of 107 km^2. The leaf litter was collected from the ground in three city areas: (i) main roads

(MRs); (ii) residential areas (RAs) and (iii) city centres (CCs). Areas differed in cleaning cycles: main roads were cleaned weekly, residential areas biweekly and the city centre was cleaned every second day. Two common large-scale collection techniques were applied: (i) the vacuum technique (VT) and (ii) the sweeping technique (ST), which were both mounted on municipal cleaning vehicles. The vacuum technique is appropriate for sites, which cannot be swept (e.g., parks, small greens along sideways) and where leaf litter is initially gathered with leaf blowers and subsequently picked up by a suction unit. The sweeping technique is usually applied on compacted surfaces and leaf litter is picked up with a rotating brush after moisturising. Leaf litter collection took place every second week at a collection point on the same day from 8 October to 10 December 2014, resulting in a total of 24 samples (4 sampling dates x 3 proveniences x 2 collection techniques). Due to the different cleaning cycles in the city, the time of ground contact of the samples differed between the city areas. Caused by the different durations of ground contact and climatic conditions, visual assessment of contamination already showed contrasts between the samples (Figure 3.1a-d). To conserve the samples for processing at a later stage they were filled into 60 L airtight polyethylene barrels, where ensiling took place. Ensiling lasted for at least 12 weeks.

***Figure 3.1** Exemplary display of leaf litter material immediately after collection by two different techniques: the vacuum technique in (**a**) residential areas during a dry period and (**b**) on main roads during a wet period; and the sweeping technique in (**c**) residential areas and (**d**) in city centres, both during a wet period.*

3.3.2 Washing Facility

The washing facility used in the present study had measures of 100 cm x 100 cm x 60 cm (width x depth x height) with a sink in the lower part with a height of 40 cm (Figure 3.2a) as a sedimentation zone for dirt and waste that were removed after washing. Approximately 550 L of water were constantly swirled by pressing air through perforated pipes (7 pipes with 6 holes each with 4 mm diameter; Figure 3.2b) at the bottom of the tank using a side channel compressor (RICO Druckluftanlagenbau GmbH, Tönisvorst, Germany, 1.1 kW, intake pressure 1000 mbar, rotational speed 2900/min). A screen basket (98 cm x 98 cm x 45 cm, width x depth x height; Figure 3.2c) with a mesh size of 1.1 cm was inserted into the washing facility, where the ascending air bubbles (Figure 3.2d) broke up leaf litter clots and mobilized adhering dirt particles that sank through the sieve into the sedimentation area. The screen basket served to hold back leafy material, which could then be evacuated from the washing area.

Figure 3.2 *Foliage cleaning machine from the side (a); pipes and water outlet valve in the bottom (b); sieve basket (c) and in operation (d).*

3.3.3 Washing of Leaf Litter

After evacuating the material from the plastic barrels, leaf litter clots were manually broken up and waste material (i.e., bottles, plastics, stones, wood, etc.) was removed. Depending on water content and degree of contamination, approximately 3 to 10 kg leaf litter was used for washing. An additional sample of 400 g was taken for determination of dry matter and ash content and elemental composition. Machine washing was conducted for 5 min at a water temperature of 10 to 12 °C.

Three kilograms of leaf litter were used for manual washing, which was assumed to represent a completely purified material and, thus, to establish a point of reference to determine the effectiveness of the machine washing. This material was stored in a freezer at -18 °C for 12 weeks. After defrosting, samples were thoroughly mixed and consecutively rinsed in 4 plastic barrels filled with fresh water at room temperature.

3.3.4 Mechanical Dehydration

The washed material was further processed by mechanical separation with a screw press (type AV, Anhydro Ltd., Kassel, Germany). The conical screw had a pitch of 1:6 and a rotational speed of 6 revolutions/min^{-1}. The cylindrical screen encapsulating the screw had a perforation of 1.5 mm. The press fluid was discarded; the press cake was sampled for further analysis

3.3.5 Laboratory Analyses of Leaf Litter

Samples for dry matter analysis were taken from the raw material, manually washed and pressed material and dried at 105 °C in a drying oven for ash and DM determination. Samples were ground with a cutting mill (Retsch, Haan, Germany, Type SM-100, motor type: AEG 1.5 Kw, rotational speed 1400 revolutions min^{-1}) to pass a 4 mm sieve. Samples were incinerated in a muffle furnace at 550 °C to determine the ash content. A second set of samples was taken for elemental composition analysis and dried at 60 °C for 48 h. These samples were also ground to 4 mm with the same cutting mill and then further processed with sample mill (1093 Cyclotec, Foss GmbH, Hamburg, Germany) to 1 mm. C, H and N concentrations in samples were determined with an elemental analyser (Vario Max CHN Elementar Analysesysteme GmbH, Hanau, Germany,). Content of K, Na, Mg, Ca, Cl, S and P were determined by X-ray fluorescence analysis by an external laboratory (Landesbetrieb Landwirtschaft Hessen, Kassel, Germany).

3.3.6 Calculation Statistical Analysis

The higher heating value (HHV) was calculated based on the concentrations of C, H, and N [g/kg DM] using the Equation (1) for bio-fuels by Friedl et al. [16]:

$$HHV\,[MJ/kg-1\,DM] = 3.55\ x\ C2 - 232\ x\ C - 2230\ x\ H + 51.2\ x\ C\ x\ H + 131 + 20.600 \quad (1)$$

Ash softening temperature (AST) was calculated on the basis of the concentrations of Ca, Mg and K [g/kg^{-1} DM] according to the formula by Hartmann [17], as equation (2):

$$AST\,[C°] = 1172 - 5.39 \times K + 25.27 \times Ca - 78.84 \times Mg \quad (2)$$

3.3.7 Statistical Analysis

Statistical analyses were conducted applying the R software (Version 3.0.2., R Foundation for Statistical Computing, Vienna, Austria) [18]. Because the assumptions to conduct an analysis of variance (ANOVA) were not given, non-parametric alternatives had to be applied. The non-parametric Kruskal Wallis test with the post hoc function “kruskalmc” was used if more than three factor levels were given in order to determine significant differences in the ash content, mineral composition, higher heating value, ash softening temperature and indices among locations (main road, residential area, city centre) and materials (unwashed, machine washed, manually washed, press cake). A non-parametric Wilcoxon signed rank test was performed to test for significant differences in ash content, mineral composition, higher heating value, ash softening temperature and indices caused by collection techniques with two factor levels (the vacuum technique and the sweeper technique).

3.4 Result and Discussion

3.4.1 Chemical Composition and Fuel Properties of Leaf Litter

According to visual and olfactory assessment, the ensiling process of the material was successful.

As shown by Piepenschneider et al. [4], ensiling of leaf litter on a laboratory scale (30–60 L polyethylene barrels) is possible in principle, provided that adequate compaction, air-tight closure and storage under cool and dark conditions is applied. Mineral and ash concentration of the parent material over all collection techniques and proveniences differed widely, shown by high standard deviations (Table 3.1, Table A3.1). In comparison to leaves collected by hand in a park area of the city of Kassel [19], the measured values for S, Mg, Na, Cl and ash were considerably higher. This might be explained by a higher contamination with soil and dirt particles due to the location and technique of collection, especially in the case of Na and Cl by contamination due to salt application for de-icing streets in autumn and winter time. Clean forest leaf litter investigated by Tyler [20] in a southern Swedish natural beech forest undisturbed for at least 50 years, collected with nets above ground, showed lower values for all elements but still an inherent level of ash of 5.28% DM. The ash concentration and mineral composition in a high quality standard fuel such as beech wood is significantly lower, with total ash values around 0.5% DM. From the chemical composition of our samples and the literature values, we calculated two indices. The K_2O/CaO Index proposed by Bühle et al. [21] serves as a measure for the risk of ash melting at low temperature. The lower the index, the lower the risk of ash melting at low temperatures. Due to the relatively high concentrations of Ca in the autumn foliage, the risk of low ash melting temperatures is very low in all leaf fractions, even lower than in beech wood. Nevertheless, the complex topic of ash melting behaviour of biomass fuels cannot be precisely predicted with a simple index involving only Ca and K, as several studies have shown [21, 22]. Thus, further laboratory research is needed. The other index, the 2S/Cl ratio, assesses the risk of high-temperature corrosion. According to Sommersacher et al. [23] and Khalsa et al. [5], the value should be ≥4 for a minor risk of corrosion, or >8 in order to rule out any corrosion risk. While the literature value for beech wood is >4, values for leaves are below this threshold due to high Cl concentrations. Thus, corrosion is likely to appear if untreated leaves are combusted. High corrosion risk has also been reported for untreated leaf litter collected in an urban park area in the city of Munich [5].

***Table 3.1** Mineral and ash concentration (% dry matter) and two indices with relevance for ash melting behaviour (K_2O/CaO) and corrosion risk (2S/Cl) in leaves from different origins compared with beech wood.*

Element/Index	Unit	City leaves [1]	Park leaves[2]	Forest leaves[3]	Beech wood[4]
S	[% DM] [7]	0.15 ± 0.04	0.08	0.08	0.02
Ca	[% DM] [7]	2.87 ± 0.62	2.17	0.87	0.29
Mg	[% DM] [7]	0.54 ± 0.36	0.30	0.12	0.04
Na	[% DM] [7]	0.13 ± 0.12	0.03	0.01	-
P	[% DM] [7]	0.14 ± 0.04	0.14	0.07	0.04
K	[% DM] [7]	0.64 ± 0.16	0.62	0.25	0.15
Cl	[% DM] [7]	0.30 ± 0.25	0.05	-	0.01
Ash	[% DM] [7]	23.73 ± 10.55	13.80	5.28	0.5
K_2O/CaO[5]		0.192	0.246	5.28	0.45
2S/Cl[6]		1.10	3.55	-	5.54

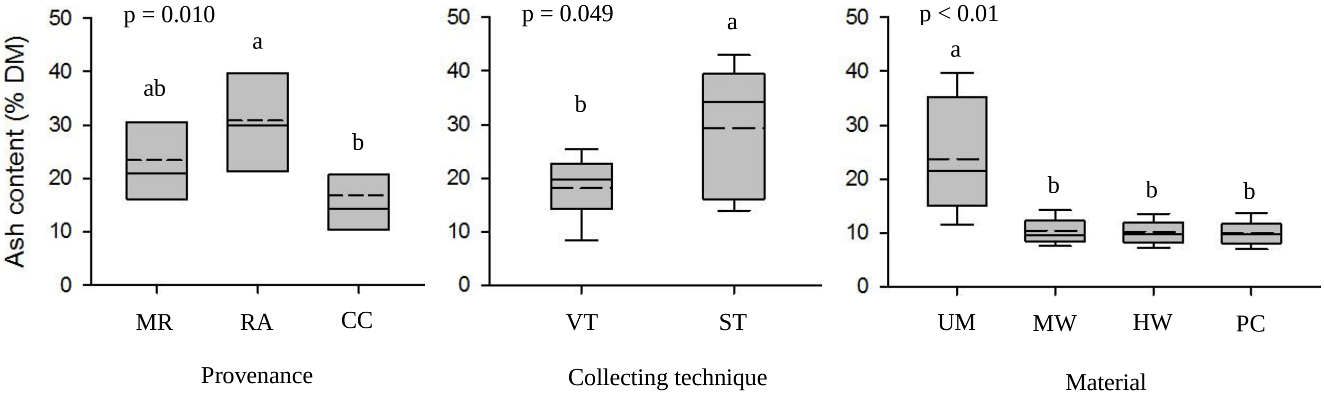
[1]Present study; [2] Piepenschneider et al. [4]; [3] Tyler [20]; [4] Hartmann [17]; [5] Slagging risk index calculated according to Bühle et al. [21]; [6] Corrosion risk index calculated according to Sommersacher et al. [23]. [7] DM: Dry matter.

Ash content in leaf litter originating from the city centre was lowest (16.8% of DM) and differed significantly from the residential area material (30.9% of DM) (Figure 3.3). Leaf litter from the main roads showed an ash content in between the other two proveniences (23.5% of DM). The collection technique also had a significant effect with a lower ash content for leaf litter collected with vacuum technique (18.2% of DM), while the use of a road sweeper increased ash content by an additional 10% of DM on average.

Machine and manual washing significantly reduced ash content by 13% of DM compared to the parent material, and both washing processes achieved similar values (10.4% and 10.2% of DM for machine and manual washing, respectively), showing that machine washing was as effective as hand washing. No further reduction of total ash could be achieved by mechanical dehydration of machine washed leaf litter (Figure 3.3). Ash content after washing was close to the threshold for solid fuels from non-woody biomasses, as defined by the German standard (10% DM, [11]).

Except for K, provenience of leaf litter material had a significant effect on its chemical composition (Figure 3.4a). Similar to its higher ash content, the residential area had higher content of Ca, Mg, Na and P, while content of S and Cl were lower than in material from the city centre and litter from the main road showed intermediate content. Although the collecting technique had an effect on overall ash content, the effect on the investigated elements was most often not statistically significant (Figure 3.4b)—only in the case of Na, where values for the vacuum technique were half the values for the suction technique. The washing treatment and the subsequent mechanical dehydration on the other hand did have a remarkable cleaning effect for all elements except Ca (Figure 3.4c).

The machine washed leaf material had significantly reduced values for Mg, Na, P, K and Cl in comparison to the freshly collected leaf litter. The comparison between washed material (MW) and washed and pressed material (PC) revealed that the PC had lower values in all cases, but statistical significance was only given in the case of P. In addition, it could be observed that the variability between the samples was much lower in the PC than in the MW or UM samples, which means that the additional treatment of mechanical dehydration leads to a homogenization of the chemical composition of such heterogeneous materials.



