Composition of waste materials and recyclables

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PhD Thesis
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Preface

The work presented in this PhD thesis was conducted at the Department of Environmental Engineering of the Technical University of Denmark (DTU) under the supervision of Associate Professor Thomas Fruergaard Astrup and the co-supervision of Associate Professor Charlotte Scheutz and Senior Researcher Alessio Boldrin. The work was conducted in the period from October 2012 to January 2016 and the necessary funds were provided by the 3R Graduate School and the Danish Strategic Research Council as part of the IRMAR project (Integrated Resource Management & Recovery; project No. 11-116775).

The thesis comprises a synopsis of the work presented in two published papers, two submitted papers and two manuscripts to be submitted. The papers will be referred to in the synopsis by the names of the respective first author and the paper number written with the Roman numerals I-VI (e.g. Götze et al., I). The papers included in this thesis are:

I **Götze, R.**, Boldrin, A., Scheutz, C., Astrup, T. F., Physico-chemical characterisation of material fractions in household waste: Overview of data in literature. *Waste Management.* DOI: 10.1016/j.wasman.2016.01.008

II **Götze, R.**, Astrup, T.F., Elemental composition of household waste materials: influence of acid digestion methods on multi-element analysis. Submitted to *International Journal of Environmental Analytical Chemistry*

III **Götze, R.**, Pivnenko, K., Boldrin, A., Scheutz, C., Astrup, T. F., Physico-chemical characterization of material fractions from residual and source-segregated household waste in Denmark. To be submitted to *Waste Management*

IV Edjabou, M. E., Jensen, M. B., **Götze, R.**, Pivnenko, K., Petersen, C., Scheutz, C., Astrup, T. F., Municipal solid waste composition: Sampling methodology, statistical analyses, and case study evaluation. *Waste Management*. DOI: 10.1016/j.wasman.2014.11.009

V Pivnenko, K., Olson, M. E., **Götze, R.**, Erikson, E., Astrup, T. F., Chemicals in the paper and board fractions of municipal solid waste. Submitted to *Waste Management*

VI Bisinella, V., **Götze, R.**, Damgaard, A., Astrup, T. F., Influence of waste characterization data in life cycle assessments of waste management systems. To be submitted to *Journal of Cleaner Production*

In this online version of the thesis, **paper I-VI** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from.

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In addition, the following publications, not included in this thesis, were also prepared during this PhD study:

- **Götze R.**, Astrup T. F., 2013. Characterisation of plastic packaging waste for recycling: problems related to current approaches. *Proceedings Sardinia 2013, Fourteenth International Waste Management and Landfill Symposium, Cagliari, Italy*. CISA Publisher.
- **Götze R.**, Astrup T.F., 2014. Optimal acid digestion for multi-element analysis of different waste matrices. *Proceedings of the 5th International Conference on Engineering for Waste and Biomass Valorisation, Rio de Janeiro, Brazil*. Mines d'Albi.

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Summary

As the valorization of waste has become a main objective of modern waste management a variety of waste technologies were developed and the complexity of management systems increased. Maximizing environmental benefits in one part of the system may lead to burdens in another. Environmentally sound decisions in waste planning thus require a holistic and systematic assessment of environmental impacts of different waste management options. Such assessment requires reliable information on the physical and chemical waste properties to model the flows of waste materials and substances throughout the entire waste management system.

The aim of this PhD project was to improve the understanding of factors influencing the quality of waste composition data during waste characterization and application in the environmental assessment of waste management systems.

Reviewing existing waste characterization studies revealed that a large variety of waste characterization approaches and analytical methods has been employed. The most frequently used approach was the chemical analysis of directly sampled waste materials which offers the highest flexibility for waste characterization studies. Direct waste analysis involves several steps to prepare the samples mechanically and/or chemically for final analysis. Not all sample preparation methods are equally well suited for specific waste characterization purposes. The correctness of results and practical feasibility of sample preparation was strongly affected by the material type of the sample and the physico-chemical parameter to be analyzed. For example, studies examining mechanical sample preparation methods suggest that plastic fractions are especially prone to de-mixing effects and that differing mechanical properties within a sample (e.g. plastic and metal) can lead to biased results. In the experimental part of this PhD project the milling of plastics and metals was especially challenging and alternative methods for preparation and analysis should be investigated. Furthermore, chemical sample preparation by means of acid digestion was found to severely affect the element content resulting from chemical analysis. Although the suitability of standardized HF-containing methods can be generally confirmed, these methods led to considerable underestimations of the element content for some combinations of element and waste material. Appropriate selection of acid digestion methods thus needs to take the waste material and the elements to be analyzed into account. The dataset obtained during this PhD project

provides information on the performance for six relevant acid mixtures for nine different waste material fractions and 64 elements and can support the selection of appropriate acid digestion method for future waste characterization studies and the comparison of data across existing studies.

A consistent dataset for 73 physico-chemical parameters in 49 residual and 24 source-segregated Danish household waste fractions was obtained and is now available for future modelling and assessment of waste management systems. The analyzed fractions were selected based on material properties with relevance for potential recycling processes. The physico-chemical analysis revealed chemical differences between residual and source-segregated samples for several fractions. The results for parameters associated with organic matter confirmed the idea of cross-contaminated recyclables in residual waste, whereas the results for heavy metals and trace elements were more complex. For many fractions rather high metal contents were found to be intrinsic properties of the recyclables. For example, the Sb content in PET packaging was 250-270 mg/kgTS. In some cases metal contents in source-segregated fractions were higher than in the respective fractions from residual waste. Rare earth elements (RRE) were quantified in all analyzed material fractions and considerably high concentrations (e.g. the Ce content in ceramics was 72 mg/kgTS) were associated with mineral and soil-like materials. This “natural background” concentrations need to be considered when concluding on the origin of REE which are typically associated with electronic/hazardous waste.

In general the use of primary physico-chemical waste characterization data for the environmental assessment of waste management systems is always preferable because many factors such as fraction definition and sampling point can be controlled. Anyhow, value ranges (as opposed to single values) should be considered due to the possibility of systematic bias (e.g. resulting from specific characterization methods) and “natural” variation. Commonly reported measurement uncertainties are not suitable to capture such effects. Thus secondary data should be considered when deriving uncertainty ranges and more research is necessary to quantify systematic effects of different characterization methods.

Considering the extensive time and costs related to physico-chemical waste characterization it is likely that environmental assessment of waste management systems will continue to draw on secondary data from literature. For some parameters the values reported in literature were found to differ

significantly. The wide range of values in literature for physico-chemical properties of individual waste materials were shown to severely affect the results of the life cycle assessment (LCA) of waste management systems, although the parameters had relatively low sensitivity. This emphasizes that sensitivity alone is not an appropriate indicator to identify critical parameters for LCA modelling. Using the literature value ranges for complete uncertainty analysis physico-chemical parameters contributed substantially to the output uncertainty of the modelling results and were in many cases more important than technology and scenario specific parameters. By selecting well-fitting data from literature the input value ranges could be potentially narrowed. Suggestions for physico-chemical data selection for environmental assessment and related uncertainty analysis are presented. At this point, however, low data availability and the large variety of used waste characterization methods limit the quantification and ranking of influencing factors via statistical data analysis of literature data. Nevertheless, it was found that the regional context of the data origin appeared to be less or equally important than other potential influencing factors (such as e.g. analytical methods, waste management system, natural variation, etc.). To consider the influence of such factors on secondary data but also primary data, LCA of waste management systems should always include a systematic uncertainty analysis for physico-chemical waste properties which needs to be based on both sensitivity and realistic uncertainty ranges for the individual physico-chemical parameters.

Dansk sammenfatning

I takt med at genanvendelse af materialeressourcerne i affald er blevet et primært formål med moderne affaldshåndtering, er nye integrerede affaldssteknologier blevet udviklet og affaldssystemet er blevet stadig mere komplekst.

Maksimering af miljømæssige gevinster i én del af affaldssystemet kan føre til miljømæssige belastninger i en anden del af systemet. Forudsætningen for at der kan tages miljømæssigt afbalancerede beslutninger i relation til affaldshåndteringen er en holistisk og systematisk analyse af miljøpåvirkningerne fra alternative affaldsteknologier. Sådanne analyser kræver relevant information om affaldets fysiske og kemiske egenskaber for at materiale- og stofstrømmene kan modelleres igennem hele affaldssystemet.

Formålet med dette ph.d.-projekt var at forbedre forståelsen af hvilke faktorer, der påvirker kvaliteten af data i relation til affaldets sammensætning samt anvendelsen af disse data ved miljøvurdering af affaldssystemer.

En kritisk gennemgang af eksisterende studier viste en stor variation i metoder til affaldskarakterisering og analyser. Den mest hyppige metode var kemisk analyse af indsamlede affaldsprøver (direkte affaldsanalyse), hvilket giver den største fleksibilitet i affaldskarakteriseringen. Direkte affaldsanalyser inkluderer flere trin i prøveforberedelsen før den endelige analyse. Ikke alle metoder til forberedelse af prøver er lige egnede i relation til affaldsmaterialer. Kvaliteten af resultaterne og den praktiske gennemførlighed af prøveforberedelsen afhang af de specifikke affaldsmaterialer og de fysisk-kemiske parametre, der skulle analyseres for. Eksempelvis viste gennemgangen af studier, at mekanisk nedknusning og håndtering af plastikfraktioner og tilstedeværelsen af forskellige mekaniske egenskaber i samme prøve (fx metal og plastik) kan potentielt føre til forkerte resultater.

Til bestemmelse af en prøves kemiske sammensætning anvendes typisk en oplukning af prøven med syre (syreoplukning). Som en del af ph.d.-projektet blev det vist, at metodevalget her signifikant påvirker de efterfølgende resultater af den kemiske analyse. På trods af at standardiseret metoder indeholdende flussyre generelt bør foretrækkes for en total oplukning, så medførte disse metoder for visse kombinationer af materialer og grundstoffer til en undervurdering af stofkoncentrationerne. Valg af metode til syreoplukning bør derfor ske i nøje afstemmelse med affaldsmaterialet og de relevante kemiske stoffer. Datasættet udarbejdet i dette ph.d.-projekt omfatter data for seks relevante syreblandinger ved anvendelse på ni forskellige affaldsmaterialer og ved analyse af 64 grundstoffer. Dette datasæt udgør et systematisk grundlag for valg af syreoplukningsmetoder i fremtidige studier indeholdende affaldskarakterisering samt for sammenligning af data på tværs af eksisterende studier.

Baseret på en omfattende undersøgelse af materialefraktioner i dansk dagrenovation blev tilvejebragt et konsistent datasæt for 73 fysisk-kemiske parametre for 49 materialefraktioner i restaffaldet og 24 kildesorterede materialefraktioner. Datasættet er tilgængeligt for fremtidige modellering og miljøvurdering af affaldssystemer. De undersøgte fraktioner var udvalgt med primært fokus på materialeegenskaber af relevans for genanvendelsesprocesser. For flere fraktioner viste analyserne signifikante kemiske forskelle mellem samme type material indsamlet via restaffaldet og via det kildesorterede affald. Resultaterne for parametre forbundet med organisk materiale bekræftede, at "forurening" af genanvendelige materialefraktioner kan ske ved indsamling via restaffaldet, hvorimod resultaterne for indhold af tungmetaller og sporstoffer ikke på samme måde var entydige. For mange genanvendelige fraktioner blev det fundet, at forholdsvis høje indhold af metaller kunne relateres til fraktioners iboende materialeegenskaber snarere end forurening fra andre materialer.

PET-emballage havde for eksempel et relativt højt Sb-indhold på 250-270 mg/kg TS. I nogle tilfælde var metalindholdet i de kildesorterede fraktioner højere end i de samme materialefraktioner i restaffaldet. Sjældne jordarter (metaller) blev fundet i alle analyserede materialefraktioner med relativt høje koncentrationer (fx var Ce-indholdet i keramik 72 mg/kg TS) forbundet med mineralske og "jordlignende" materialer. Ved kildesporing af disse sjældne jordartsmetaller (typisk associeret med elektronik/farligt affald) er det således nødvendigt at tage hensyn til disse ”naturlige baggrundskoncentrationer”.

Generelt er brugen af primære affaldsdata ved miljøvurdering af affaldssystemer altid at foretrække, da dette muliggør en bedre kontrol af faktorer som definition af materialefraktioner, prøvetagning og repræsentivitet samt relevans for miljøvurderingen. Under alle omstændigheder bør anvendes intervaller (i modsætning til enkeltværdier), således at risikoen for systematisk bias (fx fra specifikke karakteriseringsmetoder) og naturlig variation minimeres. Almindelige analytiske usikkerheder er ikke tilstrækkelige til at repræsentere usikkerheder forbundet med prøvetagning. Dermed bør sekundære data inddrages i alle tilfælde for at estimere robuste usikkerhedsintervaller.

På grund af relativt store tidsmæssige og økonomiske omkostninger ved fysisk-kemisk karakterisering af affaldsmaterialer er anvendelse af sekundære (data fra andre kilder) mest udbredt ved miljøvurdering af affaldssystemer. For mange fysisk-kemiske parametre blev der fundet en betydelig variation i værdierne i litteraturen. Baseret på intervaller for værdier i litteraturen blev det påvist, at de fysisk-kemiske parametre kan bidrage betydeligt til den samlede usikkerhed af resultater for LCA af affaldssystemer; i mange tilfælde havde disse data større betydning end teknologi- og scenario-specifikke parametre. Ved at vælge passende data fra litteraturen kan denne usikkerhed potentielt mindskes. Den lave tilgængelighed af data og den store variation i metoder til affaldskarakterisering begrænser dog muligheden for at i alle tilfælde at finde egnede data til en specifik undersøgelse. Det blev dog vist, at den regionale oprindelse for affaldsdata ikke nødvendigvis havde større betydning end andre potentielt vigtige faktorer (fx analysemetode, affaldssystem, naturlig variation, etc,). Det anbefales i alle tilfælde at inddrage en konkrete vurdering af de anvendte fysisk-kemiske affaldsdata ved LCA af affaldssystemer.

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Abbreviations

AAS	Atomic absorption spectrometry
AFS	Atomic fluorescence spectrometry
C_{bio}	Biogenic carbon content
C_{bioAnd}	Anaerobic digestible fraction of the biogenic carbon content
C_{fossil}	Fossil carbon content
DL	Detection limit
HCl	Hydrochloric acid
HDPE	High-density polyethylene
HF	Hydrofluoric acid
HHV	Higher heating value
HNO3	Nitric acid
ICP	Inductively coupled plasma
ICP-AES	ICP-atomic emission spectrometry
ICP-MS	ICP-mass spectrometry
ICP-OES	ICP-optical emission spectrometry
LCA	Life cycle assessment
LHV	Lower heating value
LIBS	Laser-induced breakdown spectrometry
MFA	Material flow analysis
MSW	Municipal solid waste
NIR	Near infrared spectrometry
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
RDF	Refuse-derived fuel
REE	Rarer earth elements
SFA	Substance flow analysis
SRF	Solid recovered fuel
WTE	Waste to energy
XRF	X-ray fluorescence spectrometry

1 Introduction

1.1 Background

Managing municipal solid waste has been acknowledged as a key principle for improving public health and environmental protection. Basic measures such as organized waste collection, treatment and disposal, prevent: littering, presence of rodents and insects, the spreading of germs and transfer of harmful waste constituents to water, air and land. Originating from combating infectious diseases in growing urban areas in the 19th century, solid waste management has since evolved to an important discipline supporting sustainable development in the industrialized and developing world (Scheinberg et al., 2010).

New driving forces like climate change and resource scarcity have broadened the objectives of solid waste management. This has led to the development of various treatment, recycling and recovery processes aiming at converting waste constituents into energy or secondary raw materials for the production of new goods. For example, to recover energy from waste a repertoire of different techniques is available today; e.g. waste incineration with heat and electricity recovery, landfill gas recovery, anaerobic digestion and pyrolysis. The recirculation of nutrients to agriculture e.g. via composting and digestion residues from organic waste materials, and the recycling of waste material fractions like glass and metal into new products, substitutes virgin raw materials and thereby avoids depletion of finite natural resources and emissions related to their production. As some of these technologies only refer to particular materials in waste, mechanical sorting processes and separate collection have to be coordinated to manage the material flows appropriately. Advanced solid waste management is thus more about managing resources and large-scale effects than just about preventing direct hazardous effects from waste on a local scale.

Managing resources from waste is also prioritized in the latest European and national legislation. The European Waste Framework Directive (EU, 2008) introduced the Waste Hierarchy defining waste prevention as the most desirable management option, followed by reuse, material recovery, energy recovery, and final disposal. The directive demands all EU member states to implement source-segregation for recyclables and to achieve defined recycling rates, which has recently caused a strategy change also in Denmark where historically waste management has been focusing on energy recovery (The Danish Government, 2013).