(a) (b) (c)

***Figure 3.3** Ash content of leaf litter from (**a**) proveniences (main roads-MRs, residential areas-RAs, city centres-CCs) collected by (**b**) the vacuum technique (VT) or the sweeper technique (ST); and (**c**) ash content of materials after different treatments (unwashed-UM, machine washed-MW, hand washed-HW, press cake-PC). Dashed lines indicate the arithmetic mean and solid lines indicate the median. Different letters indicate significant differences.*

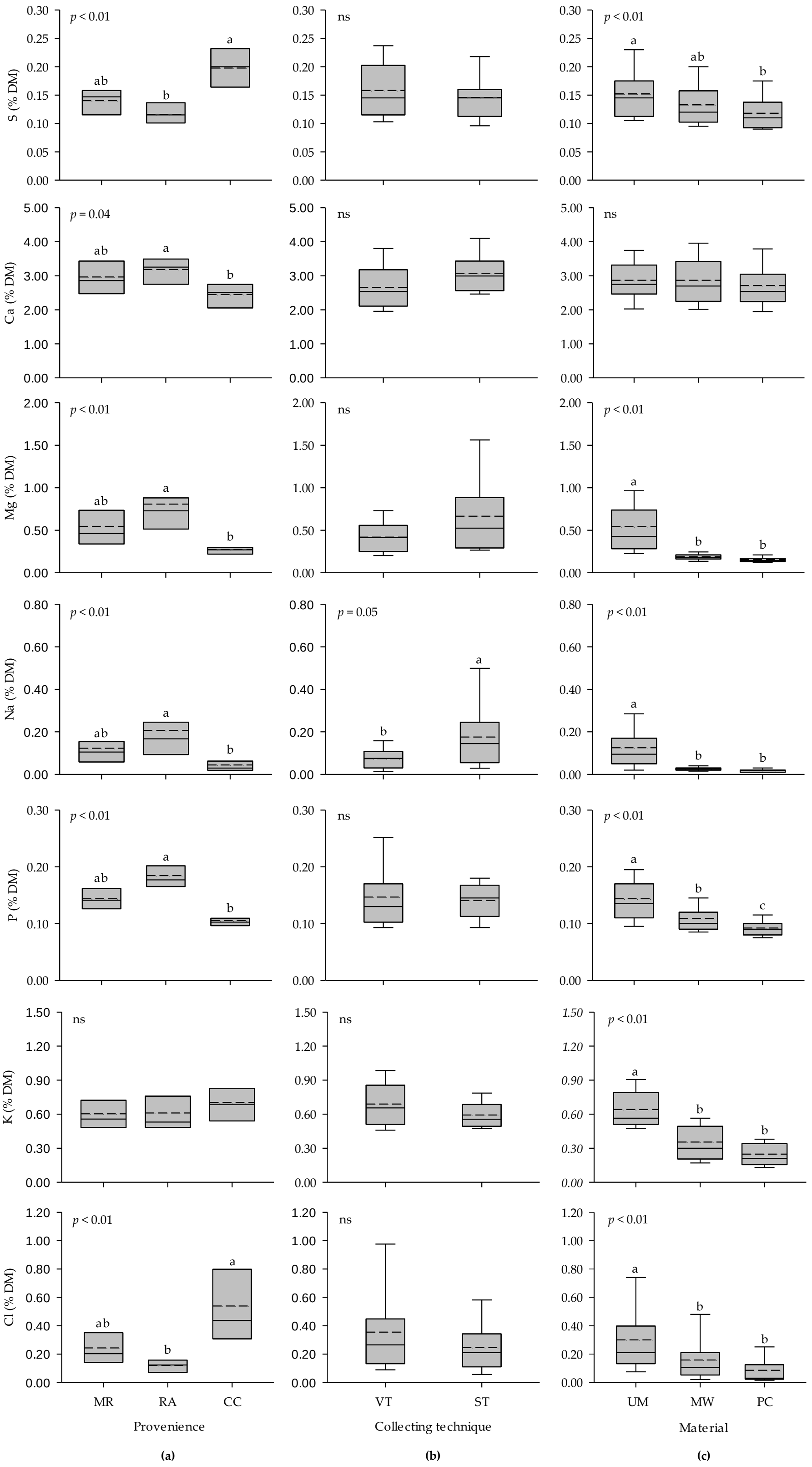


Figure 3.4 *Content of S, Ca, Mg, Na, P, K and Cl (% dry matter) in leaf litter from (**a**) various proveniences (main road-MR, residential area-RA, city centre-CC) collected by (**b**) different techniques (vacuum technique-VT and Sweeper technique-ST); The effect of different treatments is shown in (**c**) (unwashed-UM, machine washed-MW, press cake-PC). Whiskers indicate the 5th and 95th percentiles. Dashed lines indicate mean and solid lines indicate median values. Different letters indicate significant differences among, ns-not significant.*

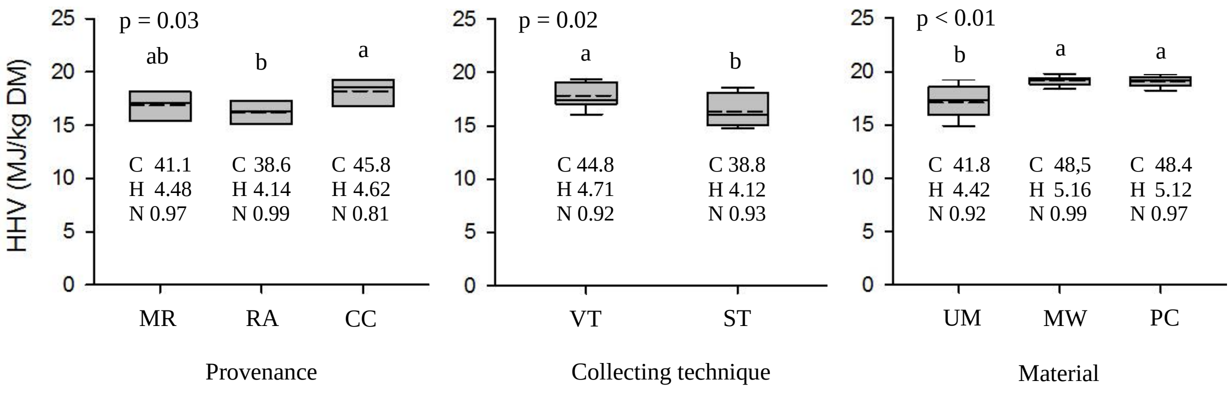
However, the washed material needs drying, if it is to be used as a fuel. By mechanical dehydration, the washed material can be dried up to DM concentrations of 50% in an efficient manner, thus the overall energy efficiency of the IFBB system is comparable to direct biomass combustion, as has been shown by Bühle et al. [24] and Hensgen et al. [15]. Leaf litter is not the only residual biomass in a city which could be used for energy conversion. Hensgen et al. [15] have shown that urban green cuts from private gardens and communal greens can also be used as a fuel after pre-treatment according to the IFBB. If a city administration should think of a system for utilizing green and wood-like residual biomass and life litter alike, the proposed system of washing and mechanical dehydration seems to be a suitable solution to produce a solid fuel for combustion.

Piepenschneider et al. [4] and Khalsa et al. [5] also investigated the effect of washing and mechanical separation on the concentrations of urban leaf litter for combustion. It can be stated that the mineral concentrations found in MW and PC material is in the range of their results, indicating that the washing step worked with the same efficiency and the minerals in the MW and PC material are those, which are inherent to the leaf litter material. In comparison to beech wood as a standard fuel, there are higher concentrations of S and Cl as well as K, Ca and Mg in treated leaf litter. However, the concentrations in leaf litter have been reduced near to or even below the guiding thresholds for unproblematic combustion stated by Obernberger et al. [12].

3.4.2 Heating Value

The calculated HHV of leaf litter showed significant differences between the proveniences (Figure 3.5), with highest values for the city centres (18.21 MJ/kg^{-1} DM) and lowest values for the residential areas (16.21 MJ/kg^{-1} DM) and intermediate values for the main roads (16.87 MJ/kg^{-1} DM). This is caused by the higher value of C in city centre leaf litter, which again might be due to the faster collection cycle, providing less time for the leaf material to decompose on the ground before collection and the lower value of ash in the samples of the city centre. HHV for material collected by the sweeping technique (16.35 MJ/kg^{-1} DM) was lower than values for the material collected by the vacuum technique (17.84 MJ/kg^{-1} DM). This may be explained by the higher ash content of the material collected by the sweeping machine.

Washing had a positive effect on HHV with an average increase from 17.10 to 19.12 MJ/kg^{-1} DM, which was mainly due to the reduction in ash content. Contrarily, mechanical dehydration did not lead to an additional increase. N concentration in the leaf litter material was below 1.0% DM; however, washing or mechanical dehydration did not reduce it further. Values for UM, MW and PC were above the threshold value of 0.6% DM, as proposed by Obernberger et al. [12] for an unproblematic combustion process considering NO_x emissions. Thus, technical measures such as air staging are necessary to prevent NO_x emissions in combustion [25, 26].

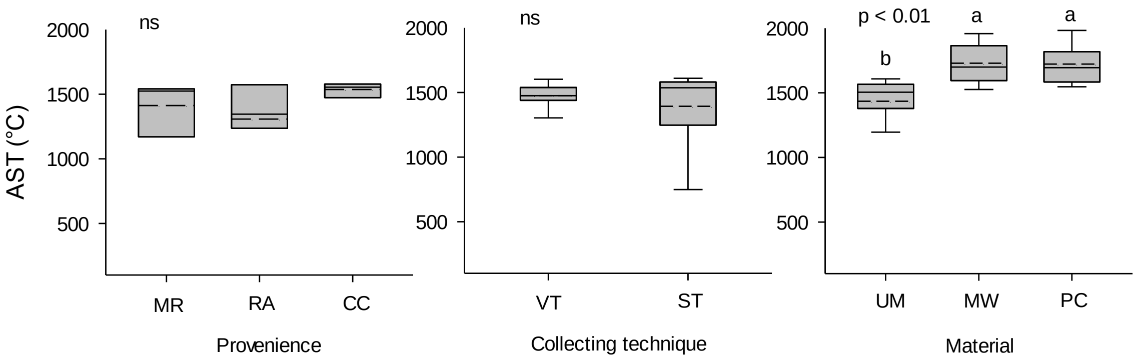


(a) (b) (c)

Figure 3.5 *Higher heating value (HHV; MJ/kg^{-1} DM) of leaf litter from (**a**) different proveniences (main roads-MRs, residential areas-RAs, city centres-CCs) collected by (**b**) the vacuum technique (VT) or the sweeper technique (ST); (**c**) HHV after different treatments (unwashed-UM, machine washed-MW, press cake-PC). Dashed lines indicate the arithmetic mean and solid lines indicate the median. Different letters indicate significant differences.*

3.4.3 Ash Softening Temperature

Ash softening temperature (AST) of the parent material was high (ca. 1500 °C), which was caused by high Ca concentrations, and no differences were found among proveniences or collection techniques (Figure 3.6a, b). Washing and mechanical dehydration increased AST further to around 1700 °C, as the relative reduction of Ca in the fuel was lower than that of K and Mg. However, as these are only calculated values, further research is necessary on the effect of washing and mechanical dehydration on leaf litter. Khalsa et al. [5] carried out combustion experiments with treated leaf litter (washing and mechanical leaching) and found a surprisingly low ash shrinkage starting temperature of 950 °C, but deformation-, hemisphere- and flow temperatures were also above 1500 °C. Piepenschneider et al. [4] investigated park leaves of five manually collected genera and measured AST both in raw leaves and in IFBB treated leaves. The mean measured AST for the untreated material was 1233 °C, whereas it was 1245 °C for the IFBB PC. This marginal difference might be, on the one hand, due to the different



(a) (b) (c)

Figure 3.6 *Ash softening temperature (AST; °C) of leaf litter from (**a**) different proveniences (main roads-MRs, residential areas-RAs, city centres-CCs) collected by (**b**) the vacuum technique (VT) or the sweeper technique (ST); (**c**) ash softening temperature after different treatments (unwashed-UM, machine washed-MW, press cake-PC). Dashed lines indicate the arithmetic mean and solid lines indicate the median. Different letters indicate significant differences, ns-not significant.*

provenience and collection techniques, as the park leaf material was comparably clean with only low amounts of adherent soil. Thus, washing and mechanical dehydration could not wash out the same amount of minerals responsible for ash melting. On the other hand, the adaptation of the IFBB system proposed in our actual study, i.e., the replacement of the mashing step of the conventional IFBB with a washing step, where the washing water is separated and omitted seems to be more efficient in removing soil and minerals. For the pre-treated leaf litter, AST is on a high level and comparable to wood [17]; therefore, ash slagging and fouling is unlikely to occur.

3.4.4 Indices

The K_2O/CaO index according to Bühle et al. [21] was calculated to estimate the slagging and fouling tendencies of the materials. There was a significant effect for provenience and material, but not for collecting technique (Table 3.2). The material from the residential area had a lower K_2O/CaO ratio, meaning that these samples are less likely to cause problems with ash slagging or fouling. However, values were generally low for all proveniences and were still reduced by washing and mechanical dehydration (from 0.20 to 0.09). The results confirmed earlier results on park leaf material by Piepenschneider et al. [4], where a reduction of the K_2O/CaO index from 0.25 to 0.15 was found with the conventional IFBB treatment. Though the study by Khalsa et al. [5] used a different index to predict problems with ash melting during combustion ((Si + P+ K)/(Ca + Mg)), they also showed that the washing and mechanical leaching treatment significantly reduced the risk of ash melting of leaf litter and nearly reached the value for wood pellets according to the European and German standard [10]. These findings together with the calculated AST indicate a very low risk of ash melting problems in combustion for such fuels.

Table 3.2 *Mean values of K_2O/CaO and 2S/Cl index for leaf litter of different origins, collecting techniques and treatment steps*

		K2O/CaO			2S/Cl		
Variable	n	Mean	Group	p-Value	Mean	Group	p-Value
Provenience							
Main road	8	0.18	ab	0.04	1.58	ab	0.02
Residential area	8	0.16	b		2.49	a	
City centre	8	0.27	a		0.94	b	
Collecting technique							
Vacuum technique	12	0.24	a	n.s.	1.52	a	n.s.
Sweeping technique	12	0.18	a		1.87	a	
Material							
Unwashed material	24	0.20	a	<0.01	1.67	b	<0.01
Machine washed	24	0.12	b		4.24	a	
Press cake	24	0.19	b		7.08	a	

ns – not significant.

The 2S/Cl index for the untreated materials indicated a high risk of corrosion (values below 2 [23]) for untreated leaf litter materials. However, there was a significant effect of provenience with highest values and therefore lowest corrosion risk for residential area material and highest corrosion risk for material from the city centre. The washing and mechanical dehydration led to a significant improvement with values between 4 and 8. This is due to the high wash out rate of Cl, which is relatively higher than that of S [14].

3.5 Conclusion

By investigating leaf litter from a full season of leaf fall, provenience was found to affect the properties of leaf litter for energetic conversion. Material collected in the city centre showed lower overall ash content and lower concentrations of specific minerals such as Ca, Mg, Na and P than the material collected in residential areas, but higher Cl concentrations. The city centre materials had higher heating values but also a higher risk of corrosion. These differences are attributed to the different cleaning cycles in the city, defining the time of ground contact for leaf litter. Collection techniques also proved significant, with leaf litter collected with the vacuum device showing lower ash and Na content and a higher heating value compared to material collected with the sweeper technique. The washing of leaf litter resulted in significantly reduced ash and element concentrations, and, thus, increased heating value as well as ash softening temperature and a lowered corrosion risk. Mechanical dehydration after machine washing did not lead to an additional substantial reduction in ash or mineral concentration of solid fuels obtained.

Appendix A

Table 3.A1. *Mean values ± standard deviation of mineral elements in different leaf litter material (unwashed, machine washed, press cake) sampled by two collecting devices (vacuum device, street sweeper) from three different city areas (main roads, residential areas, city centres).*

		Main Road		Residential Area		City Centre	
Element	Technique/Material	Vacuum Technique	Sweeping Technique	Vacuum Technique	Sweeping Technique	Vacuum Technique	Sweeping Technique
		% DM	% DM	% DM	% DM	% DM	% DM
S	Unwashed	0.14 ± 0.02	0.14 ± 0.02	0.12 ± 0.02	0.11 ± 0.02	0.22 ± 0.03	0.18 ± 0.03
	Machine washed	0.12 ± 0.03	0.13 ± 0.01	0.10 ± 0.02	0.11 ± 0.02	0.18 ± 0.04	0.16 ± 0.03
	Press cake	0.10 ± 0.01	0.11 ± 0.00	0.09 ± 0.01	0.10 ± 0.02	0.16 ± 0.02	0.14 ± 0.03
Ca	Unwashed	2.96 ± 0.76	2.97 ± 0.50	2.84 ± 0.60	3.53 ± 0.60	2.19 ± 0.28	2.72 ± 0.26
	Machine washed	3.01 ± 0.85	2.91 ± 0.45	2.92 ± 0.71	3.64 ± 0.40	2.23 ± 0.32	2.52 ± 0.42
	Press cake	3.09 ± 0.82	2.79 ± 0.52	2.76 ± 0.49	3.29 ± 0.58	2.10 ± 0.24	2.26 ± 0.40
Mg	Unwashed	0.50 ± 0.19	0.59 ± 0.32	0.53 ± 0.11	1.08 ± 0.47	0.23 ± 0.04	0.32 ± 0.07
	Machine washed	0.20 ± 0.10	0.18 ± 0.03	0.20 ± 0.05	0.19 ± 0.03	0.19 ± 0.03	0.17 ± 0.05
	Press cake	0.17 ± 0.07	0.14 ± 0.02	0.18 ± 0.03	0.15 ± 0.03	0.15 ± 0.02	0.14 ± 0.03
Na	Unwashed	0.09 ± 0.03	0.16 ± 0.11	0.11 ± 0.04	0.30 ± 0.19	0.02 ± 0.01	0.07 ± 0.04
	Machine washed	0.02 ± 0.00	0.03 ± 0.01	0.02 ± 0.00	0.03 ± 0.01	0.02 ± 0.00	0.02 ± 0.01
	Press cake	0.02 ± 0.00	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.00	0.02 ± 0.01
P	Unwashed	0.15 ± 0.02	0.14 ± 0.02	0.19 ± 0.06	0.17 ± 0.01	0.10 ± 0.01	0.11 ± 0.02
	Machine washed	0.10 ± 0.02	0.11 ± 0.01	0.13 ± 0.05	0.11 ± 0.01	0.10 ± 0.01	0.10 ± 0.01
	Press cake	0.09 ± 0.02	0.09 ± 0.01	0.11 ± 0.03	0.10 ± 0.01	0.08 ± 0.01	0.08 ± 0.01
K	Unwashed	0.59 ± 0.18	0.61 ± 0.12	0.69 ± 0.23	0.53 ± 0.06	0.78 ± 0.19	0.63 ± 0.13
	Machine washed	0.28 ± 0.11	0.30 ± 0.11	0.33 ± 0.16	0.22 ± 0.10	0.60 ± 0.17	0.40 ± 0.13
	Press cake	0.20 ± 0.08	0.19 ± 0.08	0.26 ± 0.10	0.16 ± 0.04	0.39 ± 0.08	0.28 ± 0.09
Cl	Unwashed	0.26 ± 0.10	0.23 ± 0.17	0.12 ± 0.03	0.12 ± 0.07	0.69 ± 0.30	0.39 ± 0.17
	Machine washed	0.09 ± 0.04	0.11 ± 0.08	0.04 ± 0.02	0.05 ± 0.04	0.43 ± 0.23	0.23 ± 0.13
	Press cake	0.05 ± 0.02	0.04 ± 0.04	0.03 ± 0.01	0.02 ± 0.01	0.23 ± 0.09	0.15 ± 0.10
Ash	Unwashed	20.78 ± 4.70	26.19 ± 11.00	21.72 ± 1.76	40.04 ± 3.26	12.02 ± 4.08	21.64 ± 10.56
	Machine washed	10.73 ± 2.55	10.47 ± 1.45	10.95 ± 2.45	13.45 ± 3.18	7.76 ± 0.66	9.04 ± 0.83
	Press cake	10.31 ± 1.83	11.10 ± 1.16	10.06 ± 2.13	13.63 ± 4.21	6.97 ± 1.01	8.20 ± 0.89

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4. Heavy Metals and Polycyclic Aromatic Hydrocarbons in Urban Leaf Litter Designated for Combustion

4.1 Abstract

Vast amounts of leaf litter have to be disposed of by city administrations. This biomass has the potential for energy conversion, but contamination with pollutants can adversely affect this usage. We investigated leaf litter samples from the city of Kassel by analyzing their heavy metal and polycyclic aromatic hydrocarbon (PAH) concentrations. Leaf samples were indeed contaminated with heavy metals and PAHs and contamination was influenced by provenience and collection technique. A simple cleaning system of washing and subsequent mechanical dewatering significantly reduced heavy metal concentration. Regression models were developed for contamination with heavy metals which showed that contamination could be successfully estimated using the total ash content of the sample as a predictor, with an R^2 of up to 0.77. It can be concluded that leaf litter from cities is a possible feedstock for energetic conversion, provided a cleaning step is applied.

4.2 Introduction

Every year, municipalities collect vast amounts of leaf litter, which have to be disposed of. Studies assessing the total amount of leaf litter in European cities are missing; however, the number of city trees has been a focus of recent studies. For instance, the total number of shrubs and trees in urban Sheffield, United Kingdom, increased from the 1900s to 2010 by 50.5% [1], indicating the high value of green areas in cities. A survey from England revealed that town size had no effect on tree density, and mean density was 58.4 trees and shrubs ha^{-1} [2]. Leaf litter originates from private gardens, parks and other green areas dedicated to citizens' relaxation and sport activities. While leaf litter from parks is often contaminated with soil, it may be less affected by pollutants [3], whereas leaf litter collected from the road surface may contain both soil contamination and organic, as well as inorganic pollutants.

Contamination with pollutants is a potential problem for public acceptance of biomass conversion plants fed with urban leaf litter. Up until now, there is little known about the concentration of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in leaf litter from urban roads. Heavy metals pose a serious threat to human health [4]. Past literature has reported heavy metal concentrations in soil [5, 6] and the distribution of concentrations in soil within cities, with higher values for Cd and Pb for roadside areas compared to urban park areas [7]. Plant availability and uptake of heavy metals, including the possibility of phytoremediation of soils (e.g., [8]), as well as concentrations of heavy metals in urban water (e.g., [9]) and in plants grown in urban areas (e.g., [10]) have also been determined. The general behavior of heavy metals in combustion depends on the volatility of the element in question [11]. The more volatile heavy metals (e.g., Pb, Zn, Hg) have a tendency to vaporize in combustion and condense on fine particles and, therefore, are found in cyclone or filter fly ash or escape with the flue dust into the atmosphere. However, if the combustion unit is fitted with an efficient particulate removal system, the amount of heavy metals escaping the combustion system with the exhaust is minimal [12]. Less volatile heavy metals on the other hand, such as As, Cr, Cu and Ni remain in the bottom ash of the furnace to a large extent [13]. Concentrations in the various ash fractions must be considered, as they may restrict the potential uses of the ashes and may require disposal if the concentration in the ash fraction is higher than is legally allowed for application as a fertilizer and liming agent on agricultural fields or in forests [12]. To our knowledge, there is no scientific investigation on the degree of heavy metal contamination in street leaf litter designated for combustion. Potential sources of contaminants are motor vehicle emissions, tire wear and asphalt road surfaces, as well as domestic fire emissions, gasworks and commercial incinerators [14]. Research on the concentration of inorganic, as well as organic contaminants in urban biomass has focused on detecting suitable plants as bio-indicators for pollution (e.g., metals in moss [15], grass [16], *Quercus ilex* [17] as well as in *Taraxacum officinale*, *Pinus sylvestris,* and in *Tilia cordata* [18]) and ensuring healthy food production in urban environments (e.g., [19]). Two British practical trials investigating the contamination of street leaf sweepings found that the pollution with PAHs was too high for composting purposes [20, 21].

Energy recovery from urban leaf litter may provide the opportunity to exploit a new renewable energy resource. However, for common energy recovery technologies (e.g., anaerobic digestion or direct combustion), urban leaf litter may be a problematic feedstock. Due to the high fiber and ash content of leaves, the methane yield from anaerobic digestion is low, as was shown by Kosse et al. [22] for urban chestnut leaf litter (137 l_N kg^{-1} VS) and Liew et al. [23] for an urban tree leaf litter mixture consisting mainly of maple leaves (55.4 l_N kg^{-1} VS). Concerning combustion, it is well known that high mineral concentrations in non-woody biomass may lead to problems regarding emissions of nitrogen oxides (NO_x) polychlorinated di-benzo dioxins and furans (PCDD, PCDF), sulphur oxides (SO_x), carbon-monoxide (CO) and particulate matter (PM), as well as corrosion, ash slagging and fouling due to ash melting at low temperatures [11, 24]. Recent studies have shown that the chemical composition of urban leaf litter is not as suitable for combustion as woody biomass [3, 25, 26]. In particular, the concentration of N, Mg, S, K and total ash are considerably higher. Piepenschneider et al. [3] found a mean total ash concentration of 15.92% dry matter (DM) in leaf litter. Compared to the range of ash concentrations in woody biomass (0.3% to 5.0% DM, [11]), the ash concentration was 3- to 53-fold higher in leaf litter than in woody biomass.

An integrated technique has been suggested (i.e., integrated generation of solid fuel and biogas from biomass, IFBB) to produce solid fuel from non-woody biomass with decreased mineral, N and total ash concentrations by means of a washing and dehydration treatment [27]. The IFBB process has been shown to reduce the mineral concentrations especially of water soluble elements, such as K and Cl, for semi-natural grassland [28], park leaf litter [3, 26] and urban green cut biomass [29]. However, little is known about the possible contamination of the urban input materials with heavy metals and PAHs in the IFBB system. Piepenschneider et al. [30] investigated the concentration of 16 elements (Ca, K, Mg, N, Na, P, S, Al, Cd, Cl, Cr, Cu, Mn, Pb, Si and Zn) in urban grass clippings from roadsides and found that the city grass clippings did not contain elevated heavy metal concentrations in comparison to agricultural or landscape conservation grass material. The study by Piepenschneider et al. [30] also investigated the effect of the IFBB system and found a reduction in the concentration of Ca, K, Mg, N, Na, P, S, Cl, Mn, Si, Zn and total ash, but an increase for Cr and Cu. Therefore, there is a knowledge gap regarding the organic and inorganic pollution contained in street leaf litter and the effect of the IFBB system on this potentially contaminated material.

Thus, the aims of this study were:

I. To investigate the concentrations of PAHs and heavy metals in urban leaf litter from street sweepings;
II. To determine the effect of provenience and collection technique on the concentration of PAHs and heavy metals in urban leaf litter from street sweepings;
III. To investigate the effect of washing and dehydration through the IFBB system on the heavy metal concentration;
IV. To develop a linear regression model to predict the heavy metal concentration in urban leaf litter.

4.3 Material and Methods

4.3.1 Collection of Leaf Litter

Leaf litter was collected from the city of Kassel, which is located in central Germany and has about 200,000 inhabitants within 107 km^2. Sampling was conducted in collaboration with the local cleansing department, who provided leaf litter in accordance with their routine work. Therefore, we were able to distinguish among various proveniences ((i) main road (MR); (ii) residential area (RA) and (iii) city center (CC)) and between different collection techniques ((i) vacuum technique (VT) and (ii) sweeping technique (ST)). The three proveniences had different cleaning cycles: main roads were cleaned weekly, residential areas biweekly and the city center was cleaned every second day. The vacuum technique is appropriate for sites which cannot be swept (e.g., parks and small greens along sideways) and where leaf litter is initially gathered with leaf blowers and subsequently picked up by a suction unit. The sweeping technique is usually applied on compacted surfaces and leaf litter is picked up with a rotating brush after moisturizing. Leaf litter collection took place after litter fall in calendar weeks 41, 43, 45 and 47 in 2014, resulting in 24 samples (4 dates x 3 proveniences x 2 collection techniques). For conservation, samples were ensiled in 60 L airtight polyethylene barrels for a minimum of 12 weeks.

4.3.2 Washing Facility and Washing of Leaf Litter

The washing facility is 100 x 100 x 60 cm (width x depth x height) with a sink in the lower part as a sedimentation zone for dirt and waste, which were removed after washing. Approximately 550 L of water were constantly swirled by pressing air through perforated pipes (7 pipes with 6 holes, each with a 4-mm diameter) at the bottom of the tank using a side channel compressor (RICO, 1.1 kW, intake pressure 1000 mbar, rotational speed 2900/min). A screen basket (98 x 98 x 45 cm, width x depth x height) with a mesh size of 1.1 cm was inserted into the washing facility. Ascending air bubbles broke up leaf litter clots and mobilized adhering dirt particles which sank through the sieve into the sedimentation zone. The screen basket held back leafy material, which could then be evacuated from the washing area.

After evacuating the material from the plastic barrels, the biomass was mixed and impurities (i.e., bottles, plastics, stones, wood, etc.) were removed. Depending on water content approximately 3 to 10 kg of leaf litter were used. Machine washing was conducted for 5 min at a water temperature of 10 to 12 °C. The washed material was further processed by mechanical separation with a screw press (type AV, Anhydro Ltd., Kassel, Germany). The conical screw had a pitch of 1:6 and a rotational speed of 6 r/min^{-1}. The cylindrical screen encapsulating the screw had a perforation of 1.5 mm.

4.3.3 Chemical Analyses

Subsamples of each sample were taken at each treatment stage: (i) unwashed; (ii) washed; and (iii) mechanically dehydrated. From these subsamples, dry matter was determined by drying the material at 105 °C. For elemental analysis, material was dried at 60 °C. Subsequently, material was ground with a cutting mill (SM 1, Retsch, Haan, Germany) to pass a 5-mm sieve and subsequently with a sample mill (1093 Cyclotec, Foss, Hamburg, Germany) to 1 mm. C,H and N concentrations in samples were determined with an elemental analyser (Vario Max CHN Elementar Analysesysteme, Hanau, Germany). Concentrations of Fe and Mn were determined with X-ray fluorescence spectroscopy. For determination of additional element concentrations, material was processed with microwave pressure digestion. Concentrations of Cr, Cu, Ni, as well as Zn were measured with inductively coupled plasma optical emission spectrometry, concentrations of As, Cd, Pb, as well as Tl were measured with inductively coupled plasma mass spectrometry, and Hg was measured with cold-vapor atomic spectrometry. In this study, the term “heavy metals” refers to the elements As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Tl and Zn.