These political decisions are based on assumed benefits of material recycling which are not trivial. Focusing on the recovery of one material or substance may come at the cost of another, and emissions avoided at one point in a system may cause an increase of emissions in another place. A key factor influencing the degree to which secondary raw materials from waste can actually substitute primary raw materials is their "resource quality", i.e. their physical and chemical properties. For example, heavy metal and chlorine concentrations in combustible waste materials are used as quality indicators for potential utilization as secondary fuels (RDF) (Ma et al., 2010; Rotter et al., 2004) and have been correlated with emissions from waste incinerators (Astrup et al., 2011; Zhang et al., 2008), thus limiting their application to facilities with well-equipped air pollution control. Nutrients content in organic waste materials is used to assess their potential for replacing mineral fertilizers (Hargreaves et al., 2008) and the risks of pollution related to re-utilizing organic waste on agricultural soils are assessed based on its heavy metal content (Alvarenga et al., 2007; Hansen et al., 2002; Smith, 2009; Tonini and Astrup, 2012). Elevated content of copper, tin and other so called "tramp elements" cause cracks and decrease ductility of steel products, thus limiting usability of metal scrap for certain product types (Björkman and Samuelsson, 2014). Summarizing, the relevant parameters defining the "resource quality" of a waste material depend largely on the particular material type in question, available recovery and remanufacturing processes, and anticipated application.

A systematic assessment and comparison of related environmental benefits and burdens is necessary to maximize the efficiency of complex solid waste management systems. For this purpose, decision-support tools such as substance flow analysis (SFA), material flow analysis (MFA), and life cycle assessment (LCA) have been developed. In combination they present a powerful tool to quantify recovery efficiencies, emissions and environmental impacts based on physical and chemical properties of the waste flows (Arena and Di Gregorio, 2014; Kirkeby, 2006). Thus, the assessment of waste management systems through SFA, MFA and LCA is directly influenced by the quality and reliability of available information on the physical and chemical waste composition. Furthermore, the resource quality is directly linked to physico-chemical properties. Therefore, the quantification of physico-chemical properties of waste materials is of fundamental importance for environmentally sound decisions in waste management planning.

1.2 Objectives

The overall aim of this PhD thesis is to provide a consistent and detailed data set for physico-chemical properties of materials in household waste. Based on this, improvement of the understanding of factors influencing the reliability of waste composition data both during their generation (i.e. waste characterization) and their application in the environmental assessment of waste management systems is anticipated.

The PhD project pursued the following objectives:

- Identify and evaluate importance of waste sampling and characterization methods on key parameters for waste management
- Derive a high-quality up-to-date dataset of the physico-chemical composition of waste materials and recyclables in Danish household waste
- Identify and describe key aspects for the application of waste composition data in environmental assessment
- Provide suggestions to improve current waste characterization practice and the application of waste characterization data in environmental assessment

2 Waste characterization methods

2.1 Introduction

Obtaining waste composition data is a challenging task. As the objectives and design of waste management systems for household waste vary among countries, regions and municipalities, many different methods have been used for obtaining information on the fractional and physico-chemical properties of the waste. Although for some countries technical standard methods exist, no preferred or unanimously supported method is endorsed on the European or international level (Dahlén and Lagerkvist, 2008). From a more generic perspective Brunner and Ernst (1986) have defined three approaches for the analysis of waste:

i) Direct waste analysis, which examines individual samples of waste materials by chemical analysis

ii) Waste product analysis (also referred to as indirect waste analysis), which combines chemical analysis of output materials from waste treatment facilities (typically incineration residues, but also compost or mechanically sorted waste fractions) with mass and substance balance calculations to determine the chemical composition of the input material

iii) Market product analysis, which estimates the waste composition based on national statistics on production and consumption of goods. It is only suitable if the entire national waste flow is in question and therefore it is not further discussed in this thesis.

Both direct and indirect waste analysis require considerable efforts for capturing spatial and temporal variation in physico-chemical waste properties as well as considerable attention to sampling and sample handling (e.g. Gy, 1998; Morf and Brunner, 1998; Petersen et al., 2004). A key advantage of waste product analysis over direct analysis is the minimization of uncertainties because samples of residues from incineration represent larger waste quantities entering the incinerator (e.g. Astrup et al., 2011; Brunner and Ernst, 1986). On the other hand, waste product analysis may provide limited information about individual material fractions and waste flows, as waste product analysis can only provide data for the combined waste input. Instead, direct waste analysis can be used to investigate specific material fractions within a particular waste flow, e.g. plastics in household waste from mixed and/or source-segregated collection. Thereby, direct waste analysis offers more flexibility for research as sampling point and fraction catalogue can be easily adjusted to different research questions.

This advantage of direct waste analysis is also reflected in literature. In a review of 97 publications providing physico-chemical waste composition data Götze et al. (**I**) found that 91 publications and 64% of the provided data were obtained via direct waste analysis. Especially for elements related to organic material such as C, H, N, O, S, P, and K direct waste analysis was preferred over indirect waste analysis. Therefore, the following chapters and the waste characterization activities within this PhD project focus on the direct waste analysis approach.

Direct waste analysis consists typically of the following steps: i) choosing of the sampling point and fractions to be sorted, ii) collecting the waste sample and performing the sorting procedure, iii) reducing the mass and particles' size of material fractions, and finally iv) analyzing the physico-chemical properties. The following chapters 2.2 to 2.5 include a description and discussion of key issues related to these steps.

2.2 Sampling point and fraction definition

The fractional and physico-chemical waste characteristics are closely interlinked. For example, the individual waste material fractions constituting the waste flows have a different energy and heavy metal content (Kost, 2001; Riber et al., 2009; Rotter, 2002). The fractional composition and physico-chemical waste properties are furthermore influenced by many varying aspects such as seasonal variation, regional customs and consumer behavior, local waste collection schemes and their change with time (Boldrin and Christensen, 2010; Dahlén and Lagerkvist, 2008; Matsuto and Ham, 1990; Noehammer and Byer, 1997).

The sampling point for direct waste analyses depends largely on the scope of the investigation and the waste management system in place. Dependent on which collection scheme is in place for the waste flow in question, sampling from central collection points, from households or take-back facilities can be beneficial. Sampling at central collection points is relatively easy to organize and may offer the most suitable sampling point to collect a representative amount of waste materials generated in very small quantities and/or with a large temporal variability such as garden waste and hazardous waste (e.g. Boldrin and Christensen, 2010; Fjelsted and Christensen, 2007). The main advantage of sampling at household level is that different stratification criteria (i.e. influencing factors) can be controlled. This is especially important if the study aims at evaluating the performance of different collections schemes and incentives e.g. for separation of recyclables. Dahlen et al. (2010) list many different stratification factors which are potentially relevant to consider for selecting sampling areas if the evaluation of recycling schemes is anticipated: separately collected materials, full-service or bring system, mandatory/voluntary recycling program, economic incentives, different information strategies, housing type, rural/urban area, season, tourism, private compositing, and others. However, identification and ranking of the most important influencing factors is pending. detailed investigations have found that the effect of socio-economic level and housing type are major influencing factors for the fractional composition of mixed household waste (Edjabou et al. (**IV**); Ojeda-Benítez et al., 2008). Sampling at household level requires a very big logistical effort. The waste sample should be collected without compaction to avoid mechanical stress which could enhance cross-contamination between different material fractions (Dahlén and Lagerkvist, 2008; Sfeir, 1999), thus it may require the employment of additional collection vehicles to the normal fleet.

The scope of the investigation influences the choice and definition of material fractions. Götze et al. (**I**) found that out of 97 reviewed publications only seven dealt with more than 30 distinct waste fractions and 45 did not sort the sampled waste into material fractions at all. The most frequently investigated material categories were mixed waste (49 publications), plastics (44), paper and cardboard (39), combustibles (39) and organic waste (38). Previous physico-chemical waste characterization studies have been focusing typically on rather homogeneous waste types or mixed waste as such. However, an evaluation of a recycling program's efficiency in terms of diverting contaminants and ensuring a high-quality of the recyclables requires physico-chemical composition data for detailed material fractions. Such material fractions need to reflect relevant properties affecting the respective recycling and re-manufacturing processes, or substitution rates for virgin raw materials. It has been reported that it is largely dependent on the individual polymer how well plastic can be recycled and for which application it can be used (Williams, 2013). As discussed in Götze et al. (**III**) significant differences in the physico-chemical properties were found between polymers, but also between different applications like packaging and non-packaging made from similar material (e.g. non-ferrous packaging and non-ferrous non-packaging). Please refer to chapter 3.4 and Götze et al. (**III**) for details.

Other properties can affect the recyclability of waste flows. Plastic colored with the pigment "carbon black" has been reported to be non-detectable for NIR-based optical sorting technology, which is primarily used for mechanical sorting of plastic waste into individual polymers for remanufacturing (WRAP, 2011). As a result black plastic material will end up in the reject of such facilities, will not enter remanufacturing, and thus will not substitute primary resources. Determination of the black plastic content by manually sorting black plastic items within individual plastic packaging fractions revealed the presence of considerable amounts (Table 1). The black plastic content differed for the individual polymer types and packaging made of polystyrene (PS) and polypropylene (PP) in residual waste had the highest black material contents of 34-37% and 28% respectively. Overall, 17% of rigid plastic packaging in residual and 4% in source-segregated waste were found to be black. The housing type did not have any influence on the share of black plastic in the individual fractions and collection type, except for expanded and normal PS.

Table 1: Black plastic content in different hand-sorted plastic packaging fractions from residual and source-segregated household waste from the city of Aabenraa (Denmark) in % of the total amount of the fraction

	Residual waste	**Source-segregated waste**
PET	18.8	0.8
HDPE	4.5	0.9
PP	28.0	6.2
PS	33.8	6.9
expanded PS	36.6	-
no label	8.1	6.2
Total plastic packaging excl. foil	16.6	3.9

The higher black material content in residual waste was mainly due to meat trays which are typically black in Denmark and were excluded from the source-segregation scheme for hygienic reasons. This exclusion caused the lower content of potentially non-recyclable black plastics in the source-segregated stream and thus "upgraded" the separated plastic packaging flow unintentionally. However, an exclusion of meat trays may not obtain the same effect in other geographical contexts, i.e. where meat trays typically have a different color.

Summarizing, the choices made defining the sampling point and the fractions to be sorted will influence crucially what the resulting data can be used for. Ideally, the exact purpose of the characterization and what the data shall be used for should be clear at this point.

2.3 Sorting Procedure

The sorting of fractions can be carried out in different ways. Often “hand-sorting” procedures can include the use of tools or mechanical principles, for example, the sorting of ferrous and non-ferrous metals can be easily achieved by using a magnet (Kost, 2001; Rotter, 2002). Specific materials or items can be sorted out of a material mix (positive sorting) leaving a remaining material fraction behind (negative sorting).

In many studies the waste was initially sieved to ease the sorting. The particle size where the hand-sorting was cut-off varied between 1 and 4 cm (eg. ADEME, 2007; Akinci et al., 2012; Ferrari et al., 2000; LfU, 2003; Prudent et al., 1996; RIVM, 1999; Rotter, 2002). The fine fraction was then not further sorted into individual materials but registered and analyzed as such, introducing a bias for the amount of included material fractions (Dahlén and Lagerkvist, 2008). But sieving also affects the results of the physico-chemical properties of the sorted material fractions if fine particles are excluded. To avoid such biases (Dahlén and Lagerkvist, 2008) recommended that sorting of the entire waste should be anticipated and could be manageable because small particle size fractions such as soil, cat litter, ashes, vacuum cleaner dust are usually disposed in bags. The sorting analysis performed within this PhD project was performed without sieving and confirmed that fractions of small particle sizes were mostly bagged and easily sortable (Götze et al., **III**, Edjabou et al., **IV**).

Dahlén and Lagerkvist (2008) identify moisture and food scraps sticking to their packaging and other recyclables as another error source in relation to the fractional waste composition. However, the spreading of food waste to other fractions in residual waste can hardly be avoided. On the other hand Lebersorger and Schneider (2011) pointed out that some sorting analysis categorized packed food including the packaging as food waste. This was likely done to save time and as some packaging materials have a relatively small weight compared to food waste the related error appears to be minor.

According to Lebersorger and Schneider (2011) the food packaging constituted 8% of the investigated food waste, but the effect of such sorting procedure on the packaging material fractions was not investigated. In Edjabou et al. (**IV**) the effect of the sorting practice on the complete fractional composition of residual household waste was quantified. To do so we separated food waste from its packaging and sorted the packaging items into the respective material fractions. Only small differences in the weight shares of each fraction were observed and statistical analysis revealed that these differences were not statistically significant for any of the material fractions. We concluded that sorting of food packaging with food waste does not significantly influence the fractional composition of household waste. However, the presence of packaging materials, such as plastics and metals in food waste samples influences the fraction's physico-chemical characteristics and thus has to be avoided if physico-chemical analysis is anticipated.

2.4 Mass and particle size reduction

Municipal solid waste is a heterogeneous mixture of many materials with very different properties, thus, large amounts of waste have to be sampled to obtain a representative picture. Different recommendations regarding the initial amount of waste sample have been published, some based on mass (typically not less than 100 kg), some on volume, counts of waste bins or vehicle loads and some on the number of households to be represented (see an overview in Dahlén and Lagerkvist, 2008). In any case, mass reduction is necessary to perform physico-chemical analysis which typically uses only a few milligram of pulverized material. The overall aim of mass and particle size reduction is to obtain a small amount of sample representing the properties of the initial lot as accurately as possible. The theory of sampling by Pierre Gy (Gy, 1998; Pitard, 1993) provides a mathematical description and definition of "representativity". Dahlén and Lagerkvist (2008) summarize and comment on sampling errors defined by Gy (Gy, 1998) in relation to municipal solid waste sampling. An important recommendation is that mass-reduction should be performed by flat-pile splitting instead of quartering cones. In this procedure the waste is spread along a line and split in equally sized increments. Then every second increment is selected for the sample while the other increments are discarded. This procedure may be repeated several times. A homogenization of the waste materials' particle shapes and sizes prior to this step can be achieved by coarse shredding. For the investigations of this PhD project, coarse shredding and flat-pile splitting of up to 40 kg per material fraction was performed to obtain a final sample mass of 0.5-1.5 kg (Götze et al., **III**). This procedure could be performed by a single person and took not more than 1 h per material fraction.

Particle size reduction increases the homogeneity of a sample by i) reducing the particle's diameters, ii) aligning their shapes, and iii) narrowing their particle size distribution. For this task a wide range of different grinding and milling equipment is available. Processing samples consisting of materials with rather similar mechanical properties is beneficial because the most suitable equipment can be selected and de-mixing can be reduced. For example brittle materials can be processed most easily by means of crushers (e.g. jaw crusher) and be pulverized via grinding (e.g. disc and ball mills). Grinding sets such as vibratory disc mills made of different materials (e.g. agate, hardened steel, or tungsten carbide) can be selected to respond to the samples' specific hardness. Instead, soft and malleable materials require blades or cutters, as e.g. in cutting mills. Additionally cooling agents may be necessary for some materials which develop heat due to friction and require rather long processing time. During the preparation of samples to be analyzed for Götze et al. (**III**), continuous cooling of sample material and the cutting mill with liquid nitrogen was necessary for plastic, metal and textile fractions to avoid the melting of the sample materials and damage of the cutting mill by heating.

While the processing of thin-walled non-ferrous and ferrous metal packaging was manageable, ferrous non-packaging metal included metal pieces too thick for the cutting mill (Retsch, SM2000). Instead, we pressed the material to a pellet which was then drilled at different points, and we used the turnings as sample material. This step was, however, very difficult because the sample included a lot of plastic materials which were hardly able to compress. Thus, the pellet partly disaggregated when we started drilling it. Consequently only a small amount of sample material could be obtained and its representativity is somewhat more limited relative to the other samples. Procedures used for classic metal characterization such as melting all constituents to a metal specimen and then cutting samples from its surface could be an alternative, at least for the analysis of metals and metalloids. However, such a procedure would destroy and evaporate all included organic materials, and potentially some volatile elements hindering the determination of C, H, N, O, S and halogen content in the same sample.