PAHs were determined in unwashed material shortly after opening the barrels. Therefore, samples were taken and stored at 4 °C prior to extraction and determination of PAHs with the gas chromatographic method with mass spectrometric detection. As there is a broad range of PAHs, preselection of substances was necessary. 16 PAHs, which are commonly used and recommended by the US-Environmental Protection Agency to assess the occurrence of this group of substances in the environment, were measured, namely Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(123-cd)pyrene, Dibenz(ah)anthracene, and Benzo(ghi)perylene.

4.3.4 Statistical Analyses

Figures 4.1 and 4.2 were generated with SigmaPlot, Version 12.3 (Systat Software, San Jose, CA, USA) and Figure 4.3 was generated with R, Version 3.0.2 (R Foundation for Statistical Computing, Vienna, Austria). R software was also used to detect differences in element concentrations between or among proveniences, collection techniques and degree of materials processing by applying either Wilcoxon's rank-sum test for differences between two independent groups or the Kruskal-Wallis test for differences among more than two independent groups with the post-hoc function "kruscalmc". In the case of degree of materials processing, groups were not independent, so significant results should be interpreted against this background. The dendrogram was based on Euclidean distances, which were hierarchically clustered with Ward's method. Regression analysis was conducted with R software by applying the "lm" function. Residuals were normally distributed except for Ni, Fe and Cu. Homoscedasticity was verified visually, which revealed Cu to be the only heteroscedastic element.

4.4 Result and Discussion

4.4.1 Heavy Metals

The overall observed variance of unwashed leaf litter material was high (e.g., coefficient of variation (CV) of Mn = 0.59, Fe = 0.89 and Pb = 0.70). High variance is commonly observed by scientists investigating element concentrations in street dust (e.g., CV of Zn = 0.39, Pb = 0.31 [14]; Cu = 0.89, Fe = 0.50, and Cr = 0.62 [31]).

4.4.1.1 Heavy Metals in Urban Leaf Litter

Concentrations of As, Cr, Fe, Ni, Pb and Zn in leaf litter collected from urban roads were higher than those found in forest beech litter ([32], Table 4.1). While concentrations of As, Cr and Ni were about 6- to 9-fold higher, Pb concentration was 3-fold and Zn concentration was 1.5-fold higher. The most pronounced difference was found for Fe concentration, which showed a 65-fold higher concentration in urban leaf litter collected from roads than in forest beech litter. Concentrations of Cr and Ni were in the range of concentrations detected in urban leaf litter from former studies [33, 34]. While Mn concentration was below the value detected by Heckman and Kluchinski [33], the concentration of Fe was considerably higher. Concentrations of Pb and Zn were below the concentrations previously measured in urban leaf litter [33, 34]. They exceeded values measured in vital leaves of *Quercus ilex* (Pb = 3.34 and Zn = 32.13 mg/kg^{-1} DM [17]), which might indicate that further contamination with these elements takes place while the biomass is in contact with the road surface. Cr concentrations were also lower in vital leaves (1.88 mg/kg^{-1} DM, [17]) than concentrations detected in urban leaf litter (6.04 mg/kg^{-1} DM).

Concentrations of Cd and Cu were close to values measured in forest beech litter. Cd concentration was below element levels detected in former studies on comparable biomass [33, 34]. However, the exceptional high values in urban leaf litter from Heckman and Kluchinski ([33]) show that there is a danger of elevated Cd concentrations in urban leaf litter and that the Cd concentration should be closely monitored, if urban biomass is used for energetic purposes. Cu concentration was in the range of formerly observed concentrations in urban leaf litter.

Table 4.1 *Mean concentrations of heavy metals (mg/kg^{-1} DM) ± standard error of means (s.e.) in leaf litter from different origins in comparison to wood and a German standard for pellets from non-woody material.*

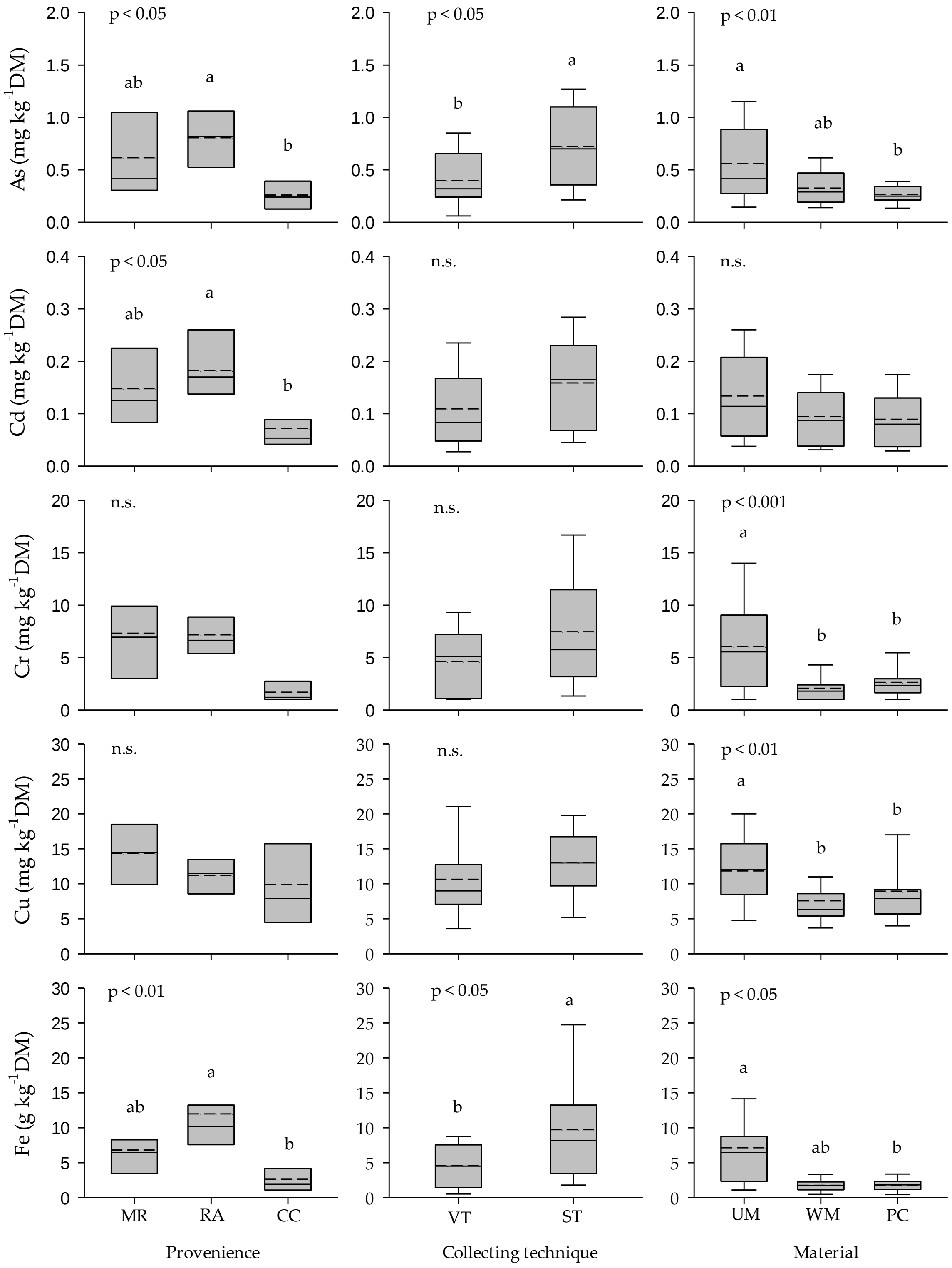
Element	Urban Leaf Litter from Roads	Forest Leaf Litter[1]	Urban leaf litter[2]	Urban Leaf Litter from Roadside Verges[3]	deciduous wood[4]	Standard for pellets from non-woody materials[5]
As	0.56 ± 0.08	0.07	-	-	≤ 1.0	≤ 1.0.0
Cd	0.13 ± 0.02	0.14	1.7	0.33	0,1	≤ 0.5
Cr[6]	6.04 ± 1.02	0.68	7.6	4.9	1.0	≤ 50.0
Cu	11.84 ± 1.04	8.3	9.2	29	2.0	≤ 20.0
Fe	7 154.46 ± 1271.02	110.0	1461.0	-	25.0	-
Mn	204.99 ± 24.47	1850.0	550.0	-	83.0	-
Ni[6]	7.20 ± 1.33	1.12	7.2	1.8	0,.5	≤ 10.0
Pb	4.14 ± 0.63	1.3	28.4	20	2.0	≤ 10.0
Zn	61.04 ± 6.95	36.0	81.0	89	10.0	≤ 100.0

[1] [32], [2] [33], [3] [34], [4] [11], [5] [35], [6] for values below the detection limit of the analytical method applied, the detection limit was used for calculation of arithmetic mean and standard error s.e.

The concentrations of all elements were considerably higher in urban leaf litter than in deciduous wood [11]. However, the concentrations were below the limits of the German standard for combustion of non-woody materials [35].

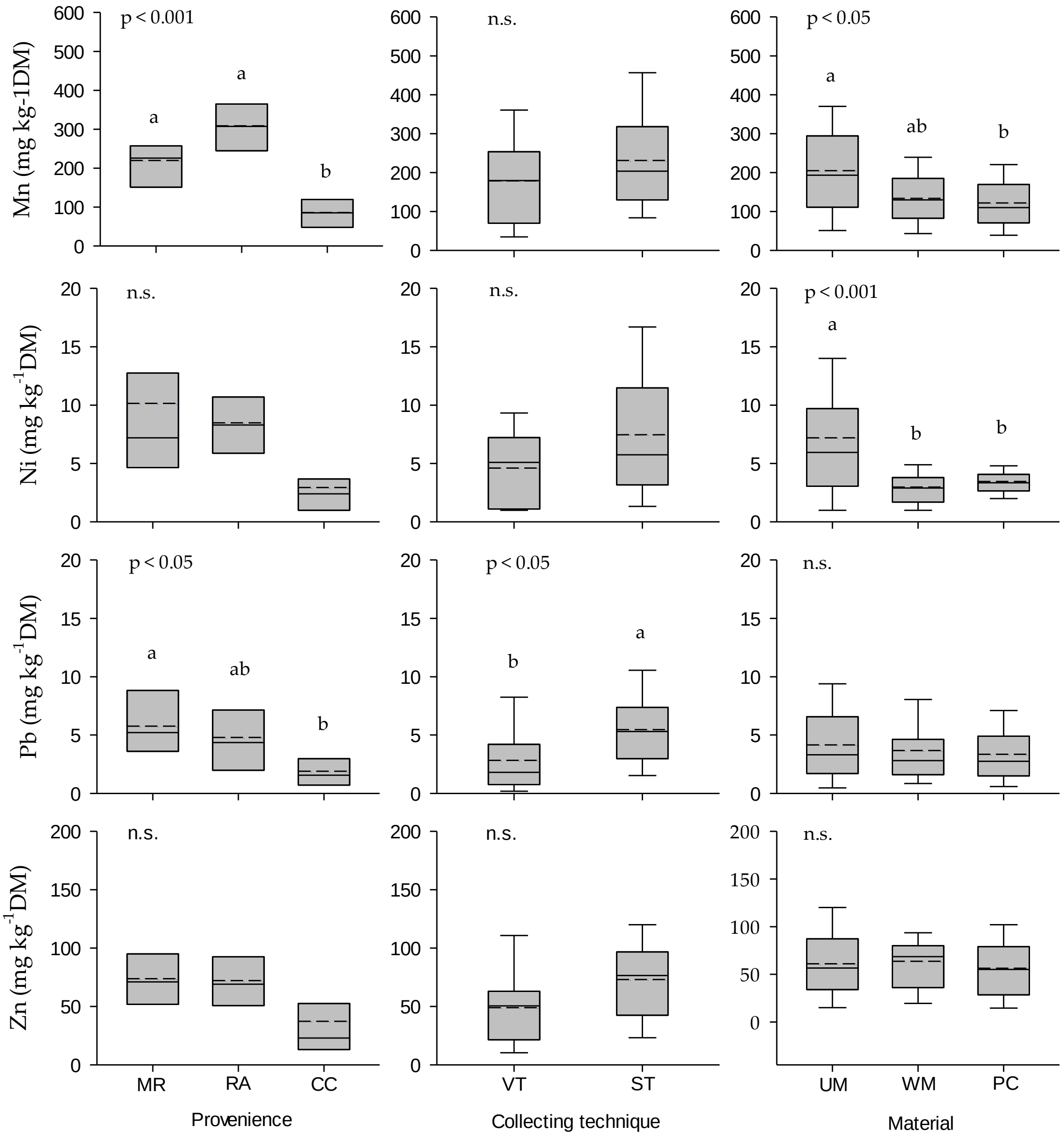
Charlesworth et al. [36] gave an overview of heavy metal concentrations (Cd, Cu, Ni, Pb, Zn) measured in the street dust of various cities, which were all higher than the concentrations detected in our study for leaf litter collected from roads (with one exception: Pb in Urbana = mg/kg^{-1} DM).

Figures 4.1a and 4.2a show the concentration of heavy metals (mg/kg^{-1} DM) in leaf litter of urban street trees from various proveniences within the city of Kassel (main roads-MR, residential areas-RA, city center-CC). Arsenic concentration differed between proveniences. Concentration in leaf litter from the CC was considerably lower than from MR and RA, with the difference between CC and RA being significant. This pattern could also be observed for Cd and Fe. While the Mn concentration of material from the CC was significantly lower than both of the other proveniences, the lower Pb concentration in leaf litter from the city center is only significant in comparison to MR. Concentrations of Cd, Cr, Cu, Ni and Zn did not differ significantly between proveniences; although the mean value of material collected from the CC was lower than the means from MR and RA in all cases. The exact cause for the differences between proveniences is unknown, but traffic characteristics (e.g., number of cars, average speed, traffic lights) and the different contact time of leaf litter with the street (two days in the CC, up to 14 days in MR and RA) might influence its contamination.



(a) (b) (c)

Figure 4.1 *Concentration of heavy metals As, Cd, Cr, Cu and Fe in leaf litter of urban street trees from (**a**) various provenience (main road-MR, residential area-RA, city center-CC) collected by (**b**) different technique (vacuum-VT and sweeping technique-ST) and (**c**) with various degrees of material processing (unwashed material-UM, washed material-WM, press cake-PC). Whiskers indicate the 5th and 95th percentiles. Dashed lines indicate mean values and solid lines indicate median values. Different letters indicate significant differences; n.s., not significant. Samples with values below the analytical detection limit were included into the dataset, using the detection limit as a conservative estimate of the concentration*



(a) (b) (c)

Figure 4.2 *Concentration of heavy metals Mn, Ni, Pb, and Zn in leaf litter of urban street trees from **(a)** various provenience (main road—MR, residential area—RA, city center—CC) collected by **(b)** different technique (vacuum—VT and sweeping technique—ST) and **(c)** with various degrees of material processing (unwashed material—UM, washed material—WM, press cake—PC). Whiskers indicate the 5th and 95th percentiles. Dashed lines indicate mean values and solid lines indicate median values. Different letters indicate significant differences; n.s., not significant. Samples with values below the analytical detection limit were included into the dataset, using the detection limit as a conservative estimate of the concentration.*

Results of Charlesworth et al. [36], investigating street dust in Birmingham, also indicate spatial clustering of contaminants potentially due to specific industries and traffic characteristics. To gain further insights into the spatial distribution of heavy metals, further research with high spatial resolution is necessary.

Figures 4.1b and 4.2b show the concentration of heavy metals (mg/kg^{-1} DM) in leaf litter of urban street trees collected with different techniques within the city of Kassel (vacuum-VT and sweeping technique-ST). Fe, As and Pb concentrations were significantly higher when collected with the ST rather than the VT. Cd, Cr, Cu, Mn, Ni and Zn concentrations did not differ significantly between collection techniques, however, a higher concentration of heavy metals in material sampled with the ST was obvious. Theoretically, this technique takes up higher quantities of road debris.

Ellis [21] sampled street leaf litter with a collection vehicle using a rotary brush as well as a vacuum device. Fresh leaves were collected together with accumulated debris [21]. As a result, heavy metal concentrations (e.g., Cu = 85.2 mg/kg^{-1} DM, Pb = 59.1 mg/kg^{-1} DM) were generally considerably higher than in the present study.

Figures 4.1c and 4.2c show the effect of washing and the IFBB system on the leaf litter material from the city of Kassel. Washing reduced the concentration of all elements with the exception of Zn. The reduction was not significant for As, Cd, Fe and Mn. The IFBB process, on the other hand, achieved a significant reduction in As, Fe and Mn concentrations compared to the unwashed material.

In the case of Cr, Cu and Ni, the concentration was significantly reduced by washing, but no further reduction occurred with the IFBB process. On the contrary, the concentration increased slightly, which was also observed by Piepenschneider et al. [30] for urban roadside cut material and can be explained by abrasion of metal within the equipment used for the IFBB system. Nicola et al. [17] also found that washing vital leaves from *Quercus ilex* reduced the concentration of heavy metals (Cr, Cu, Fe, Pb and Zn) significantly.

From a total of 24 samples, Tl and Hg could only be detected in 15 and 10 samples, respectively (Table 4.2). Thus, the minimum values in Table 4.2 are below the detection limit of 0.01 mg/kg^{-1} DM. The median concentration of both elements in unwashed material was 0.02 mg/kg^{-1} DM, while maximum values were 0.05 mg/kg^{-1} DM for Tl and 0.06 mg/kg^{-1} DM for Hg.

Table 4.2 *Concentrations of Tl and Hg (mg/kg^{-1} DM) in leaf litter of urban street trees. UM, unwashed material; WM, washed material; PC, press cake. Minimum, maximum and median values refer to the full data set of 24 samples.*

Element	Material	Number of samples with detected concentrations	Minimum value	Maximum value	Median
Tl	UM	15	< 0.01	0.05	0.02
	WM	13	< 0.01	0.04	0.02
	PC	6	< 0.01	0.04	< 0.01
Hg	UM	10	< 0.01	0.06	0.02
	WM	7	< 0.014	0.06	< 0.01
	PC	10	< 0.01	0.06	< 0.01

Nicola et al. [17] argue that accumulation of particle-bound and gaseous contaminants on the leaf surface is dependent on tree species, since leaf surface properties (morphology, chemistry of waxy components) might affect the accumulation process.

4.4.1.2 Ash Content as a Prediction for Heavy Metal Concentration

Linear regression analysis revealed a strong relationship between ash content and heavy metal concentration (Table 4.3). Linear models were significant for every element, with coefficients of determination between $R^2 = 0.77$ for As and R2 = 0.21 for Cu. Values higher than 0.5 were observed for Fe, Mn, Pb and Zn. Thus, it can be stated that if a leaf litter sample is high in ash content, it is very likely that the material is also contaminated with heavy metals.

Table 4.3 *Results of linear regression analysis determining the relationship between ash content (% DM) and heavy metal concentration (mg/kg^{-1} DM) in leaf litter of urban street trees. Residuals of the models for Ni, Fe and Cu were not normally distributed.*

Element	Intercept	Slope	R^2	Significance
As	-0.73	0.031	0.77	***
Cd	0.010	0.005	0.44	***
Cr	-0.237	0.278	0.39	**
Cu	6.629	0.219	0.21	*
Fe	-4606.400	495.620	0.71	***
Mn	8.919	8.263	0.53	***
Ni	0.061	0.317	0.29	*
Pb	-0.947	0.215	0.53	***
Zn	0.785	2.539	0.62	***

$*p < 0.05$, $** p < 0.01$, $***p < 0.001$

4.4.1.3 Relevance of Heavy Metal in Urban Leaf Litter for Combustion

The heavy metal concentration in non-woody biomass measured in this study fell below the European and German standard limits for non-woody fuel pellets [35]. Contaminated biomass types such as demolition timber and plants from phytoremediation areas have been shown to contain significantly higher concentrations of heavy metals [12]. There are two major concerns regarding heavy metals in combustion. One is emissions of heavy metals with the fly dust, which is especially applicable for the more volatile elements, such as Hg, Pb, Zn and Cd. The other concern focuses on the contamination of ash with heavy metals, making it impossible to use the ash on agricultural or forested lands. During combustion in a state of the art combustion unit, three ash fractions are generated: the bottom ash, the coarse fly ash or cyclone fly ash and the fine fly ash or filter fly ash [12, 13]. The bottom ash is the largest fraction with 60%–90% of the total ash, the cyclone fly ash is the second largest fraction 10%–35% and the filter fly ash is the smallest fraction (2%–10%). It was found that only between 1% and 21% of the ash escapes with the flue dust, with a mean of 1.6% [13]. Narodoslawsky and Obernberger [13] found that the average distribution of heavy metals for Zn, Pb, Hg and Cd was about 90% in the cyclone and fly ash and only about 10% in the bottom ash. On the other hand, about 50% of Co, Ni, Cr and V were found in the bottom ash with only about 10% of these elements in the filter fly ash. It was concluded that the gaseous emission of heavy metals during combustion is only of minor concern, except for Hg emissions [13]. However, we found Hg only in 10 out of 24 samples for the unwashed leaf litter and concentrations were only marginally higher than in beech wood (0.2 versus 0.12 mg/kg^{-1} DM, [12]) and much lower than in straw (6 mg/kg^{-1} DM, [12]) or contaminated biomass samples (2.7–1000 mg/kg^{-1} DM, [12]). The largest problem is the contaminated fly ash collected by the filters, which is a highly polluted hazardous waste that has to be disposed of [13] or industrially treated [11]. Although this fraction is the smallest, it contains the majority of the Cd and Zn, whereas between 85% and 95% of the plant nutrients are contained in the usable ash fractions [11].

4.4.2 PAHs

4.4.2.1 PAHs in Urban Leaf Litter

From the 16 PAHs investigated in this study, 5 (Naphtalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, and Dibenz (ah) anthracene) could not be detected in any sample (Table 4.4). The other 11 PAHs occurred in 1 to 13 samples of the total set of 24 samples. The most abundant substance, with the highest single and median value, was Fluoranthene, which is a pollutant originating from low-temperature and inefficient combustion. Pyrene and Benzo(b)fluoranthene were also present in higher amounts and a greater number of samples. According to Harrison et al. [37], these PAHs are especially indicative of incineration and oil combustion. Furthermore, Benzo(k)fluoranthene and Benzo(a)pyrene are indicators of road dust as an emission source. Harrison et al. [37] showed that car traffic was the most important factor influencing the PAHs concentration.

The concentration of 24 PAHs in vital leaves from *Quercus ilex* was found to be 2.1 mg/kg^{-1} DM [17], whereas Howsam et al. found 0.041 mg/kg^{-1} DM of 23 PAHs in oak leaves from a woodland area [38]. Concentration of PAHs is dependent on leaves' physiological features. Hairiness, for instance, was found to cause a significantly higher PAH concentration compared to hairless leaves [38]. The maximum concentration of Benzo(a)pyrene was 20.7 mg/kg^{-1} DM in leaf litter sweepings from urban roads when collected by a vehicle with a rotary brush and vacuum head [21]. Notably, this was lower than values detected in manually collected leaf litter [21]. The authors hypothesized that PAHs might be removed by water spray on the front of the vehicle prior to collection, but high variation in concentrations did not allow a solidified conclusion to be made. However, the detected minimum value (0.70 mg/kg^{-1} DM, [21]) was still more than twice as high as the maximum value detected in our study (0.28 mg/kg^{-1} DM). In contrast, Ellis and Keyse [21] measured less than half of the concentration found by the present study when sampling only fresh leaf litter with the vacuum device of the collection vehicle without using the rotary brush. Therefore, collection technique seems to influence the concentration of Benzo(a)pyrene in leaf litter.

***Table 4.4** Concentration of polycyclic aromatic hydrocarbons (PAHs) (mg/kg^{-1} DM) in leaf litter of urban street trees in comparison to literature values for Quercus ilex leaves from Naples, Italy [17]. Minimum, maximum and median values refer to the full data set of 24 samples.*

PAH	Chemical formula	Number of samples with detected concentrations	Minimum	Maximum	Median	Literature value[1,2]
Naphthaene	$C_{10}H_8$	0	<0.05	<0.05	<0.05	0.102
Acenaphthylene	$C_{12}H_8$	0	<0.05	<0.05	<0.05	0.052
Acenaphthene	$C_{12}H_{10}$	0	<0.05	<0.05	<0.05	0.007
Fluorene	$C_{13}H_{10}$	0	<0.05	<0.05	<0.05	0.038
Phenanthrene	$C_{14}H_{10}$	12	<0.05	0.360	<0.05	0.262
Anthracene	$C_{14}H_{10}$	0	<0.05	<0.05	<0.05	0.025
Fluoranthene	$C_{16}H_{10}$	13	<0.05	0.668	0.174	0.328
Pyrene	$C_{16}H_{10}$	8	<0.05	0.520	<0.05	0.419
Benz(a)anthracene	$C_{18}H_{12}$	6	<0.05	0.349	<0.05	0.054
Chrysene	$C_{18}H_{12}$	6	<0.05	0.282	<0.05	0.205
Benzo(b)fluoranthene	$C_{20}H_{12}$	9	<0.05	0.520	<0.05	0.127[a]
Benzo(k)fluoranthene	$C_{20}H_{12}$	1	<0.05	0.150	<0.05	0.127[a]
Benzo(a)pyrene	$C_{20}H_{12}$	5	<0.05	0.282	<0.05	0.047
Indeno(123-cd)pyren	$C_{22}H_{12}$	2	<0.05	0.179	<0.05	0.003
Dibenz(ah)anthracen	$C_{22}H_{14}$	0	<0.05	<0.05	<0.05	0.045
Benzo(ghi)perylene	$C_{22}H_{12}$	4	<0.05	0.249	<0.05	0.002
Sum	-	-	<0.05	3.053	0.267	2.10[b]

[1][17], [2] air dried, [a] benzo (b+k+j) fluoranthene, [b] Sum of 24 PAHs.

The relative abundance of single PAHs can be used to determine the source of contamination. Comparing our findings visually with the reference material SRM 1649a-Urban Dust, as cited in [14], a certain similarity was obvious. The concentration of 16 PAHs was 4.4 mg/kg^{-1} DM in street dust and 13.13 mg/kg^{-1} DM in tanker effluent [14], indicating that a certain washing effect might take place. PAHs are lipophilic compounds and less water-soluble with increasing molecular weight [39]; however, they adhere to soil and dust and thus a mobilization might take place if soil and dust particles are removed from the fuel by rain- or washing water [21]. Ellis and Keyse [21] showed that manual washing could reduce the concentration of Benzo(a)pyrene in leaf litter debris. In contrast, washing of leaves from *Quercus ilex* achieved a significant reduction of several metals, but total PAH concentration was not influenced [17].

4.4.2.2 Hierarchical Clustering of PAHs in Urban Leaf Litter

Hierarchical clustering of samples based on their PAH concentration revealed three distinguishable clusters (Figure 4.3). One cluster included all samples without any PAH contamination, a second cluster comprised all samples with a contamination of 1–4 PAHs and the third cluster included the remaining samples with a contamination of 6–7 different PAHs. Interestingly, the highly contaminated group contains no samples from the CC. This area is cleaned in a shorter cycle; leave litter is taken up every second day. Thus, the time of exposure to street dust and exhausts from cars is shorter, possibly reducing the level of pollution. Considering the time of sampling, the samples from calendar weeks 41 and 43 were found more often in the none or less polluted cluster, whereas samples from later collection dates (calendar weeks 45 and 47) were also found in the more highly polluted group. This could be due to rainfall or other environmental conditions that were not recorded in this study.

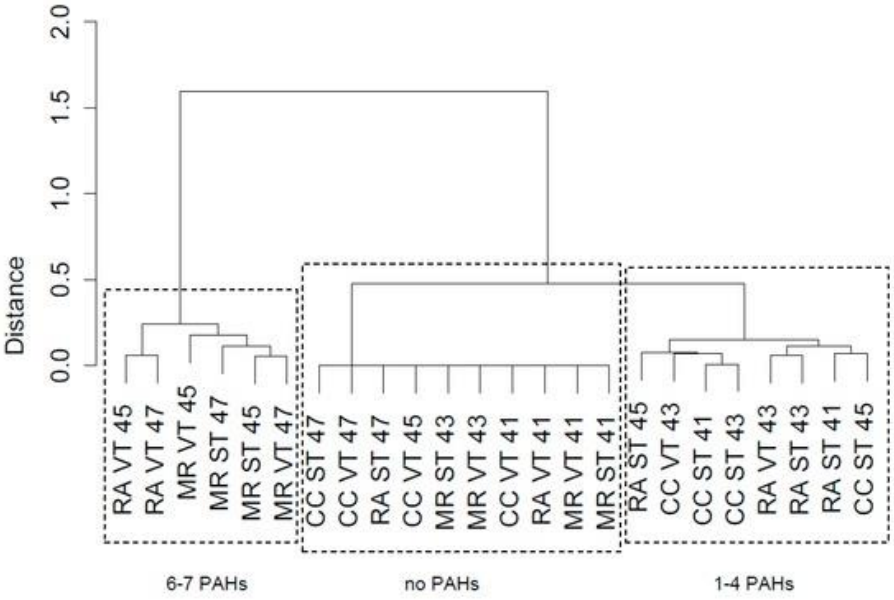


Figure 4.3 *Hierarchical clustering of 24 samples of leaf litter from urban street trees based on their PAH concentration by referring to Euclidean distance. CC, city center; MR, main road; RA, residential area; VT, vacuum technique; ST, suction technique. Numbers indicate calendar weeks during which the sample was taken.*

4.4.2.3 Relevance of PAHs in Urban Leaf Litter for Combustion

Khan et al. [40] reviewed potential problems of biomass combustion in fluidized bed boilers. The authors reported that two PAH forming mechanisms are possible. On the one hand, fragments of the aromatic structures, which were part of the fuel, are emitted. Prior to emission, pyrosynthesis might take place. On the other hand, reactions during the combustion process can lead to the formation of polycyclic compounds. The mechanisms producing PAHs seem to be dependent on combustion operation conditions and metals (e.g., Fe, Cu) may catalyze the synthesis reactions [40].