For the processing in cutting mills the maximum particle diameter is defined by the mesh size of exchangeable sieves in the outlet, and can be easily adjusted. Usually, stepwise processing of the waste materials is necessary to obtain particle diameters of 1 mm or smaller. The optimal particle diameter for accurate chemical analysis is, however, disputed. Skutan and Aschenbrenner (2012) demonstrated on synthetic plastic and paper samples spiked with metallic materials that comminution to particle sizes <0.2 mm resulted in higher precision but not always better accuracy of analyzed heavy metal contents than milling the samples to diameters <1 mm or <0.5 mm. In fact the results differed between the materials investigated. The authors concluded that insufficient particle size reduction of mixed waste material samples leads to a systematic underestimation of the heavy metal content. On the other hand, Kost (2001), Rotter (2002) and Schirmer (2007) observed selective comminution and de-mixing of certain materials (especially plastics) during the fine milling of waste fractions to diameters <0.5 mm which resulted for some plastic fractions even in a higher variance of the analyzed C and Cl contents than observed in samples milled only to diameters <1 mm. In any case, using smaller mesh sizes than 1 mm increases the time and the amount of liquid nitrogen for sample processing and thus limits the feasibility of waste characterization studies in terms of number of fractions and amount of final sample. The time necessary for such processing depends on the particular material. During the pulverization of 74 different material fractions for Götze et al. (**III**) the processing of plastic and metal fractions in the cutting mill was most time consuming especially for the fine milling step. The successive milling using mesh sizes of 4 and then 1 mm of 0.5-1 kg material took up to 4 hours per sample (excluding periods for resting and cleaning).

Another disadvantage of comminution to very fine particle sizes is the increasing stress on the equipment causing erosion of the milling equipment and thereby potentially an introduction of metallic elements to the sample (Rotter, 2002). Again, it depends very much on the particular material to which extent the milling equipment is eroded. To estimate the contamination from the equipment used during this PhD project, two types of materials and processing procedures were investigated: i) commercial gravel to simulate brittle samples was processed in jaw crusher and a tungsten carbide (WC) disc mill set, and ii) copy paper simulating soft and malleable samples was processed in a shredder and cutting mill. To obtain a “clean” sample as reference point a portion of the gravel was put in a plastic bag, broken into smaller pieces with a hammer and then ground in a vibratory disc mill set made of agate. Several sheets of copy paper were cut with titanium scissors into small pieces. Statistical analysis of the resulting element contents supports the idea that the jaw crusher and tungsten carbide disc mill introduced significant amounts of heavy metals to the sample (Table 2). Especially, the samples treated in the tungsten carbide (WC) disc mill presented 17000% higher Ni contents and 2600% higher Cr contents than the reference sample prepared in the agate disc mill. During the shredding of paper large quantities of Ca appeared to dissipate while Fe and Cr were introduced. For the processing of paper in the cutting mill statistical significance was only found for dissipative effects (for Mg, Sr, P, Ga, Nb). Based on these results we decided to prepare all brittle samples for Götze et al. (**III**), (except for ceramics), with the agate disc mill to minimize contamination.

Table 2: Differences in element contents resulting from the use of crushing and milling equipment (for selected elements) in mg/kgTS and % of the element content of the "clean" sample; "n.s.": not significant difference in ANOVA at α=0.05

	Hard sample material				**Soft sample material**			
	Jaw crusher		**WC disc mill**		**Shredder**		**Cutting mill**	
	Δ [mg/kg$_{TS}$]	*Δ [%]*	*Δ [mg/kg$_{TS}$]*	*Δ [%]*	*Δ [mg/kg$_{TS}$]*	*Δ [%]*	*Δ [mg/kg$_{TS}$]*	*Δ [%]*
Ca	30652	36	-15200	-18	-4957	-7	n.s.	n.s.
Al	-2578	-7	8872	24	n.s.	n.s.	n.s.	n.s.
Fe	4354	40	4274	40	78	41	n.s.	n.s.
Cd	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Cr	n.s.	n.s.	179	2645	2.6	174	n.s.	n.s.
Cu	1.34	31	6.5	150	n.s.	n.s.	n.s.	n.s.
Ni	n.s.	n.s.	777	17344	n.s.	n.s.	n.s.	n.s.
Mn	225	56	53.5	13	n.s.	n.s.	n.s.	n.s.
Pb	-1.02	-13	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Sb	-0.04	-25	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Zn	6.9	26	11.5	44	n.s.	n.s.	n.s.	n.s.

These results indicate that the choice on final particle size and milling equipment is a very complex task which is influenced by many factors, which still need to be understood better. Concluding from the activities in this PhD project we can only emphasize that this choice should be based on the sample material, but can also depend on the element to be analyzed. Furthermore, the extensive time needed for appropriate mass and particle size reduction must be considered when planning waste characterization studies.

2.5 Physico-chemical analysis

2.5.1 Purpose and techniques

Physical and chemical parameters of interest for waste characterization range from fuel characteristics to leaching behavior and depend very much on the purpose of the study. This PhD project focused on the total content of energy, ash and elements, i.e. CHNO, nutrients, halogens, metals and metalloids. For the determination of the content of different elements a compendium of measurement techniques exists and providing a full list of all is beyond the scope of this project. Thus the following chapters focus on methods which have been previously used for waste characterization purposes.

2.5.2 Energy and ash content

The energy content of waste materials can be expressed as the higher and the lower heating value (similar to the gross and net calorific value). The difference between the higher and lower heating value is the enthalpy (latent heat) of the vaporization of water, which is created during the reaction of hydrogen present in the solid material and oxygen in the air. The higher heating value (HHV) thus assumes that all water condensates within the system and the related energy is put into use, while the lower heating value (LHV) is the net energy that can be put into use in an open system which the water exits as vapor. The HHV can be measured based on the combustion of a portion of dried solid sample in an oxygen-filled bomb calorimeter (e.g. CEN, 2006), while the LHV needs to be calculated based on HHV and the content of hydrogen in the dry sample. Alternatively empirical equations approximate the LHV based on the content of water, C, H, N, O, S and halogens (Hulgaard and Vehlow, 2011; Kost, 2001; Schwanecke, 1976). Both values can be reported based on wet, dry or ash free sample weight. In the existing literature there is little agreement on which of the two values should be preferably provided. Götze et al. (**I**) found that the HHV was just slightly more frequently reported (366 database entries) than the LHV (341 database entries).

For metal samples the determination of the HHV with enriched oxygen atmosphere is misleading. As reported by Grosse and Conway (1958) the oxidation of metals in an oxygen atmosphere releases considerable amounts of heat. This reaction is supported by the large surface-to-volume ratio in finely milled samples. The conditions in existing thermal waste treatment processes will not promote this reaction, at least not to its full extent. Thus the measured HHV of metal samples is of no practical use for waste management technologies. Additionally, the procedure is very wearing on the employed calorimetric equipment. In the reviewed literature the heating value of metal samples was most frequently reported as “0” or below 0.1 MJ/kgTS (Götze et al., **I**). These values are likely based on the assumption that metal waste fractions are not combustible. Nevertheless, variable amounts of organic materials can be included in metal fractions which are easily combustible in thermal waste treatment processes. To estimate the heating value associated with the organic material content in metal fractions we used the empirical equation of (Schwanecke, 1976). Table 3 presents the results for the HHV of metal waste fractions obtained via the experimental method and via calculation based on the CHNOS content. The organic matter content for all metal waste fractions from residual waste resulted in HHVs (and LHVs) larger than 0.1 MJ/kgTS. Especially the non-packaging metal fractions had a considerable energy content associated to a large organic material content (Götze et al., **III**). Thus, the determination of the organic matter composition and associated energy content via calculations is important for the appropriate characterization of metal fractions from residual household waste.

Table 3: Mean values an standard deviation for the HHV [MJ/kgTS] of metal waste fractions in household waste measured by means of an oxygen-bomb calorimeter and calculated based on C, H, N, O, S contents (equation by Schwanecke, 1976); “SS”: source-segregated, “n.a.”: not analyzed

Metal waste fraction	Measured			Calculated		
metal packaging - non-ferrous	27.20	±	0.24	4.38	±	0.28
metal packaging - ferrous	8.19	±	0.25	1.27	±	0.99
metal packaging - aluminum foil	25.11	±	0.14	5.09	±	0.13
non-packaging metal - ferrous	n.a.	±	n.a.	9.43	±	0.70
non-packaging metal - non-ferrous	25.57	±	0.46	23.83	±	2.76
(SS) metal packaging - non-ferrous	28.49	±	0.02	0.65	±	0.09
(SS) metal packaging - ferrous	7.85	±	0.61	0.78	±	0.06

The ash content of waste samples is the remaining solid after burning a portion of the dried sample at temperatures higher than 500 °C for a defined period of time. However, different temperatures have been used for waste characterization purposes. Götze et al. (**I**) found that the majority of publications used a temperature of 550°C, which is recommended by several standard methods (e.g. CEN 14775, CEN 15403 and US EPA method 1684) for waste-derived fuels and biomass characterization. Others used high temperatures between 815°C and 950°C, which were prescribed by standardised methods for coal analysis (e.g. ISO 1171, ASTM D3175), but as biomass and waste have a higher content of inorganic but volatile salts (which evaporate at such high temperatures) methods designated for coal analysis systematically overestimate the VS content, thus underestimate the ash content of waste (CEN, 2009). For the ash content determination of ferrous metal samples, we found that the mass of the sample appeared to slightly increase during the treatment, resulting in ash contents slightly larger than 100% (Götze et al., **III**). This could be due to partial oxidation on the particle surfaces.

2.5.3 Carbon, hydrogen, nitrogen, oxygen and sulfur

For the simultaneous analysis of the content of C, H, N, O and S modern full-automated systems based on sample combustions are available which are very time-efficient. Such analysis was most frequently used for determination of C, H and O contents in previous waste characterization studies and accounted for 83%, 100% and 83% of experimentally obtained data in the reviewed literature (Götze et al., **I**). However, for the analysis of individual elements many different and/or less-advanced methods are available and have been used. Alternative methods for C were total organic carbon analyzers (TOC) suitable for solids and approximation via volatile solids (11% and 6% of the publications). For N determination full-automated elemental analysis (52% of the publications; 82% of data), and the Kjeldahl method (48% of publications; 18% of data) have been used. The comparatively low share of data obtained with the Kjeldahl method, reflect the extensive time required for this procedure. For determination of the S content three methods have been reported: i) ICP after acid digestion (46%), ii) elemental analysis (40% of publications), and iii) ion chromatography (IC) or titration after combusting the sample and absorbing resulting SO_2 in a solution (14%). A clear disadvantage of using full-automated elemental analyzers for determining the S content is the relatively high detection limit compared to the alternative methods.

2.5.4 Halogens

The halogen content is an important fuel characteristic due to formation of corrosive and toxic compounds during the combustion (e.g. HCl, chlorinated furans and dioxins). For the determination of the contents of Cl, F and Br the solid samples typically need to be decomposed. This can be achieved for example by combustion. Recent standardized methods use the combustion in the oxygen-bomb calorimeter during heating value determination (e.g. CEN, 2006), enabling time efficient analysis of fuel parameters. During the bomb combustion the halogens are released as gaseous emissions and then absorbed in an absorbing liquid which can be analyzed subsequently via ion chromatography (IC) or titration. However, also open combustion methods such as the Schoeninger flask combustion (e.g. European standard EN 14582) and combustion in muffle furnaces were reported (Ma et al., 2010). Other alternative methods include additional modules for Cl determination via fully automated systems for CHNOS analysis (e.g. Macro Cube, Elementar Analysesyteme GmbH) and non-destructive measurement techniques like X-ray fluorescence analysis (XRF). Combustion via oxygen bomb or Schoeniger flask followed by analysis of the absorbed halogens in the liquid phase via IC was the dominant experimental method for Cl determination, used by 63% of the publications (i.e. 55% of the experimental data) (Götze et al., **I**). Ma et al. (2010) compared different combustion-based methods for chlorine determination and found that Cl determination via bomb combustion yielded in 20% lower Cl contents in the analyzed MSW and RDF samples than via alternative methods such as water extraction for organic waste samples and Schoeninger flask combustion for plastic samples. Another method comparison revealed that for the analysis of plastic fractions non-destructive XRF measurements resulted in systematically lower Cl contents than combustion-based methods, while the methods provided similar results for analysis of paper and organic waste (Schirmer, 2007). These results suggest that the specific material matrices and chlorine species respond differently to the available analytical methods. Furthermore, Ma et al. (2010) argue that distinction of different Cl species can be important as their thermal behavior during the waste incineration differs. However, these transformation processes are at this point not well enough understood to justify such distinction during routine waste analysis.

An alternative to the sample destruction by combustion is destruction by concentrated acids; 25% of the reviewed publications (i.e. 27% of the data) used ICP technologies after destruction of the solid samples via acid digestion (Götze et al., **I**). For the determination of F and Br contents in waste materials the ICP-based approach was the most frequently reported method (limited number of data available). However, literature on analytical chemistry has reported that F content determination is not possible with ICP-MS and that generally accurate halogen analysis via ICP is difficult (Horiba Scientific, n.d.; Pröfrock and Prange, 2012). Thus, an incorrect reporting of analytical methods in the reviewed waste characterization studies cannot be precluded. Furthermore, ICP-based determination of Cl and F contents is not possible if hydrochloric acid (HCl) and hydrofluoric acid (HF) shall be used for the sample decomposition.

2.5.5 Mercury

Mercury is a very toxic and volatile metal, which typically occurs in extremely low concentrations. Due to these special properties, different techniques have been developed and have been used for waste characterization purposes: 41% of the data from direct waste analysis of Hg were measured using atomic fluorescence spectroscopy (AFS), 20% using hydride-based atomic absorption spectroscopy (AAS), and 8% using cold vapor AAS (Götze et al. **I**). All these measurement techniques require liquid inputs and thus destruction of the solid sample by acid digestion. Alternatively full-automated Hg analyzers have been developed, which thermally decompose the solid samples and separate Hg from the other formed gas constituents via amalgamation before its detection (US EPA, 2007). Only 3% of the reviewed literature data were obtained using such full-automated options.

2.5.6 Metals and metalloids

For the determination of metal and metalloid contents a large repertoire of sophisticated measurement techniques has been developed, such as atom absorption spectroscopy (AAS) and inductively coupled plasma (ICP) combined with atomic emission spectroscopy (AES), optical emission spectroscopy (OES), and mass spectroscopy (MS). Modern ICP-based technologies offer possibilities for the simultaneous determination of many elements at once and thereby require dramatically less time if many elements and samples shall be analyzed. Classic approaches such as flame-AAS, graphite-AAS, hydride-AAS, ICP-AES, ICP-OES, and ICP-MS require the dissolution of the solid samples in concentrated acids and dilution of the resulting liquids prior to the measurement. More recently developed techniques such as X-ray fluorescence analysis (XRF), but also novel sampling techniques for ICP-MS such as laser ablation (LIBS) or spark-AES and spark-OES can be applied directly on the surface of homogenized solid samples. According to Götze et al. (**I**) the most frequently used analytical methods for waste characterization purposes were classic inductively coupled plasma (ICP)-based techniques (on average 71% of publications; 59% of data) and atomic absorption spectroscopy (AAS) with flame atomizers (22%

of publications, 28% of data). X-ray fluorescence analysis (XRF) was only used in one study to analyze Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn, contributing between 3% and 10% of the respective datasets from direct waste analysis. Consequently, the majority of available data on the metal and metalloid contents of waste material rely on the assumption that the analytes have been completely (or sufficiently) transferred to the liquid phase resulting from acid digestion of the solid samples. However, little attention has been paid to the selection and appropriate reporting of acid digestion methods (Götze et al., **I** and **II**).

2.5.7 Acid digestion methods

During this PhD project extensive work has been done to improve the understanding of acid digestion methods in relation to waste characterization. For this purpose six acid digestion methods have been tested on nine different waste materials for the multi-element analysis of overall 64 elements (61 metal and metalloids, P, S, and Se). See Götze et al. (**II**) for a more detailed method description. It was found that existing waste characterization studies have used various acid mixtures for the analysis of MSW fractions. Although standardized methods for the characterization of waste exist (e.g. CEN, 2002; US EPA, 1996; US EPA, 2007), very few studies have explicitly referred to such standard methods. Consequently, a direct comparison of results across studies is very questionable. Furthermore very few waste characterization studies have used HF for the sample digestion, although HF is the only acid capable of decomposing siliceous material. The detailed investigation of Götze et al. (**II**) generally confirmed that for most elements the HF-containing standard methods resulted in higher element content than HF-free methods.

However, some elements in some waste materials presented considerably better recovery with HF-free methods, e.g. As in paper and cardboard, and composites, and P in paper and cardboard, plastic and metal. The results indicated that using any other digestion method than Aqua Regia (method B) for the analysis of As in paper and cardboard leads to a substantial underestimation of the As content by at least 75% (Table 4). For the analysis of combustible waste the HF-containing European standard method (D) EN 13656 (CEN, 2002) performed for most elements worse than the other tested methods. Consequently, the best performing acid digestion methods is a function of the respective waste material and element(s) in question.