Investigating pyrolysis of olive residues, Jauhiainen et al. [41] observed increasing PAH formation with the elevation of reaction temperature for compounds with various aromatic rings. However, the yield of light hydrocarbons decreased with increasing reaction temperature. In addition, Naphthalene and Anthracene emissions were rather stable at each temperature and, therefore, did not decompose easily [41]. Finally, air rich conditions diminished the total amount of hydrocarbons produced [41].

Regarding the total amount of PAH emissions, Lee et al. [42] measured a concentration of 25 mg PAH kg^{-1} fuel (comprising 33 different PAHs) when burning coal in an experimental combustion unit with an open fire setting. In contrast, the combustion of several biomass-derived fuels in a small-scale modern pellet boiler led to total PAH emissions of 0.5 to 1.9 mg/kg^{-1} DM fuel [43]. Coal combustion is known to have naturally high PAH emissions [40]. The extent to which PAHs, contained in street leaf sweepings, are destroyed or emitted during combustion must be examined in combustion experiments with boiler technologies, which are well adapted to the biomass feedstock. The complex processes during pyrolysis do not allow such a prognosis to be made.

PAHs are not only emitted, but are also part of ash. Kosnar et al. [39] found significantly higher levels of PAHs in fly ash than in bottom ash and considerably higher values combusting phytomass (agricultural residues) than dendromass. However, Kosnar et al. [39] conclude that PAH concentrations in bottom ash from phytomass still allow the utilization of ash as fertilizer. Fly ash from urban street leaf litter will likely have to be disposed of like the fly ash from other fuels.

4.5 Conclusion

The investigated urban leaf samples were partly contaminated with heavy metals and PAHs. Concentrations of heavy metals were considerably higher than those found in wood, but still below the limiting values of the German standard for non-woody materials. Concerning the investigated organic pollutants, the concentrations of PAHs in the material were lower than expected. There was a clear effect of provenience for both heavy metal and PAH contamination, with the samples from the city center being the least contaminated, whereas samples from main roads and residential areas had higher concentrations of contaminants. A possible explanation for this finding might be the different collection cycles, with the shortest collection cycle occurring in the city center. It is logical that fast collection after leaf fall will reduce contamination with road dust and soil. Hence, if leaves are used for energetic purposes, fast collection is advisable. The effect of collection technique was not always a significant factor, but for As, Pb and Fe, collection with the sweeping technique resulted in significantly higher contamination than the suction technique. Thus, it is advisable to use the suction technique where possible to produce a cleaner material. The washing and subsequent dewatering with the IFBB process proved to be successful in reducing heavy metal contamination in the biomass, especially for As, Cr, Cu, Fe, Mn and Ni. However, these elements will be contained in the wash water or the press liquid, so further research is necessary to investigate the safe disposal of both. A linear regression model was developed with total ash concentration as a useful indicator for heavy metal contamination. Further research is necessary regarding the evaluation and development of more complex models to predict heavy metal and other contaminants more precisely. The urban leaf litter collected in the present study had heavy metal contaminations that would allow for direct combustion. Furthermore, these levels could even be reduced by a washing and dewatering step, which would ensure that heavy metal contamination is well below critical values.

4.6 References

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5. Diskussion

5.1 Verfahren

In der ersten Untersuchung mit dem sauberen Parklaub (Kapitel 2) wurden seine Eigenschaften durch das IFBB-Verfahren [1] untersucht. Für das Straßenlaub in der zweiten Untersuchung (Kapitel 3 und 4) wurde das IFBB-Verfahren anders gestaltet. Da das schmutzige Straßenlaub einen deutlichen Reinigungsbedarf aufwies, wurde eine Waschanlage entwickelt und in der zweiten Untersuchung, vor dem IFBB-Verfahren eingesetzt. Die Ergebnisse beider Untersuchungen wurden miteinander verglichen. Ein wichtiges Merkmal der Waschanlage ist, dass sie sich von der Maischanlage des typischen IFBB-Verfahrens durch ihre Laub-Schmutz-Trennung unterscheidet. Während die Maischanlage des IFBB-Verfahrens für eine saubere Biomasse ohne Reinigungsbedarf geeignet ist und das Maischen in einem geschlossenen Mischer stattfindet, ist die Waschanlage für das schmutzige Laub so entworfen worden, dass die Ausgangsmasse durch die Laub-Schmutz-Trennung gesäubert werden kann. Die Trennung basiert auf einem Schwimm-Sink-Verfahren, wobei der Schmutz durch den Siebkorb nach unten wandert und das Laub im Siebkorb zurückgehalten wird. Das Waschen fand auch nicht im Warmwasser, sondern mit kaltem Leitungswasser statt. Der Pressprozess blieb unverändert, jedoch wurde der daraus entstandene Presssaft in beiden Untersuchungen aufgrund seiner geringen Methanausbeute [2, 3] nicht gegoren.

5.2 Das Verhalten des Laubs in der Waschanlage

Die Beschreibung des Verhaltens des Laubs in der Waschanlage basiert lediglich auf visuellen Beobachtungen während des Waschens im Zeitraum von 5 Minuten. Für eine effiziente Reinigung sollte das Material möglichst auf der Wasseroberfläche schwimmen. Die durch die Seitenkanalverdichter erzeugten Luftblasen hätten das Blatt hierfür in Drehung bringen sollen, damit am Blatt anhaftender Schmutz sich vom Laub trennen konnte. Das in den Waschprozess eingeführte Laubmaterial verhielt sich allerdings anders. Der größte Teil des Materials sank wegen seines hohen Wassergehalts bereits nach wenigen Sekunden auf den Boden des Siebkorbs. Das Laub im mittleren Bereich des Siebkorbs konnte aufgrund der Vielzahl der Luftdüsen bis zur Wasseroberfläche transportiert werden. Die Luftdüsen sorgten auch dafür, dass das Laub sich während des Waschens vielfach an den Ecken und Rändern des Siebkorbs gedrückt wurde. Dazu kam noch eine rasche Sättigung durch das Wasser und die Klumpenbildung des Laubs. Aufgrund dessen war es nötig, die Masse ab und zu per Hand in die Mitte zu bewegen. Wenngleich diese Schwächen in der weiteren Entwicklung technisch gelöst werden müssen, konnte in den vorliegenden Untersuchungen dennoch eine Laub-Schmutz-Trennung realisiert werden. Alle Partikel < 11 mm passierten schon in den ersten Minuten das Sieb und sammelten sich um den Schmutzwasserablasshahn, wo sie zum weiteren Sieb abgeleitet werden konnten.

5.3 Störstoffe

Bei den Störstoffen handelt sich um die Gegenstände, die durch beide Sammelverfahren in der Laubmasse landeten, wie z.B. Steine, Plastik, Metall, Papier, Glasbrüche. Solcherlei Stoffe können den Verarbeitungsprozess teilweise oder komplett verhindern. Da es sich in Kapitel 2 um naturbelassenes Parklaub handelte, waren dort solche Störstoffe nicht zu finden. Gegenüber dem Parklaub hatte das Straßenlaub einen deutlich höheren Störstoffgehalt. Die Laubwaschanlage war für die Trennung von Störstoffen wie Steine, Flaschen, Dosen Zeitungen und Holzstücke nicht geeignet. Deswegen wurden sie bereits bei der Vorbereitung (Auflockerung) zum Waschen aus der Masse entfernt. Kleine Störstoffe (Steine, Glaspartikel, Plastikverpackungen, Zigarettenreste und Flaschendeckel), die bei der Vorbereitung nicht auffielen, wurden nach dem Waschen bei einer optischen Kontrolle aus dem Siebkorb per Hand entfernt.

Nach Herkunftskategorien betrachtet, weist die Hauptstraße (Main road (MR)) im Durchschnitt 0.74 % TM Störstoff auf, das Wohngebiet (Residential area (RA)) hingegen 0.66 % TM (Tab 5.1). Proben aus dem Stadtzentrum (City centre (CC)) hatten hierbei, im Gegensatz zu denen der anderen beiden Herkünfte, geringere Gehalte (0.40% TM). Dieses geringe Vorkommen im Stadtzentrum ist vermutlich durch die oftmalige Reinigungsperiode zu klären. Erntetechnisch gesehen, kann die Hypothese, dass die Kehrmaschine ein stärker belastetes Material liefert, bestätigt werden: der mittlere Wert der Störstoffe der Kehrmaschine (Sweeping technique (ST)) ist fast doppelt so hoch (0.78% TM) wie für die Saugmaschine (Vacuum technique (VT)) (0.46% TM).

5.4 Sediment

Als Sediment wurde das Material (Sand, Kies, Metallpartikel) definiert, welches sich während des Waschens von der Lauboberfläche getrennt, das Sieb passiert und sich um das Ablassrohr gesammelt hat. Die durch 11 mm Sieblochung durchflossenen Laubkrümel waren auch Teil des Sediments. Um den schweren Kies und Sand von leichten Laubkrümeln zu trennen, wurde das gesamte Sediment in ein weiteres Sieb (Bogensieb) eingeleitet.

Tabelle 5.1Menge der Trockenmasse, Störstoffe, Sediment und Presskuchenanteil des städtischen Laubs (% TM) (Daten unveröffentlicht).

	Ausgangsmaterial (Input)	**TM Gehalt**	**Störstoffe**	**Sediment**	**Laubverlust bei Waschen**
Herkunft	**g TM**	**%**	**% TM**	**% TM**	**% TM**
Hauptstraße	4677.81 ± 37.13	27.54 ± 2.34	0.74 ± 0.90	7.58 ± 2.60	0.99 ± 0.62
Wohngebiet	4856.23 ± 36.16	29.33 ± 2.42	0.66 ± 0.86	9.76 ± 2.04	1.10 ± 0.61
Stadtzentrum	2881.36 ± 35.97	36.84 ± 2.98	0.40 ± 0.52	9.51 ± 2.82	1.03 ± 0.92
Sammeltechnik					
Saugmaschine	3440.80 ± 37.56	33.65 ± 3.05	0.46 ± 0.75	6.23 ± 1.84	1.14 ± 0.75
Kehrmaschine	5064.70 ± 34.92	27.81 ± 1.85	0.78 ± 0.86	11.57 ± 2.66	0.94 ± 0.69

Das Bogensieb hielt die schweren Partikel in einer Kammer zurück und die leichteren blieben auf dem gebogenen Sieb zurück. Laut der Tabelle 5.1 unterscheiden sich die Sedimentmengen nach Herkunftskategorien nicht stark. Während das Laub von der Hauptstraße 7.58 % TM Sand und Kies beinhaltet, liegt der Wert in dem Wohngebiet bei 9.76 % und im Stadtzentrum bei 9.51 % TM. Der Unterschied zwischen den zwei Sammelverfahren ist allerding groß. Während das gesaugte Laub einen Wert von 6.23 % TM aufweist, liegt der Wert für gekehrtes Laub etwa doppelt so hoch (11.57 % TM).

Die sich im Sediment befindenden feinen Laubpartikel (Laubkrümel) sind wahrscheinlich auf den Straßen entstanden. Denn die Fahrzeuge könnten mehrmals über sie rübergefahren sein. Auch die Kehrmaschine könnte mit ihrer Metallbürste die Laubmasse zerkleinert haben. Dagegen sollte das Laub auf den Straßen durch das Saugverfahren unbeschädigt aufgenommen worden sein. Gegenüber den Straßen hätten die Grünstreifen entlang der Straßen geringere Mengen an Laubkrümel nachweisen sollen. Da aber in der Methode keine Rücksicht auf die genaue Entstehung der feinen Laubmasse (Laubkrümel) genommen wurde, kann nicht bestimmt werden, worauf sie zurückzuführen ist. Im Allgemeinen machte dieses Material im Sediment sowohl in den drei Herkunftskategorien, als auch in den zwei Sammelverfahren etwa 1.0 % TM aus. Die feinen Laubpartikel wurden als Verlust der Biomasse während des Waschens betrachtet.

5.5 Aschegehalt

Die Aschegehalte haben für die weitere Verwertung organischer Reststoffe eine wesentliche Bedeutung. Aufgrund hoher Gehalte und schwieriger Zusammensetzung der Asche, ist häufig lediglich eine Deponierung des Materials möglich. Da das Deponieren mit hohen Kosten verbunden ist, strebt die IFBB-Technologie an, den Aschegehalt eines Festbrennstoffs möglichst gering zu halten.

Die erste Untersuchung (Kapitel 2) weist darauf hin, dass das Rohmaterial aus der Parkanlage 13.80 % TM Aschegehalt besitzt und nach dem IFBB-Prozess bei 40°C Konditionierung bis auf 12.06 % TM bzw. um etwa 1 % reduziert werden kann. Das städtische Laub, welches in der Waschanlage nur bei 10-12 °C und nur 5 Minuten gewaschen wurde, wies dagegen deutlich höhere Werte auf (Hauptstraße 23.48 % TM, Wohngebiet 30.88 % TM, Stadtzentrum 16.83 % TM). Sammeltechnisch gesehen besitzt die Biomasse des Saugverfahrens 18.17 % TM Asche, wobei der Gehalt des Kehrverfahrens 10 % höherer ist. Daher stand vor der Waschanlage die Aufgabe, aus hochaschehaltigem Laub einen standardmäßigen Festbrennstoff (Aschegehalt ca. 10 % TM) [4] zu realisieren.

Um den Effekt des maschinellen Waschens zu untersuchen, wurde der Aschegehalt des maschinell gewaschenen Laubs mit handgewaschenem Laub verglichen. Der Aschegehalt des Laubs aus der Waschanlage wies gleiche Aschegehalte (10.40 % TM) wie das im Labor handgewaschene Material (10.22 % TM) auf. Damit hat die Waschanlage nicht nur den Aschewert des Ausgangsmaterials um mehr als 13% reduziert, sondern es ist ihr auch gelungen, sich dem DIN-Standard von 10 % TM anzunähern [4]. Die Asche hat sich nach dem Pressen bzw. im Presskuchen weiterhin bis auf 10.05 TM [4] verringert.