Table 4: Arsenic (As) recoveries of the tested acid digestion methods (A-F) relative to the highest result obtained for each waste material; “n_{sig}”: statistical significance; “$n_{<DL}$”: indicates not quantifiable element-material combinations; A: HNO_3 (US EPA, 2007); B: Aqua Regia (HNO_3, HCl); C: HNO_3, HCl, HF (US EPA, 1996); D: HNO_3, HCl, HF (CEN, 2002); E & F: material dependent

Waste material	**n_{sig}**	**$n_{<DL}$**	**A**	**B**	**C**	**D**	**E**	**F**
Food Waste			0.51	0.50	0.94	1.00	0.35	0.26
Gardening Waste	sign		0.88	0.87	1.00	0.96	0.77	0.69
Paper & Cardboard Waste	sign		0.01	1.00	0.17	0.25	0.01	0.01
Composite Waste	sign		0.02	1.00	0.19	0.20	0.02	0.02
Plastic Waste	-	<DL	-	-	-	-	-	-
Combustible Waste	sign		0.99	0.68	1.00	0.21	0.55	0.81
Metal Waste	sign		0.31	0.99	0.90	1.00	0.74	0.79
Glass Waste	sign		0.50	0.50	1.00	0.88	0.63	0.71
Inert Waste	sign		0.34	0.35	1.00	0.88	0.93	0.95

The dataset attached to Götze et al. (**II**), quantifies the differences between the tested acid digestion methods for each element and material (as for As Table 4 for an example) and can thus provide a comprehensive basis for determining the most suitable acid digestion method for a specific waste material and set of elements in question. While matching different acid digestion methods to individual material samples is manageable, the employment of a single acid digestion method for all elements is likely, due to practical and economic constraints. The obtained dataset could also be potentially used post-analysis to obtain a better estimate of the total element content of individual element-material combination and to support comparison across different studies using different acid digestion methods.

3 Physico-chemical properties of material fractions from household waste

3.1 Introduction

To derive a consistent dataset on the physico-chemical composition of Danish household waste 49 fractions from residual waste and 24 fractions from source-segregated waste were investigated. The sampled waste was generated by 100 households in a single-family housing area in the Danish city Aabenraa within a two-week period. Further details on the sorting and the fractional composition are provided in Edjabou et al. (**IV**) and Götze et al. (**III**). The sorted fractions were dried, mass and size reduced and finally analyzed for the contents of 71 elements, HHV, LHV and ash content (details see Götze et al., **III**). The acid digestion methods were selected for each material type individually based on the result of Götze et al., (**II**). The entire dataset (including mean values, standard deviation, number of replicates, number of replicates below the detection limit, and detection limits) is available in the supplemental material of Götze et al. (**III**). The following chapters are organized by material types to summarize important aspects for their valorization and key findings from the performed physico-chemical characterization and literature review (Götze et al., **I** and **III**). Throughout this thesis the material fractions in Table 5 are followed.

Table 5: Material types and waste fractions analyzed for Götze et al. (**III**)

Material type	Analyzed waste fractions
Organic waste	Animal-derived food waste; vegetable food waste; plant material; woody plant material; humus; animal excrements from dogs; animal excrements from cats; animal bedding
Paper and cardboard waste	Magazines and advertisement; newsprint; office paper; books; tissue paper; other paper; cardboard and paperboard; paper and cardboard composites
Plastic waste	*Plastic packaging:* PET; HDPE; PP; PS; expanded PS; resin identification code 7; no polymer resin identification code; plastic foil; metal-plastic laminate; *Non-packaging plastic:* PET; PP; LDPE; no resin identification code
Metal waste	*Metal packaging:* ferrous; non-ferrous; aluminium foil; *Non–packaging metal:* ferrous; non-ferrous
Glass waste	*Glass packaging:* clear, green, brown; *Non packaging glass:* kitchen and table ware glass; other/special glass
Combustible waste	Sanitary products; textiles, leather and rubber; wood; vacuum cleaner bags; other combustibles
Inert Waste	Ceramics; ashes, cat litter; gravel, sand and stone; other non-combustibles

3.2 Organic waste

Organic waste is easily biodegradable and contains valuable nutrients. Organic waste management options include biogas production via anaerobic digestion or composting. In both cases solid outputs are applied on land to recirculate the nutrients. Compost additionally improves the soil texture and can thereby promote higher crop yields. On the other hand, the application of organic waste fractions or organic waste treatment residues on land can introduce heavy metals to the soil. To minimize heavy metal accumulation many European member states have implemented regulations for waste-derived fertilizers (e.g. compost) limiting the concentrations of Cd, Cr, Cu, Hg, Ni, Pb, and Zn (Barth et al., 2008). Nevertheless, environmental impacts can result also from other metals. To assure sufficient quality of organic waste materials for such purposes, monitoring of heavy metal contents as well as the identification and separation of carrier materials is important. Lately special attention has been paid to food waste and its prevention (e.g. Lebersorger and Schneider, 2011). However, the physico-chemical characterization of total element contents is less interesting in this context.

In line with the characterization activities for Götze et al. (**III**) eight organic samples, consisting of two food waste and six gardening waste fractions (including animal excrements), were analyzed. An overview on selected properties of food and gardening waste is provided in Table 6.

Table 6: Selected physico-chemical properties of the analyzed organic waste fractions (Götze et al., **III**) and as reported in the reviewed literature (Götze et al., **I**)

		Food waste		**Gardening waste**	
	Unit	**Analyzed fractions**	**Literature**	**Analyzed fractions**	**Literature**
N	%TS	2.0 - 4.4	0 - 12.2	1.2 - 2.9	0.1 - 3.4
P	mg/kgTS	2209 - 11782	489 - 30455	991 - 98988	21 - 15900
K	mg/kgTS	4729 - 10957	0 - 41800	6181 - 13852	161 - 27300
Cd	mg/kgTS	0.06 - 0.09	0 - 7.30	0.16 - 1.67	0.11 - 10.85
Cr	mg/kgTS	4.5 - 14.1	0 - 952	7.0 - 38.9	4.5 - 188.7
Cu	mg/kgTS	5.1 - 16.8	0 - 1168	20.5 - 80.9	0.2 - 1238
Hg	µg/kgTS	5.9 - 9.2	0 - 6250	6.6 - 48.8	0 - 2170
Ni	mg/kgTS	11.0 - 11.5*	0 - 162	4.0 - 12.1	1 - 45.6
Pb	mg/kgTS	0.82 - 2.00	0 - 667	2.0 - 12.8	0 - 255
Zn	mg/kgTS	39 - 57	8 - 931	68 - 940	0 - 696

The results of the physico-chemical analysis revealed significant differences among the fractions with respect to many elements. Key parameters for utilizing organic waste fractions as a fertilizer-substitute are the N, P, and K content. The fractions *animal-derived food waste* and *animal excrements from cats and dogs* had significantly higher P contents than the other organic fractions analyzed (Figure 1).

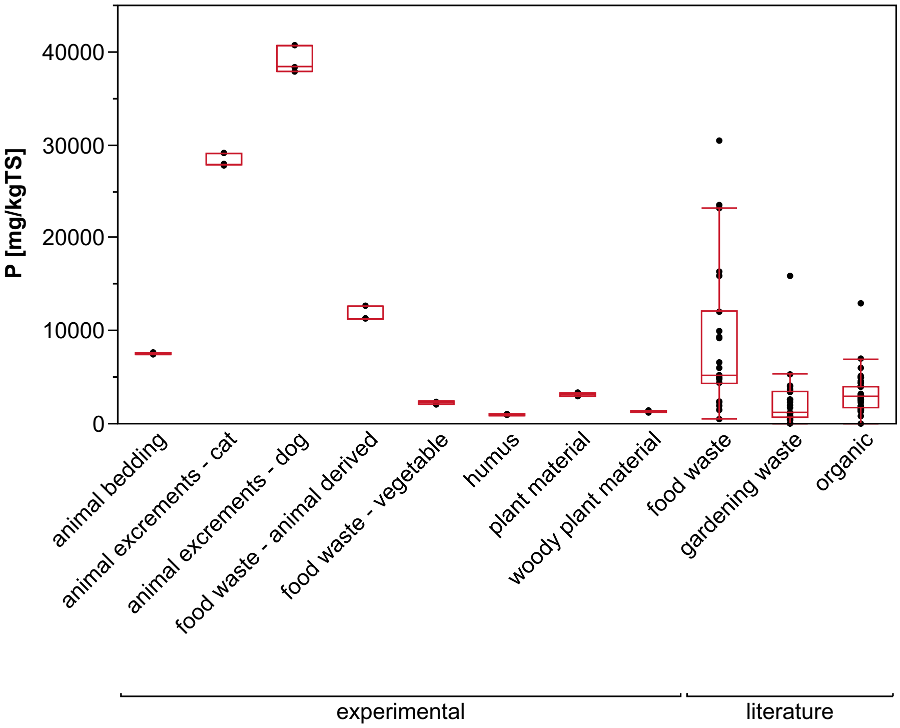

Figure 1: Boxplots of phosphorous concentration measured in organic waste fractions (Götze et al., **III**) and values from reviewed literature (Götze et al., **I**) for food waste, gardening waste and mixed organics

Furthermore, these P contents were in the upper quarter of the literature dataset for food waste and similar or higher than the maximum reported for gardening and mixed organic waste. *Animal-derived food waste* had also clearly higher contents of N and K than *vegetable food waste*. These N and K concentration fit with the highest 10% of the literature dataset. Thus the presence of such fractions will crucially determine the overall P content of organic waste. The sample *plant material* which also included substantial amounts of fine and inert material had significantly higher contents of Cu, Cr, Fe, Hg, Mn, Ni and W than found in most of the other samples. For many of these elements the sample *humus* had second highest or comparable concentrations. Additionally, *humus* had significantly higher Mo and V contents. We concluded that the presence of many heavy metals in the analyzed organic waste materials are associated with soil-like materials, which are natural and are thus of little concern for nutrient recycling. Another interesting finding was that *animal bedding* presented an up to 14 times higher Sb content than the other organic fractions, possibly resulting from preservatives in the included wood chips. *Animal-derived food waste* had three times higher Sn content than *vegetable food waste*. Compared to earlier characterization studies on organic waste materials we found relatively high levels of Al, Fe and Mn at the level of the 75th percentile or in the higher range of the literature dataset (Götze et al, **I**). In contrast the concentrations of Cd, Hg, Mo and Pb were comparatively low; the Cd, Mo and Pb concentrations are comparable to the lowest 10% of the respective datasets and the Hg concentrations were 4 times smaller than the 25th percentile.

3.3 Paper and cardboard waste

Paper and cardboard consist mainly of cellulose which has a high carbon content, and is easily combustible and biodegradable. Paper and cardboard waste can thus potentially function as secondary fuel and as substrate for anaerobic digestion or fuel production via thermo-chemical conversion processes. On the other hand, material recycling of paper and cardboard is widely established. The key component for the recycling of paper and cardboard are the contained cellulose fibers: 57% of fiber used in the paper industry originate from recycled paper and cardboard (Grossmann et al., 2014) and about 38% of recovered paper originates from households (Baeyens et al., 2010a). However, due to its biodegradability, separation of paper and cardboard from moisture and food scraps is crucial to maintain good quality. The paper quality depends on the fibers' strength and length, which are reduced during each remanufacturing cycle. Thus fibers can be recycled only 4 to 8 times (Baeyens et al., 2010a; Martens, 2011). In complex process chains (e.g. flotation, hydro-cyclones and de-inking) the fibers are separated from unwanted constituents that are introduced by the paper product itself (e.g. printing inks, mineral particles) or during its use and subsequent collection (e.g. food scraps and leftovers, sand, glass) (Grossmann et al., 2014). Heavy metals and other contaminants are transferred to the deinking-sludge (Baeyens et al., 2010a).

In line with the characterization activities for Götze et al. (**III**) and Pivnenko et al. (**V**) 29 samples from residual and 28 samples from source-segregated paper and cardboard waste were analyzed. An overview on selected properties of paper and cardboard waste is provided in Table 7.

Table 7: Selected physico-chemical properties of the analyzed paper and cardboard waste fractions (Götze et al., **III** and Pivnenko et al., **V**) and as reported in the reviewed literature (Götze et al., **I**)

		Analyzed samples		Literature
	Unit	Residual	Source-segregated	
LHV	MJ/kgTS	10.2 - 23.3	10.9 - 19.9	6.7 - 23.0
ash	%TS	3.9 - 39.5	4.8 - 34.2	0 - 35.4
C	%TS	32.1 - 51.5	33.7 - 48.8	30.2 - 53.4
Ca	mg/kgTS	5025 - 124,900	5552 - 112,470	0 - 101,000
As	mg/kgTS	0.9 - 16.7	0.9 - 3.3	0 - 35
Cd	mg/kgTS	0.05 - 6.12	0.05 - 0.32	0 - 11
Cr	mg/kgTS	0.7 - 90.0	1.3 - 22.6	2.5 - 292
Hg	µg/kgTS	<2.4 - 46	<2.4 - 269	0 - 16,160
Pb	mg/kgTS	0.8 - 36.4	0.7 - 28.8	0 - 316
Ce	mg/kgTS	0.5 - 9.1	0.6 - 10.3	no data

As the fibers are combustible the ash content indicates the content of non-recyclable constituents. The highest ash contents (about 30% TS) were found in *magazines and advertisements*, and *books* from both residual and source-segregated waste flows. This was associated with higher Ca contents suggesting a high abundance of calcium carbonate fillers in these fractions (Auhorn, 2012). Also the highest concentrations of REE in paper and cardboard fractions were found in *magazines and advertisement* and could thus be related to the used filler materials. Previous studies have reported ash and Ca contents of 0%TS, which appears unlikely based on these results. Moreover, these results confirm that especially high grades of paper (e.g. used for magazines) reportedly contain large amounts of additives, such as clay, which can make such paper less economically attractive for recycling due to lower yield of paper vs. sludge (Baeyens et al., 2010a). Lower yields of paper vs sludge also relates to substitution of virgin materials and increasing emission factors per quantity of paper waste send to recycling thus overall to lower “resource quality” of the paper waste material.

The contents of heavy metals are important quality indicators for paper recycling as limit values were established for particular paper products e.g. for Cd, Cr(VI), Hg and Pb packaging (EU, 1994), and Cd, Hg and Pb in food packaging (CEPI and CITPA, 2012). The fractions *tissue paper*, *other paper*, and *corrugated cardboard boxes* had higher Hg contents than the remaining paper and cardboard samples. The overall highest Hg content was found in *cards and labels* (sub fraction of *other paper*) from source-segregated waste (269 µg/kgTS). However, the same fraction sampled from residual waste presented a much lower Hg content (13.2 µg/kgTS). *Self-adhesives* (sub fraction of *office paper*) presented the highest Cr content possibly due to fine particles sticking to the adhesive film (Pivnenko et al., **V**). The contents of Cr and Pb were consistently lower in *newsprints*, *office paper* and *books* than in other fractions. Also Cu in *office paper* and *books*, was at considerably lower concentration than observed in other samples (Figure 2). This might be due to different types of inks used (Pivnenko et al., 2015).