5.6 Mineralstoffe

Die Mineralstoffe (Ca, Cl, K, Mg, Na, P, S) des Stadtlaubs unterschieden sich je nach Herkunft. Das im Verbrennungsprozess Schmelzpunkt erhöhend wirkende Ca kommt in unterschiedlichen Mengen vor. Das naturbelassene Laub aus dem Wald weist einen Ca-Gehalt von 0.87 % TM auf [5]. Der Gehalt des Parklaubs liegt bei 2.17 und kann durch Konditionierung bei 40°C und Pressen bis auf 2.13 % reduziert werden. Der Ca-Gehalt des Laubs aus den drei Stadtteilen ähnelt dem des Parklaubs. Während die Materialien von der Hauptstraße (2.97 % TM) und aus dem Stadtzentrum (2.45 % TM) einen Gehalt unterhalb von 3.0 % TM zeigen, weist das Wohngebiet einen 3.19 prozentigen Ca-Gehalt in der Trockenmasse auf. Diese Werte ähneln den Ergebnissen (3.16% TM) von Khalsa et al. [6] Somit liegen alle Werte weit unterhalb des empfohlenen Werts in Höhe von 15-35% TM [7].

Chlor ist das Element, welches vor allem in gedüngten Kulturpflanzen in hoher Konzentration auftritt. Es darf den europäischen Standardwert von 0.10 % für die Brennstoffe aus Nicht-Holzartige-Pellets [4] nicht überschreiten. Der Cl-Gehalt im Parklaub lag im Durchschnitt ohnehin lediglich bei 0.05 %, konnte aber durch IFBB noch bis 0.01 reduziert werden. Dieser Gehalt ist allerdings im städtischen Laub höher. Nach Herkunftskategorien differenziert, besitzt schon das Material aus dem Wohngebiet 0.12% Cl und ist im Laub aus der Hauptstraße doppelt so hoch (0.24%), im Stadtzentrum sogar vervierfacht (0.54%). Sammeltechnisch gesehen sind die Gehalte beim gesaugtem Laub höher (0.36% TM) als im gekehrten (0.25% TM). Ein großer Erfolg ist es, dass die durchschnittliche Chlor-Menge von 0.3 % TM im Ausgansmaterial, durch Waschen bis auf 0.2 % TM verringert wurde. Durch das Pressen fielen die Werte sogar unterhalb des DIN-Grenzwertes von 0.1 % TM.

Das Korrosion verursachende Kalium [8] kommt im Waldlaub mit 0.25% TM [5] und im urbanen Laub mit etwa 0.38 bis 0.48 % TM [9] vor. Untersuchungen von Khalsa et al [6] zeigen auch, dass das städtische Laub 0.14 % TM Kalium besitzt. Das durch den IFBB-Prozess bearbeitete Rohmaterial aus der Parkanlage wies einen 0.62 prozentigen Gehalt auf, der aber durch die Konditionierung bei 40°C und durch das Pressen halbiert (0.36% TM) werden konnte. Die K-Gehalte des Stadtlaubes, getrennt nach Herkunftskategorien und Sammelverfahren, liegen zwischen 0.60 und 0.70 % TM und halbierten sich nach dem Waschen mit kaltem Wasser (10-12°C) auf 0.35% TM. Nach dem Pressen sanken sie sogar bis auf 0.25% TM. Nach Angaben von Obernberger et al. [7] wird K dann als schädlich eingestuft, wenn es in der Biomasse mit mehr als 7.0% vorkommt. Die im Laub gefundenen Zahlen liegen damit deutlich unterhalb dieses Grenzwertes. Der zur Abschätzung einer möglichen Schlackebildung abgeleitete K_2O/CaO-Index lag im Ausgangsmaterial des Parklaubs bei 0.25 und wurde durch den IFBB-Prozess bis auf 0.15 reduziert. Denselben Effekt zeigte auch das Waschen des Stadtlaubs, in dem der Index von 0.20 im Rohmaterial bis auf 0.09 nach dem Pressen reduziert wurde.

Tortosa Masia et al. [10] berichtet, dass die Werte unterschiedlicher Biomassen zwischen 0.2 und 0.9 lagen. Pronobis [11] und Dunnu [12] berechneten 4.1 bzw. 2.4 für verschiedene Holzmaterialien. Der K_2O/CaO-Index, der Indikator des Schlackebildungsrisikos, wurde ursprünglich für fossile Energieträger – Steinkohle entwickelt. Deswegen kann man diesen Index nicht ohne weiteres auf die Biomasse anwenden, da sich diese stark von den fossilen Energieträgern unterscheidet. Außer die Literaturwerte für diesen Index existiert kein standartmäßiger Wert [10].

Wie für die oben erwähnten Mineralstoffe ist auch für Schwefel ein Grenzwert vorgeschrieben. Laut DIN 14961-6:2012 [4] darf der S-Inhalt der Festbrennstoffe aus nicht holzartigen Biomassen einen Wert von 0,1 % nicht überschreiten. Die Werte aus drei Stadteilen zeigen, dass die Biomassen des Wohngebietes (0.12 % TM) und der Hauptstraße (0.14 % TM) den Grenzwert leicht überschreiten. Dagegen ist der Gehalt des Stadtzentrums mit bis zu 0.20 % TM etwa doppelt so hoch. Sammeltechnisch gesehen, hat das Material der Saug- und Kehrmaschine einen etwa 0.15 prozentigen S-Gehalt. Durch das Waschen wurde angestrebt, diesen Gehalt auf das Grenzwertniveau von (0.1 % TM) zu bringen. Es wurden jedoch nur bis zu 0.13% erreicht. Auch der Presskuchen beinhaltete immer noch 0.12% TM Schwefel. Im Gegensatz zu städtischem Laub beinhaltet das Waldlaub 0.08 % S in der Trockenmasse [5]. Auch das Parklaub, welches ins IFBB-Verfahren eingeführt wurde (Kapitel 2), besaß vor dem Prozess 0.08 % TM und im Presskuchen 0.07 % TM Schwefel. Zum gleichem Ergebnis (0.06% TM) kam auch Khalsa et al. [6]. Der aus dem S und Cl-Gehalt ermittelte 2S/Cl-Index, ein Indikator für Korrosion, stellt unterhalb des Wertes 2 ein hohes Risiko dar. Der Index nach Sommersacher et al. [13] sollte über 4, im besten Fall bei 8 liegen. Der 2S/Cl-Index beträgt im unbehandelten Stadtlaub 1.67. Dieses Niveau wurde bereits durch das Waschen auf 4.24 und nach dem Pressen bis auf 7.08 erhöht. Dieser Effekt ergab sich daraus, dass durch die Reinigung ein großer Teil von Cl ausgewaschen werden konnte. Somit hat der Wert des Presskuchens vom Stadtlaub das Niveau von Holz (etwa 8.0) erreicht [13].

Ein Grenzwert für Na ist nicht bekannt. Es kann zusammen mit Cl, S und K eine Rolle bei der Korrosion des Ofens spielen [8]. Na ist meistens in der Asche zu finden und kommt auch in den flüchtigen Partikeln vor. Der Na-Gehalt ist beim Waldlaub 0.01% TM [5] und in den krautigen Materialien 0.1% TM [7]. Ein ähnliches Ergebnis zum Waldlaub zeigt auch das Parklaub (0.03% TM), welches durch das IFBB-Verfahren bearbeitet wurde (Kapitel 2). Das Natrium ist allerding im städtischen Laub (Kapitel 2 und 3) aus der Hauptstraße (0.12% TM) und dem Wohngebiet (0.21% TM) im Vergleich zum Parklaub deutlich höher. Aber das Laub aus dem Stadtzentrum besitzt einen deutlich geringeren Inhalt (0.04% TM) wie das Parklaub. Ein großer Unterschied besteht auch zwischen den Sammelverfahren. Während das gesaugte Laub 0.07 % TM Na aufweist, ist es bei gekehrtem Laub 0.18 % TM. Dieser Effekt könnte damit erklärt werden, dass im Zeitraum der Probennahme in der Stadt Na-Salz gegen Frost gestreut worden war und es sich über die

Kehrmaschine im Laub wiederfand. Alle Na-Mengen verringern sich direkt nach dem Waschen bis auf 0.03 % TM. Ein weiterer Rückgang um 1 % wurde durch Pressen erreicht.

Mg und P kommt im Buchenholz mit 0.04% und im Pappelholz mit bis zu 0.10 % TM vor [8]. Beide Elemente wirken positiv auf den Düngerwert der Aschen. Das Parklaub besaß 0.30 % TM Mg und 0.14 % TM P vor dem Prozess. Durch die IFBB-Vorbehandlung konnten beide Elemente im Parklaub um 0.03 % verringert werden. Im Durchschnitt enthielt das Laub aus der Stadt 0.54 % TM Mg, ging aber durch das Waschen bis auf 0.19 TM % zurück. Nach dem Pressen wurde dieser Inhalt noch mal bis auf 0.16 % TM reduziert. Der mittlere Wert des Phosphors im urbanen Laub lag damit bei 0.14 % TM und wurde über Reinigung bei kaltem Wasser bis auf 0.11 % TM und nach dem Pressen bis auf 0.09 % TM reduziert.

5.7 Brennwert und Ascheschmelztemperatur

Der Brennwert des Laubs von den Grünstreifen der Stadt Kassel lag nach Angaben von Piepenschneider et al. [14] bei 16.98 MJ/Kg TM im Ausgangsmaterial. Dieser Gehalt wurde durch Konditionierung bei 40°C und Entwässerung durch die Schneckenpresse bis auf 20.34 MJ/Kg TM gesteigert. Khalsa et al. [6] dagegen fanden Brennwerte von 20.53 MJ/Kg TM. Der Brennwert des Parklaubs (Kapitel 2) erreichte nach der Vorbehandlung die Literaturwerte in Höhe von 20.0 MJ/Kg TM [14] [6]. Das Ausgangsmaterial städtischen Laubs wies dagegen 17.10 MJ/Kg TM im Durchschnitt auf. Dieser Wert wurde durch den Wascheffekt mit kaltem Wasser bis auf 19.13 MJ/Kg TM angehoben und hat sich im Presskuchen nicht mehr verändert (19.08 MJ/Kg TM). Damit erbrachte das Parklaub (2. Kapitel), welches durch das typische IFBB-Verfahren bei 40°C für 15 Minuten konditioniert wurde, einen höheren Brennwert im Vergleich zum städtischen Laub, das bei 10-12°C temperierten Wasser nur 5 Minuten gewaschen wurde. Allerdings ist zu beachten, dass es sich hier nicht um den in einer Brennkammer gemessen Brennwert handelt, sondern nach Friedl et al [15] die berechnete Brennwertsumme anhand des C, H, N – Gehalts. Daher ist es möglich, dass hier eingegebene Werte etwa 2-3 MJ/Kg TM höher sein können als die Messerwerte in einer dafür geeigneten Brennanlage.

Die Ascheschmelztemperatur des Parklaubs (Kapitel 2) wurde nach DIN 51750 untersucht. Die Ergebnisse zeigten, dass der Schmelzpunkt des Ausgangsmaterials des Parklaubs bei 1233°C liegt und durch das Pressen bis auf 1245°C erhöht wurde. Gegenüber dem Parklaub wurde das Straßenlaub nach Hartmann H. [16] anhand der K, Ca, Mg-Gehalte berechnet. Nach dieser Berechnung wies schon das Rohmaterial des Straßenlaubs (Kapitel 3) eine höhere Temperatur (1434°C) als Parklaub auf. Diese Temperatur konnte bereits durch das Waschen bis 1729°C erhöht werden. Das Pressen des gewaschenen Materials beeinflusste nicht den Schmelzpunkt. Somit blieb die Temperatur bei 1722°C Demgegenüber wurde die Ascheschmelztemperatur des städtischen Laubabfalls bei Khalsa et al [6] nach DIN CEN/TS 15370-1 gemessen. Hierbei lag der Schmelzpunkt des Materials bei 1500°C.

5.8 Schwermetalle und PAK

Die Schwermetalle bleiben überwiegend in der Asche des Festbrennstoffs zurück und kommen in unterschiedlichen Mengen vor. Sie können die Aschequalität negativ beeinflussen, sodass sie nicht als Dünger verwendet werden kann. Asche mit hohem Schwermetallgehalt kann nur deponiert werden. Manche Schwermetalle sind flüchtig und ihre Emission kann nur durch komplizierte Filterverfahren verhindert werden [8]. So wie es für die Mineralstoffe eine Gehaltsbegrenzung gibt, existieren auch für die Spurenelemente Grenzwerte. Während die DIN 14961-6:2012 [4] Höchstwerte für die Elemente vorschreibt (As 1.0 mg/Kg TM, Cd 0.5 mg Kg/TM, Cr 50.0 mg/Kg TM, Cu 20.0 mg/Kg TM, Ni 10.0 mg/Kg TM, Pb 10.0 mg/Kg TM, Zn 100 mg/Kg TM), empfehlen Kaltschmidt et al. [8] zum Teil geringere Werte (As 0.8 mg/Kg TM, Cd 0.5 mg/Kg TM, Cr 8.0 mg, Cu 5.0 mg, Pb 10.0 mg, Zn 100 mg).

Die Spurenelemente waren im Parklaub (Kapitel 2) geringer. Der Wert des Kupfers im Rohmaterial lag bei 7.17 mg/Kg TM und nach dem Prozess im Presskuchen bei 6.90 mg/Kg TM. Die Mn- (RM 128 mg/Kg TM, PK 116.0 mg/Kg TM) und Zn-Gehalte (RM 26.63 mg/Kg TM, PK 24.17 mg/Kg TM) lagen, verglichen mit dem Stadtlaub, bei weniger als der Hälfte.

Während die Konzentration der fünf Elemente Cr, Cu, Ni, Pb und Zn im Ausgangsmaterial von der Hauptstraße am höchsten waren, lagen die Werte im Stadtzentrum am niedrigsten. Das Wohngebiet wies aber höhere Gehalte an As (0.81 mg/Kg TM), Cd (0.18 mg/Kg TM) und Mn (309.0 mg/Kg TM) gegenüber dem Material von der Hauptstraße (As 0.62, Cd 0.15 und Mn 0.15 mg/Kg TM) auf. Im Stadtzentrum kommen auch As (0.26 mg/Kg TM), Cd (0.07 mg/Kg TM) und Mn (86.10 mg/Kg TM) im Vergleich zu Hauptstraße und Wohngebiet am geringsten vor. Der geringe Schwermetallgehalt des Stadtzentrums könnte an der häufigen Reinigung (3 Mal die Woche) liegen. Je kürzer das Laub liegenbleibt, desto geringer ist der Schwermetallgehalt.

Thallium wurde auch im Stadtlaub identifiziert, wobei allerdings von 24 Proben nur in 15 unbehandelten und 13 gewaschenen Proben und in 6 Presskuchen Tl gefunden wurde. Während die Gehalte der ungewaschenen und gewaschenen Materialien bei 0.02 mg/Kg TM lagen, wiesen die Presskuchen weniger als 0.01 mg/Kg TM auf. Genauso wurde auch Quecksilber in nur 10 Proben des ungewaschenen, gewaschenen und abgepressten Materials festgestellt. Alle Hg-Werte (0.02 mg/Kg TM) lagen sowohl unterhalb der DIN-Grenzwerte (0.1 mg/Kg TM) [4] als auch unter den empfohlenen Höchstwerten (0.05 mg/Kg TM) von Kaltschmidt et al. [8].

Innerhalb der Elemente ist Eisen in höchster Konzentration im städtischen Laub vorhanden. Mit 11.99 g/Kg TM wies das Laub aus dem Wohngebiet den höchsten Wert gegenüber dem Material von der Hauptstraße (6.82 g/Kg TM) und Stadtzentrum (2.66 g/Kg TM) auf. Der Fe-Gehalt war bei dem Kehrverfahren (9.73 g/Kg TM) höher als bei dem Saugverfahren (4.58 g/Kg TM). Auch Khalsa et al. [6] berichten darüber, dass das urbane Laub nach der Behandlung 1.2 g/Kg TM Eisen enthielt.

Generell haben die Biomassen beim Kehrverfahren durchschnittlich höhere Schwermetallgehalte. Dieses Phänomen könnte dadurch erklärt werden, dass die Kehrmaschine über ihre Besen und die Saugvorrichtung mehr Metallpartikel von der Straßenoberfläche aufsammeln kann, als nur für gehäufelte Laubmasse geeignete Saugmaschinen. Dadurch, dass die Besen mit Metallkehrbürsten ausgerüstet sind, besteht die Möglichkeit, dass sich auch die abgenutzten Besenpartikel im Laub wiederfinden. Interessanterweise gehen die Gehalte bereits direkt nach dem Waschen stark zurück. Das unbehandelte Laub wurde auf 16 unterschiedliche PAKs untersucht. Von insgesamt 16 Proben konnten allerdings nur in 10 Proben PAKs identifiziert werden. Die einzelnen PAKs wurden nur im unbehandelten Laub untersucht und nur in sehr geringen Mengen gefunden. Die Summe aller PAKs lag im Saug- und Kehrichtlaub bei 0.267 mg/Kg TM. Die Brennstoffe aus verschiedenen Biomassen setzten dagegen bei der Verbrennung im speziellen Ofen 0.5 bis 1.9 mg/Kg PAKs frei [15]. Da für die Festbrennstoffe aus der Biomasse keine Grenzwerte existieren, und die Gehalte im Laub die Literaturwerte nicht überschreiten, kann gesagt werden, dass wegen der PAK-Grenzwerte Festbrennstoffproduktion aus städtischem Laub nicht verhindert werden kann.

5.9 Literatur

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6. Zusammenfassung und Empfehlung

Die Ergebnisse dieser Arbeit zum städtischen Laub und seiner energetischen Verwertung lassen sich wie folgt zusammenfassen:

I. **Vorbehandlung des Laubs durch Waschung**: In einer ersten Untersuchung mit Parklaub wurde festgestellt, dass die Konditionierung alleine den Aschegehalt des Laubs nicht reduzieren kann. Für eine deutliche Reduzierung bedarf es eines Waschvorgangs. Diese Hypothese ließ sich bei einer zweiten Untersuchung mit stark verschmutztem Straßenlaub beweisen. Durch die Reinigung, bzw. Laub-Schmutz-Trennung mit kaltem Wasser, kann eine starke Ascheverringerung realisiert werden. Dadurch wurde die Erkenntnis gewonnen, dass für die Aschereduktion die Reinigung eine wichtigere Rolle spielt, als die Konditionierung mit Warmwasser (40°C).

II. **Störstoffe:** Die Biomasse aus den Grün- und Parkanlagen kann mit Boden belastet sein. Dagegen beinhaltet das städtische Straßenlaub unterschiedliche Störstoffarten in unterschiedlichen Anteilen. Die Anzahl großer Partikel ist gering. Dessen Menge im Stadtlaub war etwa 1.0 % TM. Sie können technisch aus dem Sauglaub sowohl während der Ernte, als auch bei der Sortierung (magnetisch und mit Luftdruck) leicht entfernt werden. Das Sediment in Form von Sand und Kies macht einen erheblichen Teil (etwa 10.0% TM) aus. Sie sind im Kehrichtlaub in hohen Mengen vorhanden, können allerdings durch eine Laub-Schmutz-Trennung aus der Biomasse ausgewaschen werden.

III. **Mineralstoffe:** S- und Cl- Gehalte im Ausgangsmaterial des Parklaubs und im Presskuchen sind geringer als der Grenzwert nach DIN 14961-6.2012-04. Alle anderen Elemente (Ca, K, Na, Mg und P) kamen auch in geringen Mengen vor und lagen mit den Literaturwerten auf gleicher Höhe. Aufgrund der sehr geringen Mengen der Mineralstoffe konnten sie im Parklaub durch die Konditionierung bei 40°C nicht mehr reduziert werden. Der Effekt der Auswaschung durch die Laub-Schmutz-Trennung in der Waschanlage war bei Cl, K, Mg und Na hoch. Dagegen ließen sich Ca, P und S nur schwer reduzieren. Trotz unterschiedlicher Wirkung des Waschens auf Elemente, blieben alle Mineralstoffe unterhalb der Grenzwerte. Der aus den Mineralstoffgehalten berechnete Heizwert sowie die Ascheschmelztemperaturen wiesen akzeptable Werte auf. Das Waschen beeinflusst den Aschegehalt positiv und reduziert ihn bis zum standardmäßigen Wert. Das Laub besitzt generell aufgrund seines hohen Ligningehalts einen hohen Brennwert, der nach dem Prozess weiter gesteigert werden kann. Die Ascheschmelztemperatur hat direkt nach dem Waschen ihren maximalen Wert erreicht. Selbst durch das Pressen konnte dieser Wert nicht gesteigert werden.

IV. **Schwermetalle und PAKs**: Die Werte von Cu und Zn lagen unterhalb der Grenzwerte der DIN 14961-6.2012-04. Die Mn-Gehalte im Parklaub lagen niedriger als die Literaturwerte. Das Waschen beeinflusste den Schwermetallgehalt des Stadtlaubs positiv und deren Gehalt konnte dadurch stark minimiert werden. Im Durchschnitt waren Schwermetalle wie As, Cd, Cr, Cu, Hg, Ni, Pb und Zn im unbehandelten Stadtlaub unter dem Grenzwert der DIN 14961-6.2012-04. Mn und Tl kamen auch in geringen Mengen vor. Dass die Gehalte an Cr, Cu und Ni nach dem Pressen steigen, weist allerdings darauf hin, dass die abgenutzten Anlagenprofile sich im gepressten Material wiederfinden können.

V. **Potenzial:** Der Wassergehalt des Kehrichtlaubs ist sehr hoch und es besitzt in großen Mengen Sedimente. Daraus resultierend lässt sich relativ wenig Festbrennstoffanteil gewinnen. Dagegen beinhaltet Sauglaub eine hohe Trockenmasse und geringere Störstoffanteile. Sein Festbrennstoffanteil ist doppelt so hoch wie der des Kehrichtlaubs. Dieses Material kann sauberer erfasst und gemessen werden, wodurch sein Potenzial geschätzt werden kann. Die bislang nicht verwertete Biomasse hat jetzt aufgrund des politischen Interesses eine Chance, energetisch verwendet zu werden. Die Förderung der Reststoffverwertung bietet eine Entwicklungsmöglichkeit für die städtischen Biomassen. Das energetische Potenzial des Laubs kann bisher nur in Großstädten mit hohem Laubvorkommen wie Berlin, Hamburg und München, anhand jährlich erhobener Daten, berechnet werden. Eine konkrete Berechnung der Energiepotenziale unter Berücksichtigung der aufgewendeten Energiemengen für einzelne Kommunen und Städte steht bislang aus. Nach Angaben kleinerer Städte, kann das Potenzial durch die Integrierung des Laubsackes erhöht werden. Auf diese Art und Weise können kleinere Kommunen ein Laublieferant für den Festbrennstoffhersteller werden. Denn in den Säcken gepacktes Laub lässt sich leicht transportieren.

VI. **Empfehlung:** Die aus dieser Arbeit gewonnenen Erfahrungen und Erkenntnisse prädestinieren weitere wissenschaftliche Untersuchungen, das Laubmaterial aus anderen Großstädten in ähnlicher Größe wie Kassel auf seinen Störstoff- und Sedimentgehalt zu untersuchen. So könnte der Störstoff- und Sedimentgehalt in Höhe von 11.0 % TM aus der Stadt Kassel mit einer anderen Stadt verglichen werden. Des Weiteren kann gesagt werden, dass das Laub nach seinem Anteil im Kehrichtmaterial gründlich untersucht werden soll. Im Fall einer zu geringen Menge, könnte darauf verzichtet werden, es energetisch zu verwerten. Technisch gesehen, ist es möglich, grobe Störstoffe während des Zusammenfegens und Saugens zu beseitigen, sodass der Reinigungsprozess erleichtert werden kann. Im technischen Sinne sollte man sich auch darüber Gedanken machen, wie man das verbrauchte Wasser recyceln kann. Es ist auch wichtig, eine Verwendung für das Sediment zu finden und es wiederzuverwerten.

Aus der Sicht dieser Arbeit und anderen Untersuchungen können keine Daten über die Rentabilität der Festbrennstoffproduktion aus dem städtischen Laub gemacht werden. Daher ist es zu empfehlen, die Wirtschaftlichkeit des durch das IFBB Verfahrens behandelten Laubs zu erforschen. Dabei sollen unterschiedliche Verwertungswege wie Kompostierung, Festbrennstoffherstellung mit Beseitigung über die Müllverbrennung verglichen werden

7. Zusammenfassung

In der vorliegenden Arbeit wurden das relativ saubere Parklaub und das verschmutzte städtische Straßenlaub durch das IFBB-Verfahren nach seiner energetischen Verwertbarkeit untersucht. Das Parklaub wurde durch das typische IFBB-Verfahren verarbeitet. Da das Straßenlaub durch Störstoffe (Sand, Kies, Plastik, Papier, Metallstücke) belastet war, bestand die Notwendigkeit es gründlich zu reinigen. Deswegen wurde der Vorgang der Konditionierung des IFBB-Verfahrens bei 40°C bei Straßenlaub durch den Reinigungsprozess bei 10-12°C ersetzt. Das Pressen in Presssaft und Presskuchen blieb jedoch unverändert. Aufgrund eines hohen Ligningehalts des Laubs wurde nur der Presskuchen untersucht. Der Presssaft wurde nicht berücksichtigt. Das unbehandelte und bei der Verarbeitung entstandene gewaschene Material und der Presskuchen wurden auf ihren Asche-, Schwermetall-, und Mineralstoffgehalt, sowie auf ihre Energiedichte und Ascheschmelztemperatur untersucht und miteinander verglichen.

Der Schmutz aus dem Straßenlaub konnte mit großem Erfolg durch die Waschanlage entfernt werden, sodass der Aschegehalt von 30-40 % TM auf 10-11 % reduziert werden konnte. Somit erreichte das Straßenlaub seine maximale Aschereduktion und konnte nicht mehr durch das Pressen weiter verringert werden.

Sowohl Schwermetalle (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Tl, Zn) als auch Mineralstoffe (Ca, Cl, K, Mg, P, S) kamen im Allgemeinen im Ausgangsmaterial des Park- und Straßenlaubs in geringeren Mengen als DIN EN 14961-2:2011 vor. Nur wenige Elemente im Straßenlaub wiesen einen höheren Gehalt auf. Diese Stoffe konnten bereits durch das Waschen deutlich verringert werden. Die Energiedichte des unbehandelten Laubs lag bei 17 MJ/Kg TM, die durch das Waschen bis 19 MJ/Kg TM erhöht werden konnte. Durch das Pressen konnte diese nicht verbessert werden. Eine Werterhöhung wurde auch bei der Ascheschmelztemperatur beobachtet. Die Temperatur im unbehandelten Material betrug 1500°C, im gewaschenen Laub wurden 1700°C gemessen. Auch hier konnte die Ascheschmelztemperatur im Presskuchen nicht gesteigert werden. Die K_2O/CaO und 2S/Cl Indizes verbesserten sich nach der Verarbeitung deutlich.

Vom Aufwand her, ist das Straßenlaub bei der Verarbeitung arbeits- und kostenintensiv. Betrachtet man es aber genauer, unterscheidet sich gesaugtes Laub durch sein sauberes Vorkommen vom gekehrten Laub. Daher empfiehlt es sich, bei der energetischen Verwertung auf das Kehrichtlaub nicht nur wegen seiner starken Verschmutzung zu verzichten, sondern auch aufgrund seiner geringen Menge. Das Laub in den Parks und auf den Grünstreifen in den Städten kann durch die Laubsaugmaschinen sauberer gesammelt werden. Außerdem lässt es sich in wenigen Schritten verladen und in großen Volumen transportieren. Das ist aber bei vielen 2 m^3 Kehrmaschinen nicht möglich.

8. Summary

In the present paper, relative clean tree leaves collected from a city park and dirty leaves collected from urban streets were analyzed for their energetic usability in the IFBB procedure (Integrated Generation of Solid Fuel and Biogas from Biomass). The park leaves were processed according to the normal IFBB procedure. As the street leaves were negatively affected by contaminations (sand, gravel, plastics, pieces of paper, metallic items), it was necessary to clean them thoroughly. Therefore, the conditioning of the IFBB procedure at 40 degrees for street leaves was replaced by a cleansing process at 10-12 degrees. However, the pressing procedure to separate the press fluid and the press cake remained unchanged. Due to a high lignin content of the leaves, only the press cake was investigated while the press fluid was disregarded. The untreated material and the cleaned material resulting from processing as well as the press cake were examined for their ash, heavy metal and mineral content, energy density and ash melting temperature.

The removal of the dirt in the street leaves during the washing procedure was found to reduce the ash content from 30-40 % DM to 10-11 %. Pressing had no further effect on reducing the ash content. Most of the heavy metals (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Tl, Zn) as well as minerals (Ca, Cl, K, Mg, P, S) occurred only in small quantities in the raw materials from the park and the street as suggested by DIN EN 14961-2:2011. These substances could already be significantly diminished by washing. The energy density of the untreated leaves amounted to 17 MJ/Kg TM, which could be increase up to 19 MJ/Kg TM with washing. Energy density did not improve with pressing. A difference in melting temperature of the ash was observed, with that in the untreated leaves melting at 1500°C and that in the washed leaves melting at 1700°C. The pressing process had no effect on the ash melting temperature. The index of K_2O/CaO and 2S/Cl was enhanced considerably through processing.

Use of street leaves renders the IFBB processing more costly and labour intensive. However, upon closer scrutiny it appears that leaf cleanliness depends on whether they are collected through vacuuming or sweeping. It is therefore appropriate to avoid swept leaves not only because of their heavy contamination, but also because they are normally available only in smaller quantities. Leaves on the grounds of city parks and lawns are regularly collected with vacuums, which results in cleaner leaf materials. Furthermore, these leaves can be collected in just a few steps and can also be transported in large quantities, which is not possible when it comes to the standard 2 m^3 road sweepers.