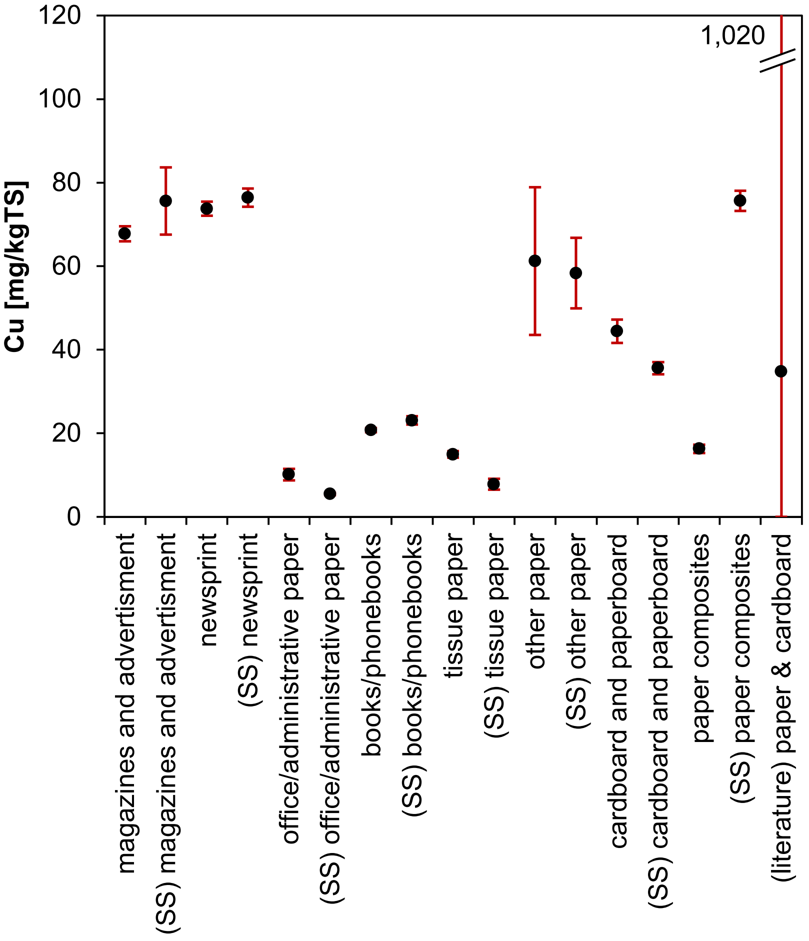

Figure 2: Weighted averages and standard deviation of copper concentrations in aggregated paper and cardboard fractions from residual and source-segregated waste (Götze et al., **III**) and median, minimum and maximum of literature values (Götze et al., **I**)

Generally, the measured heavy metal contents in many samples were in the lower half of the literature datasets and for all samples much lower than the respective maximum values reported in literature. However, in comparison to previous Danish and German studies the measured Pb concentrations were slightly higher (Pivnenko et al., **V**). The Cu content of many samples matches with values in the upper half of the respective dataset but are nevertheless much lower than the reported maximum value. Some fractions in source-segregated waste in fact presented higher contents of metals and potentially toxic elements. Overall the results show that higher concentrations of metals are not necessarily a result of cross-contamination from materials other than paper due to mixed waste collection, but may be intrinsic properties of the paper products (e.g. inks and fillers).

3.4 Plastic waste

Polymers have a large content of C and energy, which makes plastic waste interesting for energy recovery via incineration or for fuel production via gasification. But also material and feedstock recycling (via pyrolysis, hydrocracking, gasification) of plastics are very much desired options which aim at the substitution of fossil petrochemicals as feedstock for production. Energy recovery and mechanical recycling of plastic are currently the most common techniques and mechanical recycling is with a recycling rate of about 50% especially successful for production scraps (Baeyens et al., 2010b). Nevertheless, plastic recycling rates for post-consumer plastic waste are generally lower than for many other waste materials and about 40% of post-consumer plastic waste collected for recycling can finally not be recycled (Shen and Worrell, 2014).This is related to the large diversity of plastic materials: they vary in polymer type, intermolecular bonding, and added inorganic fillers, stabilizers and pigments which affects their mechanical properties (Martens, 2011). Furthermore, concentration of Cd, Cr(VI), Hg and Pb in newly manufactured plastic packaging applications must comply with EU Directive 94/62/EC (1994).

The investigated plastic fractions were sampled based on waste flows (source-segregated or residual), function (packaging or non-packaging), and polymers (PET, PE, PP, PS, others). Overall 20 samples - 13 fractions from residual and seven fractions from source-segregated waste - were analyzed for Götze et al. (**III**). An overview on selected physico-chemical properties of plastic waste is provided in Table 8. For many physico-chemical parameters significant differences between the analyzed plastic samples were found. The LHV and ash content differed substantially between polymer types, but were within the range reported in literature.

Table 8: Selected physico-chemical properties of the analyzed plastic waste fractions (Götze et al., **III**) and as reported in the reviewed literature (Götze et al., **I**)

		Analyzed samples		Literature
	Unit	Residual	Source-segregated	
LHV	MJ/kgTS	22.9 - 41.7	23.2 - 41.9	10.8 - 45.5
ash	%TS	1.0 - 12.1	0.1 - 9.1	0 - 60
C	%TS	64.0 - 84.6	63.6 - 88.8	33.3 - 92.1
Cl	%TS	0.02 - 3.05	0.004 - 2.452	0 - 56.8
As	mg/kgTS	2.1 - 4.1	2.1 - 5.1	0 - 44.8
Cd	mg/kgTS	<0.4 - 5.1	<0.4 - 50.8	0 - 388
Cr	mg/kgTS	4.2 - 78.5	4.2 - 47.0	0.4 - 853
Hg	µg/kgTS	<2.4 - 9.6	<2.4 - 6.2	0 - 12150
Pb	mg/kgTS	0.7 -219.0	0.5 - 81.6	0.8 - 1595
Sb	mg/kgTS	0.5 - 270.9	0.4 - 254.5	0 - 271

In particular, the LHV, C and H content of *PET packaging* was considerably lower than found in the other polymer types. Packaging and non-packaging plastic fractions without a label identifying the polymer resin, and *plastic-metal laminates* presented a significantly higher Cl content (1.6-3.6%TS) than the other plastic fractions, suggesting an abundance of PVC (polyvinylchloride), which includes Cl atoms in its molecular structure. Generally, higher metal contents were found in *plastic-metal laminates*, non-packaging fractions and *packaging without polymer resin label*. The highest Sb concentration was found in *PET packaging* (Figure 3). Sb has a high toxicity potential and is widely used in PET manufacturing as a catalyst. The high Sb content in *PET packaging* is thus not a waste-specific impurity but a potential problem of the product itself. Tests revealed that only a small fraction of the total Sb content is leachable into water (Westerhoff et al., 2008) but whether the release rate could be altered by recycling and increase the risks for human health and environment is unclear at this point.

We found only few significant differences between fractions from residual and source-segregated waste. P, S, Cl and Hg concentrations were higher in some fractions from residual waste than in the respective source-segregated fractions, while for the heating value opposite results were found. The measured concentrations of many heavy metals match with the lower half of the respective literature datasets and for Hg and Pb even with the lowest 25%.

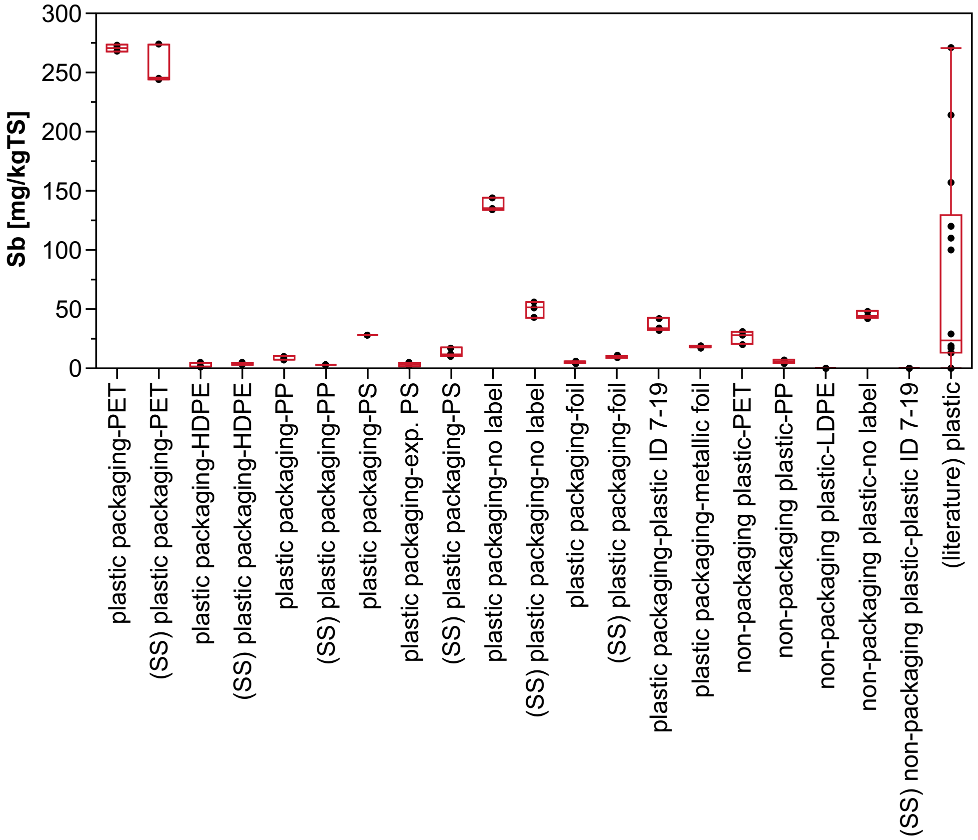

Figure 3: Boxplots of antimony concentration measured in plastic waste fractions (Götze et al., **III**) and values reported in the reviewed literature (Götze et al., **I**)

Overall the results of the physico-chemical analysis of plastic waste fractions emphasize the importance of distinguishing plastic fractions by application (e.g. packaging vs. non-packaging) and polymer type. Based on the results for heavy metals the distinction between residual and source-segregated waste flows appears to be of little relevance for plastic waste.

3.5 Metal waste

Metal waste disposed in household waste consists mainly of packaging (Edjabou et al., **IV**) which is either made of steel or aluminium. In fact different types of steel are used to produce steel packaging; i) tin coated steel for all applications, ii) chromium coated steel covered with organic lacquer or polymers for food cans, and iii) blackplate which is the basic component for the previous two types but without metallic or organic coatings (ArcelorMittal, 2015; Baeyens et al., 2010b). Aluminium cans consist of aluminium sheet alloyed with Mn and Mg which is coated with organic lacquer (Baeyens et al., 2010a). Generally the recycling of metals requires lower amount of energy than virgin material production and emissions from raw material extraction can be avoided. Thus metal recycling has been an integral part of metal production for a long time. European recycling rates are at 75% for steel packaging and at 62% for aluminium packaging (APEAL, 2015; Baeyens et al., 2010a). Metals are also often recovered from solid MSW incineration residues. Due to its magnetic properties ferritic and martensitic steel is easy to separate from other waste streams and metals, so that very clean material flows can be sorted. However, austenitic steel does not respond to magnets and thus remains mixed with other metals during magnetic sorting. Austenitic steel, aluminium and other non-ferrous metals can be separated via eddy-current separators but this is less efficient. While inorganic impurities decrease metal yield and increase the energy consumption of the smelting process, excessive presence of organic materials can result in safety problems as they can cause flashfires (Martens, 2011). Fe and Al act as impurities in the complementary remanufacturing process and other metallic elements can have negative effects on material strength and ductility. Tolerated levels depend very much on the specific remanufacturing process and anticipated product/alloy. As a guideline, a rough overview of the roles of different elements in individual metal production processes is provided in the “Metal Wheel” as presented e.g. in UNEP (2013).

The metal waste fractions investigated for Götze et al. (**III**) were sampled based on waste flows (source-segregated or residual), function (packaging or non-packaging), and were further distinguished into ferrous, non-ferrous, and aluminium foil. Overall five samples from residual and two samples from source-segregated waste were analyzed. An overview of selected physico-chemical properties of ferrous and non-ferrous metal waste is provided in Table 9.

Table 9: Selected physico-chemical properties of the analyzed metal waste fractions subdivided into ferrous and non-ferrous metal (Götze et al., **III**) and as reported in the reviewed literature (Götze et al., **I**)

		Analyzed samples		Literature
	Unit	Ferrous metal	Non-ferrous metal	
LHV	MJ/kgTS	0.8 - 8.8	0.6 - 22.3	-0.1 - 10.7
C	%TS	2.0 - 18.6	1.5 - 46.2	0 - 76.2
Al	%TS	2.3 - 6.1	9.7 - 32.3	0.09 - 86.1
Fe	%TS	51.9 - 84.0	0.4 - 1.7	0.015 - 98
As	mg/kgTS	15.9 - 30.6	1.7 - 5.3	0 - 539
Cd	mg/kgTS	<0.1 - 2.4	<0.1 - 1.0	0 - 53
Cr	mg/kgTS	229 - 1399	41 - 458	0 - 4702
Cu	mg/kgTS	163 - 2594	69 - 45705	0 - 45100
Hg	µg/kgTS	<2.4 - 2.8	<2.4 - 12.3	0 - 8500
Sn	mg/kgTS	770 - 2759	15 - 76	67 - 3710

As already described in chapter 2.5.2 the direct measurement of the HHV of pulverized metal samples following the standard procedure leads to misleading results, as the reaction of metals with an oxygen-enriched atmosphere releases large amount of heat (Grosse and Conway, 1958). The lower heating value of the analyzed metal samples was estimated based on the contents of C, H, N, O, and S and thus represents the energy content related to combustible materials attached to the metal items, such as paper labels, organic lacquer and polymer linings, and food residues. The amount of organic matter in the non-packaging metal fractions was substantially higher than in metal packaging fractions as indicated by higher LHVs (8.8 and 22.3 MJ/kgTS) and lower ash contents (36.9%TS) (Table 9). Also in comparison to previous studies the organic matter content of the analyzed non-packaging metal fractions was rather high; ash contents were smaller than the minimum and C, H, N and Na contents higher than the maximum of the literature dataset. To put this in an overall perspective non-packaging metal fractions had a higher LHV and lower ash content than *other combustibles* (LHV: 14.9 MJ/kgTS; ash: 59.7%TS), emphasizing the problem in generalizing even basic properties of macro-fractions such as metals and combustibles, as the range for certain sub-fractions may overlap. The ash content of *ferrous metal packaging* from source-segregated waste exceeded 100%TS (104%TS), indicating a slight increase in the sample mass during the trial, which could be due to the partial oxidation of the metal particles' surfaces in absence of volatile organic matter. Significant differences between the analyzed metal samples were found with respect to many heavy metals and trace elements. *Ferrous metal packaging* was associated with higher Sn contents (Figure 4), reflecting the tin coated steel type used for steel packaging.

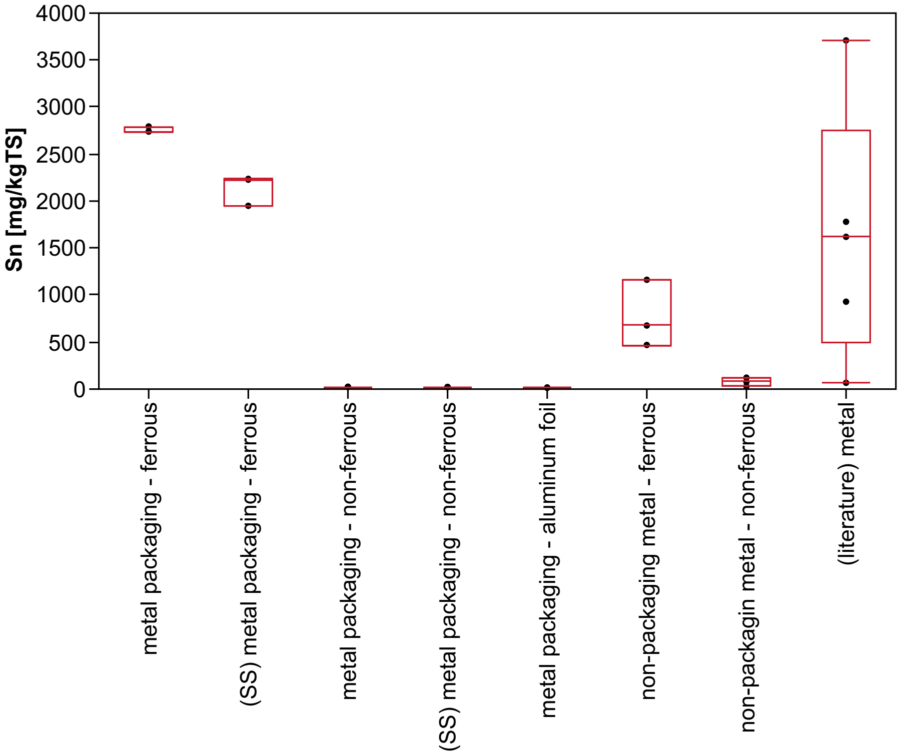

Figure 4: Boxplots of tin concentration measured in metal waste fractions (Götze et al., **III**) and values reported in the reviewed literature (Götze et al., **I**)

All ferrous metal fractions presented higher concentrations of As, Co, and Ge than the non-ferrous fractions. Conversely, the non-ferrous fractions had higher contents of Ga, Mg, Mn, Na, Hf and Zr than the ferrous metal fractions. *Aluminium foil* had a significantly higher Hg concentration than the other metal fractions. The highest concentrations of Cd, Cr, Ni, Pb, Sb and Zn were found in the non-packaging fractions (ferrous and non-ferrous) suggesting that these fractions are a concentrated source for many heavy metals. Also the concentrations of Zn, Pb, Sb and Ba in these samples match values in the upper quartile or are close to the maximum values of the literature datasets. *Aluminium foil* presented higher S, Na, P, V and K contents than the maximum values found for metal waste in literature.

Only metal packaging fractions were found in the source-segregated waste flow and thus a comparison of residual and source-segregated waste was only possible for metal packaging fractions. The samples from residual waste had significantly higher concentrations of several heavy metals and trace elements than the samples from source-segregated waste.

3.6 Glass waste

Glass waste consists mainly of amorphous SiO_2 and can be in principle re-melted without any loss for the remanufacturing of new glass. Depending on the specific application of the glass different chemical components are added during manufacturing to improve hardness and chemical resistance for the anticipated purpose. Thus, mixing glass from different applications is undesirable. The most relevant glass type in household waste is glass packaging which is made of soda-lime glass consisting of approximately 70% SiO_2, 15% Na_2O and 9% CaO_2 (Dyer, 2014). Recycling of post-consumer glass packaging is very common; it constitutes about 50% of the feedstock for glass packaging production (Baeyens et al., 2010b). Glass of other applications, ceramics, metal, paper and food scraps are unwanted impurities in the remanufacturing process for glass packaging (Martens, 2011). Furthermore, the production of clear glass requires absence of any colored glass pieces. Most of these impurities and color requirements can be handled today by mechanical and optical sensor-based sorting, and washing. Other management options of post-consumer glass packaging include reuse and other open-loop recycling options such as using glass in concrete, pavements or in abrasive media (Dyer, 2014). When disposed in mixed waste glass ends up in MSW incineration bottom ash or landfills. During incineration organic components such as labels and food scraps incinerate under heat release.

The glass waste fractions characterized for Götze et al. (**III**) were sampled based on waste streams (source-segregated or residual), function (packaging or non-packaging) and color (clear, brown, green). Five fractions from residual waste and 4 fractions from source-segregated waste were analyzed. An overview of selected physico-chemical properties of ferrous and non-ferrous metal waste is provided in Table 10.

Table 10: Selected physico-chemical properties of the analyzed glass waste fractions subdivided into packaging and non-packaging applications (Götze et al., **III**) and as reported in the reviewed literature (Götze et al., **I**)

		Analyzed Samples		Literature
	Unit	Packaging	Non-packaging	
LHV	MJ/kgTS	<0.2 - 0.6	<0.2 - 0.7	0 - 0.7
ash	%TS	96.1 - 99.6	95.2 - 99.8	83.5 - 100
As	mg/kgTS	6.8 - 13.6	2.4 - 1535	0 - 1664
Cd	mg/kgTS	0.1 - 1.1	0.5 - 1.3	0 - 8.4
Ce	mg/kgTS	15.8 - 48.6	96.8 - 229.6	-
Cr	mg/kgTS	12.3 - 1187.4	3.9 - 16.0	0 - 1236.8
Cu	mg/kgTS	4.8 - 24.6	4.2 - 266.3	0 - 268
Fe	mg/kgTS	478 - 2934	297 - 1013	477 - 3567
Pb	mg/kgTS	65.2 - 163.8	26.2 - 41.2	0 - 889
Sb	mg/kgTS	6.4 - 26.9	5.5 - 45.4	5.9 - 81.2

The results for LHV, ash content, C and H content indicate that the organic matter content in glass samples from residual waste were considerably higher than in the samples from source-segregated waste, likely due to cross-contamination. The LHV and ash content of all samples fit very well with the range of respective datasets while C and H content fit with the upper half of the literature dataset. Some heavy metals could be associated with the color of the analyzed glass packaging fractions; i.e. Cr with *green glass packaging* (Figure 5), Fe with *brown* and *green glass packaging*, and Sb in *clear glass packaging*. In fact many heavy metals and trace elements have reportedly been used to adjust color and optical properties of glass (De Jong et al., 2011). Higher concentrations of As, Ba, Be, Cu, Sb, Ga, Ce, Nd, and Sb were found in non-packaging glass samples than in the packaging ones. Compared to values from previous studies the fraction *kitchen and table ware* had contents of Mg, Na, Cu, Zn and Sn similar or higher than the maximum values reported in literature. However, the heavy metal and trace element contents in source-segregated non-packaging glass were substantially higher than in the residual sample. Given the heterogeneity of these fractions and small amounts found these differences are likely due to differences in disposed items.

Overall, the results of the physico-chemical analysis of glass waste fractions revealed considerable differences in the concentration of heavy metals and trace elements depending on the glass application (packaging or non-packaging) and the color of glass packaging.

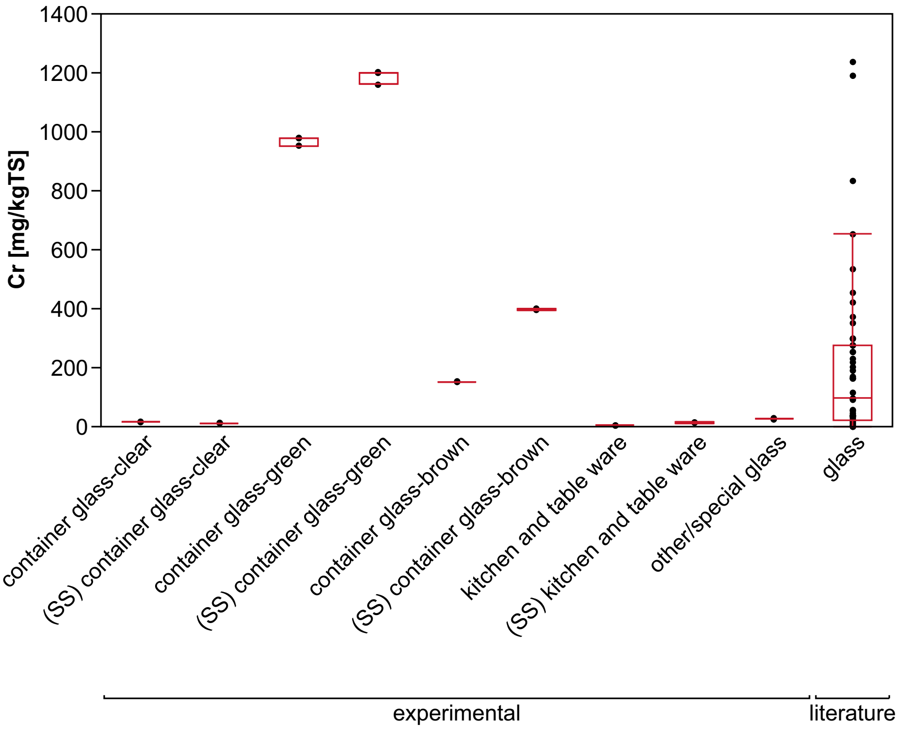

Figure 5: Boxplots of chromium concentrations measured glass waste fractions from residual and source-segregated (SS) waste (Götze et al., **III**) and values reported in the reviewed literature (Götze et al., **I**)

3.7 Combustible waste

In a household waste context combustible waste generally refers to materials which are hardly recyclable and hardly biodegradable while their high energy content suggests a preference for energy recovery, e.g. via direct incineration or thermo-chemical conversion to fuel, such as pyrolysis (Wu and Williams, 2013). Although the exact definition can differ dependent on local waste management systems it typically includes sanitary products, vacuum cleaner bags, and small items consisting of multiple materials e.g. cigarette butts. Also other small items made of wood, textiles, leather, rubber, polymers and combinations of those (e.g. shoes) are often included, while large items (e.g. carpets and furniture) are typically handled separately as “bulky waste”. For clothing often separate collection via charity systems exist, aiming at second-hand sale and reuse. Non-reusable textiles can be potentially recycled e.g. to stuffing materials (Hawley, 2014). However, a lack of economic incentives results commonly in routing even source-segregated textile products to WTE facilities (Thewissen et al., 2014). Source-segregated clean wood can be potentially recycled for the production of particleboard, oriented strand board, medium density fiberboard and animal bedding and mulches (Dodoo et al., 2014). However, in EU average recycling and energy recovery of post-consumer wood are equally common as wood is a popular renewable energy source (Mantau et al., 2010). For several heavy metals and the chlorine content limit concentrations have been established for the utilization of combustible material as secondary fuel (SRF/RDF) by several European countries(Rotter et al., 2004). Thus, monitoring of such element contents, the heating value and ash contents and tracing contaminants to individual materials is of special relevance for combustible waste materials.

The investigated combustible waste samples comprised five material fractions from residual waste and one material fraction from source-segregated waste. An overview of selected physico-chemical properties of ferrous and non-ferrous metal waste is provided in Table 11.

Table 11: Selected physico-chemical properties of the analyzed combustible waste fractions (Götze et al., **III**) and as reported in the reviewed literature (Götze et al., **I**)

	Unit	Analyzed Samples	Literature
LHV	MJ/kgTS	7.6 - 23.7	6.0 - 37.4
ash	%TS	1.5 - 59.7	0.1 - 3.6
Cl	%TS	0.1 - 3.6	0 - 23
As	mg/kgTS	2.7 - 44.6	0 - 400
Cd	mg/kgTS	0.4 - 1.4	0 - 250
Cr	mg/kgTS	7.1 - 372.1	0 - 9000
Cu	mg/kgTS	9.8 - 306.0	0 - 9240
Hg	µg/kgTS	5.1 - 160	0 - 7030
Pb	mg/kgTS	1.3 - 78.5	0 - 6900
Sb	mg/kgTS	1.0 - 53.1	0 - 86.3

Significant differences in LHV, ash content, and C and H content were observed among the analyzed combustible fractions (Figure 6). The lowest LHV (7.6 MJ/kgTS), C content (23.2%TS), H content (3.2%TS), and highest ash content (59.7%TS) were found in *vacuum cleaner bags*. These results are comparable to the lowest HHV, C and H content and the highest ash content of the literature datasets reported by Götze et al. (**III**). Additionally, *vacuum cleaner bags* and *other combustibles* presented the highest concentrations of many macro and trace elements among all combustible waste fractions.

Especially the Hg concentration in *vacuum cleaner bags* (160 µg/kgTS) was by far the highest. This suggest that these trace elements are accumulated in small inorganic particles i.e. dust. However, compared to values reported in literature Hg concentration was among the lowest 25% of data. The highest As concentration was found in *wood* (44.6 mg/kgTS) and likely originated from wood preservatives (Loferski, 1999). *Textiles, leather and rubber* presented the highest concentrations of Cu, Cr, Sb, and Zn among the combustible fractions. *Sanitary products* and *other combustibles* presented a significantly higher Sn concentration (37.7 mg/kgTS) than the remaining combustible waste samples. The Mn and V content in the samples *vacuum cleaner bags* and *other combustibles*, and the Sn content in *sanitary products* and *other combustibles*, exceeded the maximum value of the literature dataset.

We found only small amounts of misplaced materials fitting the fraction *textiles, leather and rubber* in the source-segregated waste flow. The LHV and concentrations of Cl, N and some trace metals were significantly higher in the source-segregated *textile, leather and rubber* sample than in the one from residual waste. This is likely a result of intrinsic differences among the discarded products within this fraction. Generalization is however difficult especially because the sample from source-segregated waste originated from a rather small amount of misplaced material.

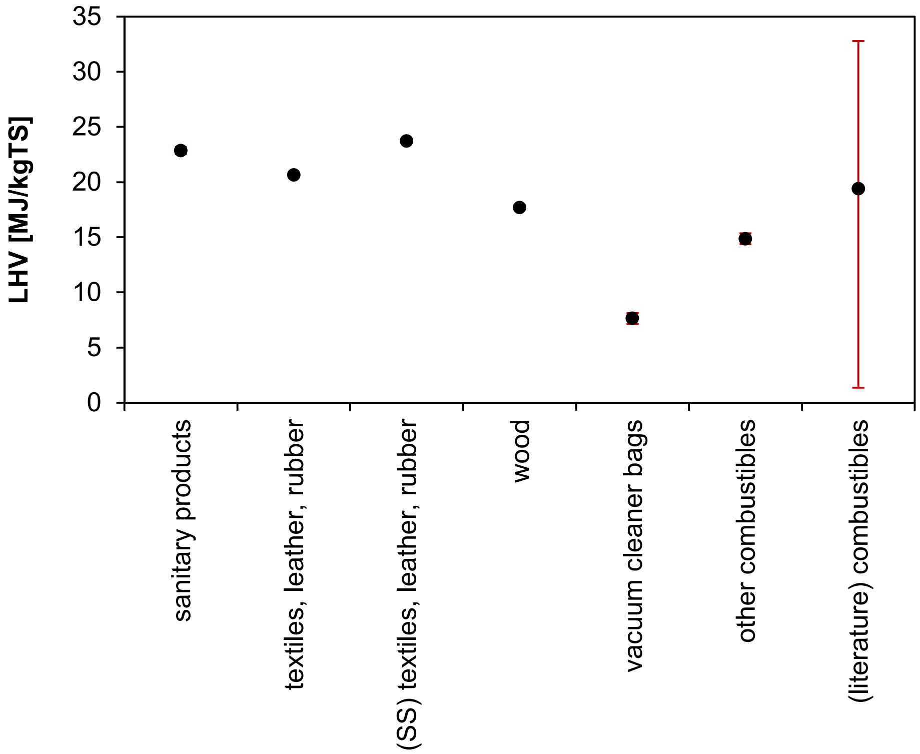

Figure 6: Mean values and standard deviation of the LHV in the analyzed combustible waste fractions from residual and source-segregated waste (Götze et al., **III**) and median, minimum and maximum of literature values (Götze et al., **I**)

3.8 Inert waste

In the category inert waste we discuss inorganic materials typically made of mineral raw materials such as ceramics, cat litter, ashes and materials used for construction e.g. cement, plaster, sand, gravel, stone. While such materials are found in large quantities in waste from the construction and demolition industry also small amounts arising in private households can be disposed in household waste. Owing to the absence or very low contents of organic matter inert waste materials provide no benefit for energy recovery. According to Martens (2011) the incentives for recycling inert waste materials are primarily the saving of landfill volume and avoiding contamination of soil, while substitution of natural resources and related energy consumption are only a secondary objective. The recycling to secondary raw materials for production of ceramics or construction materials is often not possible due to high purity requirements but after crushing and classifying, the materials can be utilized e.g. in the construction of roads, sport fields and parks or as filling material (Martens, 2011). To assure that such application is safe the materials have to be characterized for their stability (e.g. organic/degradable material content) and comply with limit values for heavy metal contents established by many countries for individual application types.

The investigated inert waste samples comprised four material fractions from residual waste and two material fractions from source-segregated waste. An overview of selected physico-chemical properties of the samples from the two waste flows is provided in Table 12.

Table 12: Selected physico-chemical properties of the analyzed inert waste fractions (Götze et al., **III**) and as reported in the reviewed literature (Götze et al., **I**)

		Analyzed samples		**Literature**
	Unit	**Residual**	**Source-segregated**	
LHV	MJ/kgTS	<-0.03 - 0.53	<0.17	0 - 18.5
ash	%TS	93.8 - 99.2	99.3 - 99.7	43.9 - 100
Al	%TS	0.22 - 9.57	0.01 - 11.15	0.7 - 5.8
Ca	%TS	0.5 - 36.7	1.6 - 39.0	0 - 11.2
As	mg/kgTS	<2.8 - 18.4	<2.6 - 65.9	0 - 1153
Cd	mg/kgTS	0.1 - 2.9	0.4 - 0.7	0 - 341
Ce	mg/kgTS	4.0 - 72.0	0.1 - 60.3	-
Cr	mg/kgTS	6.3 - 96.4	1.3 - 85.3	0 - 1075
Hg	µg/kgTS	<2.4 - 32.9	3.6 - 16.8	0 - 3420
Pb	mg/kgTS	2.8 - 190.2	2.0 - 1947.7	0 - 11740

The HHV in many samples was below the detection limit, but the quantified ones fit well with the values found in literature. The ash content of all samples fit very well with the literature value range and analyzed C and H content fit with the upper half of the literature dataset. The nutrient, metal and trace element content differ substantially among the individual fractions. *Ashes* presented significantly higher contents of P and Mn than the other inert fractions and compared to the literature datasets *ashes* had high S, K, Mg, P and Zn contents which were similar or higher than the maximum. *Ceramics* and *cat litter* presented higher contents of Al, Be, Co, Ge, Fe, Hg, Nb, Pb, Th, and U and many REE than the other inert fractions. The RRE concentrations in *ceramics* (e.g. Ce: 72 mg/kgTS; and Nd: 29.0 mg/kgTS) were higher than in any other analyzed waste fraction. This suggests certain mineral raw materials as a possible source for REE in non-hazardous household waste fractions. Previously REE in MSW have been only associated with the presence of electronic/hazardous waste (e.g. Morf et al., 2013).

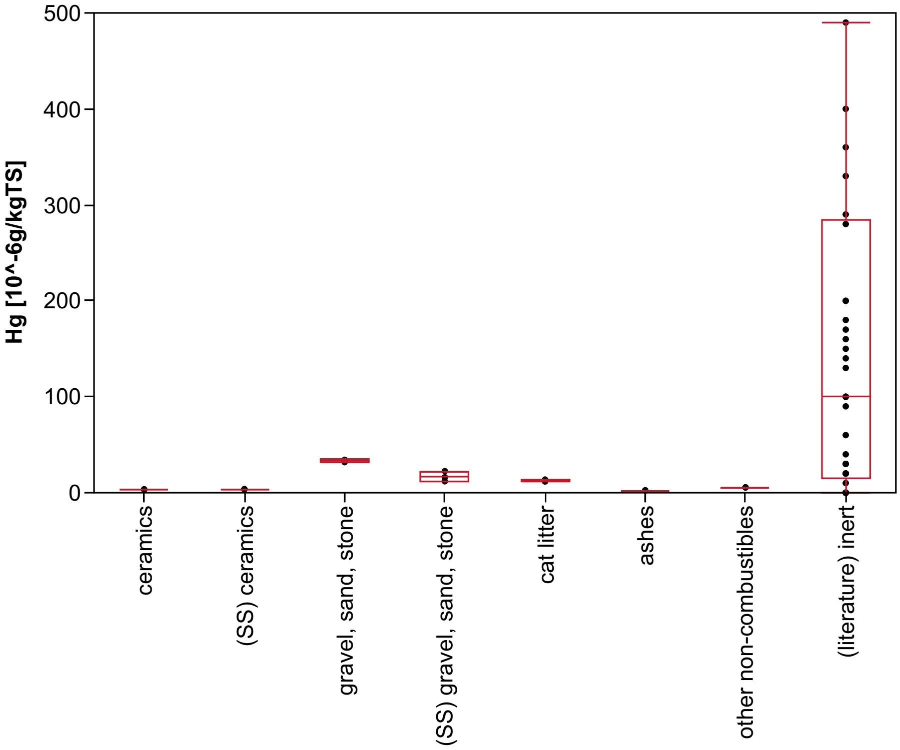

Figure 7: Boxplots of mercury concentrations measured in inert waste fractions from residual and source-segregated (SS) waste (Götze et al., **III**) and values reported in the reviewed literature (Götze et al., **I**). Literature values higher than 500 µg/kgTS were excluded to enable an appropriate visual presentation; the maximum value reported was 3420 µg/kgTS.

The result for the C and H content suggest a possible cross-contamination with organic material in the sample from residual waste. *Gravel, sand and stone* from residual waste had significantly higher C, H, Cl, K, Al, Fe, Ca, Hg, REE and precious metals content and significantly lower content of ash, Au, Ca, Co, Pb, Rh, Sn and Ta than the corresponding fractions in source-segregated waste. Considering the very small amounts of *gravel, sand and stone* found in the source-segregated waste a sheer difference between the disposed items is very likely and general conclusions on heavy metals and trace elements cannot be drawn.

4 Application of waste composition data in environmental assessment

4.1 Introduction

The complexity of waste management systems requires a systematic procedure for assessing related environmental impacts to support environmentally sound decisions in waste management planning. Relevant decision-support tools include e.g. risk assessment, SFA, MFA, and LCA. Especially LCA has become increasingly popular for the assessment of the environmental performance of waste management systems (Laurent et al., 2014a). LCA is an internationally standardized procedure (ISO 14040 and 14044) to assess environmental impacts arising from all life cycle stages (e.g. extraction of resources, production and disposal) of products and systems. It consists of four phases:

i) Goal and scope definition where aim of the study, functional unit and system boundaries are defined,

ii) Life cycle inventory analysis where cumulative emissions to air, water and soil are calculated,

iii) Life cycle impact assessment, where emissions are converted to environmental impacts by multiplication with so-called characterization factors. Different impact assessment methods are available which define different environmental impact categories and related characterization factors (e.g. Hauschild et al., 2013).

iv) Interpretation.

Several authors pointed out that considering physical and chemical properties of waste flows in the environmental assessment of waste management systems is of significant importance to obtain realistic results (Arena and Di Gregorio, 2014; Brunner and Ma, 2009; Kirkeby, 2006; Laurent et al., 2014b). As the emissions are linked to waste input properties, the results of waste systems LCAs have been shown to strongly depend on the fractional and physico-chemical waste composition data used for the modelling (e.g. Slagstad and Brattebø, 2013; Turconi et al., 2011). However, deriving a well-fitting and consistent dataset on the physico-chemical waste composition from literature is not a trivial task; even when primary data are used, the choice of characterization methods can influence the results of the waste characterization to the point where it affects the outcome of the environmental assessment. In this chapter key challenges in selecting appropriate physico-chemical waste composition data for environmental assessment purposes are identified, presented and discussed; based on these findings a list of recommendations is provided.

4.2 Key challenges

4.2.1 Limited data availability

The importance of applying appropriate waste composition data reflecting the spatial and temporal scope of the assessment has been pointed out in several cases (e.g. Clavreul et al., 2012; Fruergaard and Astrup, 2011). By reviewing 97 online-available publications providing physico-chemical waste composition data Götze et al. (**I**) found substantial differences in data availability between regions and countries (Figure 8). While relatively many data were available for European countries (58.2% of all data) very few were found e.g. for Africa (1.9%) and South America (6.3%). The most data were found for the countries China (25%), Denmark (18%), and Germany (9%). However, for many large countries no relevant data were found at all (e.g. Russia). Thanks to many Chinese publications, Asia appeared to be relatively well represented. However, composition data from other Asian countries, especially tropical ones, were very scarce. Overall, there is a clear data gap for developing and emerging economies, which is challenging especially when considering that lifestyles, income levels, demographics and legislation may differ considerably from industrialized countries and likely affect the physico-chemical characteristics of waste. However, this only outlines the overall frequency of waste characterization activities in different regions while for individual physico-chemical parameters (i.e. elements, energy and ash content) and materials very differing distributions of geographical origin were found.

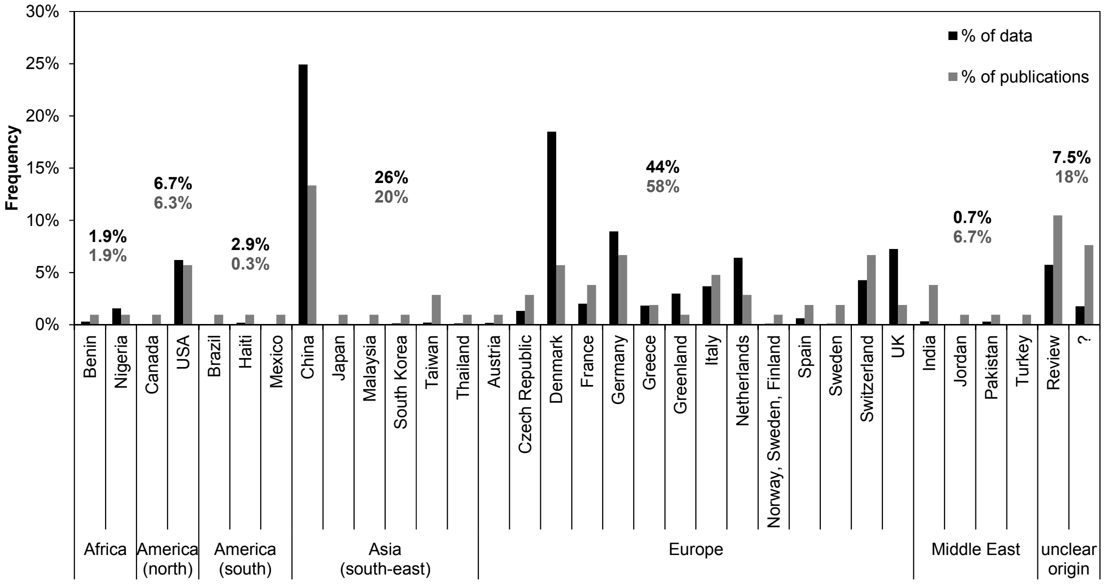

Figure 8: Overview on the availability of physico-chemical waste composition data in literature by country (columns) and region (values)

The most frequently reported physico-chemical parameters were the contents of some particular heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn), CHNOS, Cl, ash and energy. Contents of Al, Be, Co, Fe, Mn, Mo, Sb, Sn, V where less commonly analyzed. The data availability of these elements was especially low for the fractions glass, metal and plastic. Extremely little or no data was found for elements used in high-tech applications, e.g. precious metals and REE, which clearly limits the assessment of resource efficiencies and dissipation of such critical raw materials in waste management systems.

The best data availability was found for combustible waste fractions reflecting a strong focus on waste-to-energy options in previous characterization activities. Generally rather little information was found for glass, metal and composite fractions pointing to clear limitations for modelling recycling scenarios for these materials. For paper and plastic more data was found than for metal and glass, but the types of fractions are not in all cases very suitable for the modelling of recycling chains. Götze et al. (**I** & **III**) has shown that the physico-chemical properties can differ significantly e.g. between ferrous and non-ferrous metal, and polymer resins which are typically mechanically sorted for recycling. However, only few waste characterization studies sorted metal and plastics into more detailed fractions and even less by criteria relevant for recycling technologies. This shows that there is a clear need for characterization studies focusing on the quality of recyclables.

Another finding of Götze et al. (**I**) was that the publication rate for waste characterization studies (number of publications per year) fluctuated but did not show any increasing trend. On the other hand, the number of yearly publications of waste systems LCAs has been steadily increasing in the last decade (Laurent et al., 2014a). This implies that many waste LCA studies rely on the same old existing waste composition data and combination of those.

As already discussed in chapter 2.2 the fraction definition depends very much on the objective and purpose of the waste characterization study. Thus, in the ideal case the objectives of the characterization activity are aligned with the objective of the modelling, i.e. primary data need to be obtained. However, in reality even primary data will have some limitations because waste LCA modelling typically includes scenarios that do not exist yet (e.g. new waste collection schemes) and something that does not exist cannot be experimentally characterized. This is of special relevance for physico-chemical waste characteristics which can be altered easily by presence/absence of certain products. Thus the application of waste composition data for LCA modelling will always - to a certain degree - require using data out of their original scope.

As discussed in chapter 2, the choice of characterization methods can affect the resulting values for physico-chemical properties of waste fractions. Even though the geographical origin has been obviously accepted as a selection criterion for waste characterization data by the waste LCA community, the database established by Götze et al. (**I**) does not reveal clear differences between macro-regions as presented for the examples Cd and Hg (Figure 9 and Figure 10). This overview on the data distributions for combinations of parameters, material fraction and regional origin suggests that the regional context alone may actually be not as important as assumed. As described in Götze et al., (**I**) the level of detail of the fractioning in the individual studies played an important role. A consistent in-depth statistical analysis of the relevance of other factors such as characterization methods, socio-economic aspects, and waste management system based on these datasets was unfortunately not possible due to insufficient data quantity.

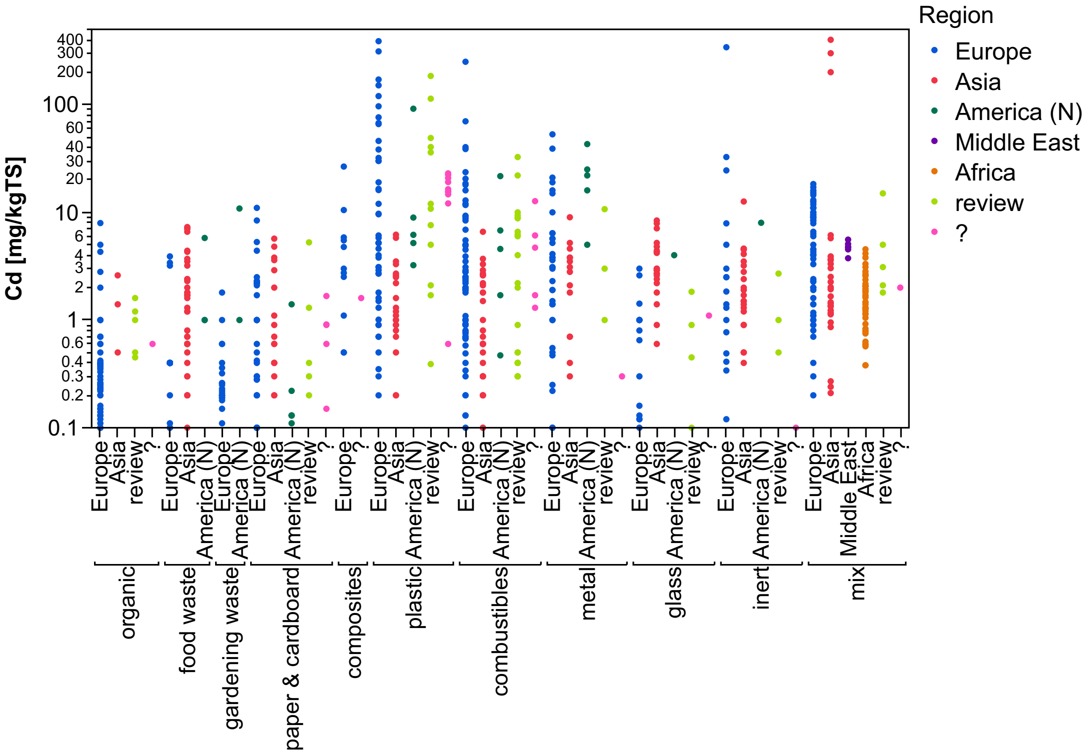

Figure 9: Cd content of different waste materials by regional origin (color code)

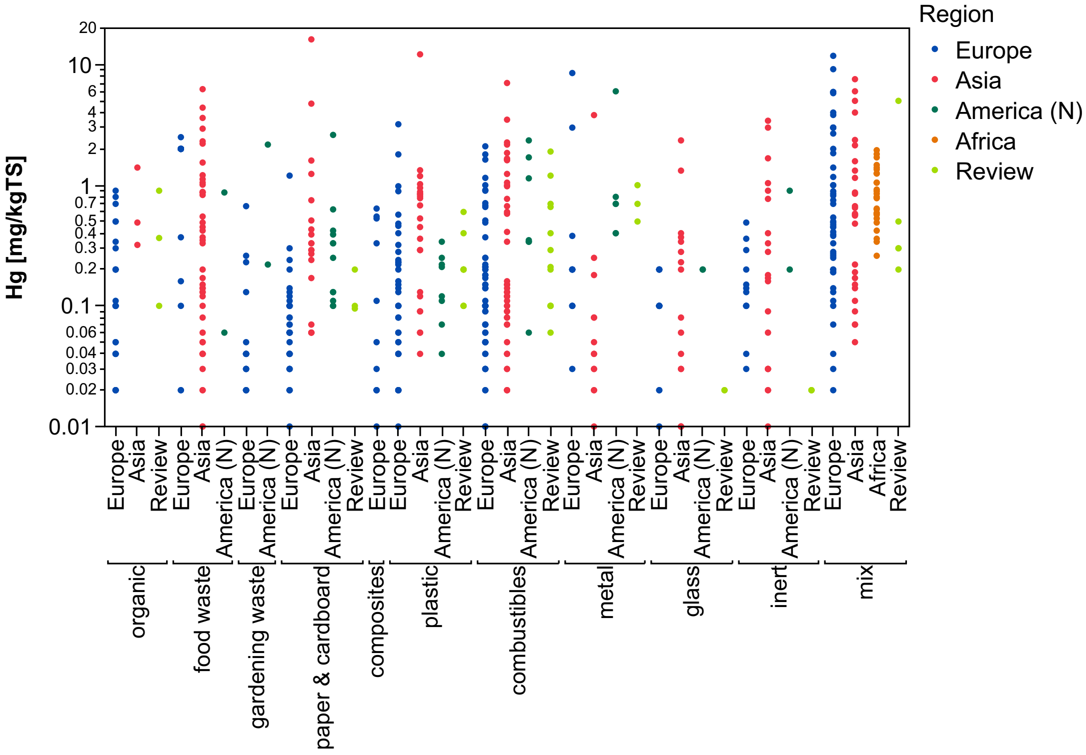

Figure 10: Hg content of different waste materials by regional origin (colour code)

4.2.2 Data reporting

Even though correct data reporting may seem to be trivial we observed substantial and reoccurring flaws while reviewing publications for Götze et al. (**I**). Modelling practitioners will experience similar confusion when extracting data for a concrete modelling purpose and have to make choices which introduce uncertainty to the modelling. In the following texts these problems are described in detail and recommendations for correct reporting provided. A summary is provided in Table 13. The provided recommendations address mainly researchers performing waste characterization studies, because it is clearly the responsibility of the authors presenting waste composition data to provide sufficient and correct information, whereas modelling practitioners cannot do much more than choosing other data or compensating with assumptions. The listed problems could, however, serve modelers as quality indicators for data quality and selection.

Table 13: Summary on reoccurring problems related to the reporting of physico-chemical waste composition data and recommendation for accurate reporting

Problem	Solution
Unclear whether data on wet, dry or ash-free basis	Clear and consistent labelling of units and captions e.g. by using indices
Unclear whether net or gross calorific value	Clearly state, avoid locally influenced terminology
Missing or incorrect units	Always report units, check results with literature values to identify potential errors
Local units (especially common for energy parameters)	Always report in SI units
Reporting measurements below the detection limit as zero	Provide detection limit
Ambiguous fraction naming	Avoid subjective expressions, such as “soft”, “hard”, “recyclable” and if you have to use them, clearly define them
Presentation of results in figures only	Always provide (additional) data tables
Insufficient description of analytical methods	Always state basic principle in addition to standard method number, always describe employed acid digestion procedure and measurement equipment
Publication in local languages and non-ISI journals	Likely unavoidable, but manageable by systematic reviews

In several publications (e.g. Abu-Qudais and Abu-Qdais, 2000; Chandrappa and Das, 2012; Hanc et al., 2011; Tchobanoglous et al., 1993), data-presenting tables did not state expressively whether the values were reported based on wet or dry material weight. This information, however, is crucial for appropriate quantification of substance and energy flows associated with the waste and thus accurate quantification of waste-specific emissions. To prevent misinterpretations, we recommend clear labelling in table captions and/or in the reported units. Common options for the labelling of units in waste characterization is adding abbreviations such as “TS” (total solids) or “DM” (dry matter) e.g. as indices ($\%_{TS}$ or $\%_{DM}$). In conventional fuel analysis, abbreviations such as “db” (dry basis), “ar” (as received) and “daf” (dry ash-free) may also be suitable in the context of waste characterization, especially when the publication focuses on energy recovery.

We found that also the terminology used to describe the energy content of materials was often ambiguous. Authors should therefore make sure that they differentiate clearly between higher and lower heating value (or net and gross calorific value) and also state whether the presented values refer to dry materials (“db”), materials as received (“ar”) or dry ash-free (“daf”).

Although this point may seem obvious, we found several tables with ambiguous or inconsistent unit presentation (e.g. Granados et al., 2004; Olajire and Ayodele, 1998; Topanou, 2011). Especially for energy content clear statement of units is critical, because many units are commonly used depending on the regional context (e.g. BTU/lb, kcal/t and kJ/kg) requiring frequent unit conversion. Furthermore we found many values which were obviously labelled with wrong units, as they differed from other publications’ results by factors of 1,000 or 1,000,000 (e.g. Gidarakos et al., 2006). An error by factor 1000 or more can have logically serious effects on the modelling results. While such errors are relatively easy to identify for the energy content and ash content, they can hardly be distinguished from outliers or peak concentrations of trace elements. All presented data on physical and chemical parameters, whether in tables, figures or the text body, should be labelled unambiguously with the correct unit.

The value “0” was very frequently reported. However, most of the measurement results have a detection limit larger than a true “0”. Innovation and improvement of measurement technologies over time typically results in a decrease of detection limits. To estimate how well the detection limits fit with state of the art analytical techniques reporting of “0” is insufficient. Furthermore, considering the fact that concentrations are often used for flow modelling which involves multiplication with large amounts of waste, some trace elements - potentially with critical environmental relevance - cannot be properly accounted for. Especially, for advanced statistical data analysis, which considers constraints of compositional data (e.g. concentrations cannot be negative and not more than 100%, 10^6 mg/kg, etc.) values of "0" are a problem as typically logarithmic transformation are used and the logarithm of zero is not defined. In fact there is not a single rule of how to use the results from measurements below the detection limit (Aerts et al., 2013; Cohen and Ryan, 1989; Palarea-Albaladejo et al., 2014), but to enable a conscious choice the respective concentrations should be reported and results below the detection limit be labelled accordingly.

We observed many cases of ambiguous naming of waste material fractions. Especially names including terms such as "recyclable" and "non-recyclable", "soft" and "hard", "light" and "heavy" are difficult to interpret, as they are very subjective to personal perceptions and dependent on local conditions, and should consequently be avoided. Data for fractions labelled "composites" were found particularly difficult to interpret; the term was used for multi-material laminates as well as for items consisting of assembled or glued parts made from different materials, though many authors did not describe the related materials at all. Thus a clear agreement on the meaning of this term for waste management purposes should be pursued.

A clear description of analytical methods must be provided, to enable researchers from different countries and backgrounds to access, evaluate and apply waste characterization data properly. We found publications citing a standardized method but not providing any further details on the involved digestion or measurement methods (e.g. Ferrari et al., 2000; Zhang et al., 2005). This is especially a challenge in relation to regional/national standards, which are not always accessible, for example because of cost or language issues. Regardless of whether the experimental methods are standardized or not, it is recommended to provide a short description of the method principles together with some form of reference. In particular, information on acid digestion methods or other decomposition methods applied to solid waste samples prior to the actual measurement was lacking or poorly described in several publications (e.g. la Cour Jansen et al., 2004; WRAP, 2010).

Another obstacle for finding fitting data for a particular modelling purpose can be the publishing language and type of publication. Götze et al (**I**) found that a significant amount of valuable data on physico-chemical composition of waste were published in non-ISI publications, e.g. grey literature, reports and theses. Publishing data in grey literature or local languages is understandable, but this may also limit access to the data by the global scientific community. Considering the extensive economic costs and time required for waste characterization research, it is crucial to put existing characterization data into an easily accessible format. An outstanding example is a review by Zhou et al., (2014), where data from numerous studies previously published only in Chinese were gathered and made available to a larger audience in a well-structured appendix.

4.2.3 Total content data

The work of this PhD project has been executed under the premise that data on the total content of substances in the generated waste materials are needed for the modelling of substance flows and related emissions in waste management systems. However, the total content is most often not equal to the amount released to the environment or available for recovery. On the other hand, waste characterization data need to be useful for a multitude of purposes, such as substance flow analysis, estimating a pollution potential or risk assessment of different systems and contexts. Thus, the total content of elements in solid waste materials is likely the most suitable option for a general purpose value and release rates and partitioning should be selected for the specific modelling purpose.

An example for an element with relevance for recovery is aluminium. Aluminium is one of the most abundant elements in the earth crust and constitutes many natural minerals and clay which is a common soil material. Although from a recovery and recycling perspective only metallic aluminium is relevant the element aluminium is practically omnipresent. When analyzing the total Al content of a waste material it is not possible to distinguish between aluminium bound to minerals and metallic aluminium.

An example for a potentially toxic element is Chromium, which was for example found in high concentrations in green glass packaging. During MSW incineration glass ends up in the bottom ash, which can be utilized as a road construction material. The release and speciation of Cr from MSW incineration bottom ash has been studied extensively by (Allegrini et al., 2015; Astrup et al., 2005). They found complex release dynamics, which were strongly influenced by the pH value and presence of organic matter. Such dynamics are not reflected by total element contents.

Furthermore, the specific waste treatment processes applied influence the transfer of individual substances present in generated waste materials to the different output flows. For example, for MSW incineration it was shown that As, Cr, Cu, Pb and Zn contents in the input waste were mainly transferred to the bottom ash while Cd and Hg were transferred mainly to air pollution control residues (Zhang et al., 2008). The waste treatment processes can also alter the chemical bonds and thereby change release rates of the output material, as e.g. described for a thermo-chemical phosphorous recovery process by Adam et al. (2009).

Summarizing, how much of the total content of heavy metals and nutrients are finally released to different environmental compartments depends on many different factors such as the total content in the initial waste material, the transfer of materials and substances in the particular treatment processes, the matrix properties of the output materials and the environmental conditions during their utilization or final disposal. In theory all these partitioning can be handled during the modelling of substance flows and LCA by transfer coefficients and/or release models as demonstrated by Allegrini et al. (2015) and Butera et al. (2015). But two conditions must be fulfilled: i) the modeler is aware of such partitioning, and ii) sufficient research results are available describing the partitioning. Thus, awareness about chemical issues needs to be promoted in the modelling community and extensive effort put into establishing accurate process and chemical release models.

There is also a clear message for the waste characterization community. It is obvious that quantifying the release to environmental media is a complex matter and that the total content of elements in generated waste is just one part of the entire picture. Nevertheless this fact has been used as an argument against using hydrofluoric acid (HF) for total sample destruction prior to chemical analysis of waste samples. As described in Götze et al (**II**) only very few waste characterization studies have used HF-containing acid digestion methods for the analysis of household waste fractions. However, acid digestion methods using other concentrated inorganic acids are in no way suitable to simulate realistic conditions in the environment either. Neither are they able to substitute modelling of material and substance-flows in waste management systems and complex chemical processes. Instead employing a sub-optimal acid digestion method has been shown to lead to substantial underestimations of total element contents in generated waste materials (Götze et al., **II**) and thus it leads to a biased perception of the total “hazardous capacity” of the respective substance and the modelling results of models based on it.

4.3 Quantifying the importance of waste input properties in LCA

Very often waste systems LCA have to rely on secondary data due to time and budget constraints and due to limited data availability as discussed in chapter 4.2.1. If a modeler has to rely on secondary data, shortcomings from one characterization study can only be overcome by retrieval of additional information from other studies and assumptions. Consequently, mixing of data from different sources is very likely, and often little attention is devoted to the focus and origin, and the sampling and analytical methods applied.

To address the consequences of such choices made by the modeler a systematic sensitivity and uncertainty analysis should be performed (Clavreul et al., 2012; Laurent et al., 2014b). Certain physico-chemical waste characteristics have been reported to be very sensitive for the modelling of waste management systems or certain waste technologies (e.g. Boldrin et al., 2011; Riber, 2007; Turconi et al., 2011). However, the overall variance of the modelling result does not only depend on the sensitivity of the parameter in the specific model but also on its actual uncertainty. In fact the overall variance of the modelling result is the sum of the individual variances of each parameter, which in turn can be described as the product of the sensitivity coefficient and the uncertainty of the parameter (Bisinella et al., 2015). Thus, the quantification of the contribution of physico-chemical waste composition data to the overall uncertainty of the results of LCA modelling requires a full uncertainty analysis including sensitivity and propagation of realistic uncertainty intervals for the individual parameters.

The value ranges derived from the literature review (Götze et al., **I**) for individual physico-chemical parameters in waste material fractions were very wide. These ranges include many different factors that can potentially influence the results of physico-chemical characterization of waste, such as characterization approach, sampling and analytical methods, region and related waste management systems. As described earlier it is very difficult to isolate distinct factors affecting the characterization results and quantify their influence, so that beside regional aspects a definition of concrete selection criteria is pending. As discussed previously limitations in data availability can require mixing and selecting data from various publications. Currently there is little quantitative information available on how the selection of physico-chemical waste characterization data affects the final LCA modelling results. In Bisinella et al (**VI**) we aimed at investigating the relevance of selecting physico-chemical waste composition data from literature for the overall uncertainty of results from waste systems LCAs considering the whole span of errors associated with such data. To do so we used the value ranges from literature derived by Götze et al. (**I**) as uncertainty ranges for the specific physico-chemical parameters in individual waste fractions. As the data were clearly not normally distributed we chose a simpler triangular distribution for the uncertainty propagation of the physico-chemical parameters based on minimum, maximum and mode of the individual datasets. Also process-specific parameters (e.g. efficiency of electricity generation) were varied in realistic ranges. Three full waste management scenarios for the treatment of household waste were defined for this investigation; i) source-segregation of paper, cardboard and glass and incineration of the residual waste with energy recovery, ii) same as the first scenario with additional source-segregation of organic waste routed to anaerobic digestion and application on land, and iii) same as first scenario but landfilling of residual fraction. The modelling was performed with the LCA software EASETECH (Clavreul et al., 2014), which allows simultaneous balancing of energy and substance flows, and environmental impact assessment.

The contribution of physico-chemical waste properties to the overall model output uncertainty differed very much between the individual impact categories and scenarios (Table 14).

Overall, physico-chemical waste properties contributed to a substantial share of the output uncertainty in all scenarios, but especially for the scenarios including incineration (scenario 1 & 2) and anaerobic digestion followed by application of the digestate on land (scenario 2). Considering that the landfill process model in scenario 3 used leachate generation rates based on the quantity of landfilled waste but did not track any substance flows to the leachate it is obvious that there are clear limits to which scenario 3 can be affected by individual substances. Scenario 2 was the most influenced by variation of physico-chemical waste characterization data: here even for the least affected impact categories (ozone depletion and fossil resource depletion) physico-chemical waste properties still contributed to 72% of the output uncertainty.

Table 14: Contribution of physico-chemical waste characterization data to the LCA modelling output uncertainty in the investigated scenarios and environmental impact categories as % of total output uncertainty

Impact category	Scenario 1	Scenario 2	Scenario 3
Climate change (GW)	98	97	93
Ozone depletion (OD)	74	72	0
Human toxicity - cancer effects (HTC)	100	100	4
Human toxicity - non-cancer effects (HTNC)	99	100	38
Ionizing radiation, human health (IR)	74	72	41
Photochemical ozone formation (POF)	86	88	81
Fresh water eutrophication (FE)	0	100	5
Marine Eutrophication (ME)	85	98	5
Ecotoxicity (ET)	53	100	7
Resource depletion - fossil (RDFOS)	92	74	62
Resource depletion - mineral (RD)	100	93	47
Terrestrial acidification (TA)	94	97	1
Terrestrial eutrophication (TE)	85	96	45
Particulate matter (PM)	96	96	61
Average	81	92	35

In general the output uncertainties were considerably high when compared to the average impact scores. Except for POF and PM the 90% confidence interval of all impact categories included a possible shift of the mean by more than 400% either in positive (less environmentally beneficial) or negative (more environmentally beneficial) direction. Combining this with the contribution of physico-chemical parameters to the overall uncertainty we can estimate the capacity of physico-chemical waste composition data to shift the average results (Table 15).

The capacity to severely shift the average impact score was overall highest for the impact category RD in scenario 2 where a negative shift of the average impact score by 34000% was possible due to physico-chemical data variation. This uncertainty was mainly caused by variation of the ash content/VS of plastic, combustibles and food waste. The second highest possible shift due to physico-chemical parameters (7000% of impact score in positive direction) was identified for HTNC in scenario 1. In several cases the resulting uncertainty ranges included a shift from environmental benefit to burden, which is especially critical (Figure 11). In particular this was the case for GW in scenario 3, as well as HTC, HTNC, ET, POF, RDFOS, and TE in scenario 2.

Table 15: Possible shift of average impact scores in positive and negative direction caused by variation of physico-chemical waste composition data expressed as % of the normalized impact score (maximal three significant digits presented)

	Scenario 1		**Scenario 2**		**Scenario 3**	
Impact category	**+**	**-**	**+**	**-**	**+**	**-**
Climate change (GW)	45	73	35	213	55	570
Ozone depletion (OD)	10	8	13	0	0	0
Human toxicity - cancer effects (HTC)	72	21	10300	566	2	1
Human toxicity - non-cancer effects (HTNC)	6970	98	819	586	103	108
Ionizing radiation, human health (IR)	12	16	17	409	0	6
Photochemical ozone formation (POF)	53	68	29	68	17	11
Fresh water eutrophication (FE)	8	1	565	788	7	20
Marine Eutrophication (ME)	86	65	230	657	1	1
Ecotoxicity (ET)	46	35	1050	508	2	2
Resource depletion - fossil (RDFOS)	0	0	32	122	1	2
Resource depletion - mineral (RD)	148	66	20	33900	0	0
Terrestrial acidification (TA)	12	19	23	461	0	3
Terrestrial eutrophication (TE)	92	638	47	112	31	15
Particulate matter (PM)	16	23	2	126	1	7

In absolute terms the normalized impact scores and uncertainty for the impact categories HTC and ET in scenario 2 out scaled the results for all other impact categories (Figure 12). The uncertainty originated mainly from the variation of Cu and Zn contents which were considered as directly emitted to the environment via application of digestate on agricultural land. These results are, however, difficult to interpret. It is likely that a large fraction of the total content of metals is bound to the soil materials and inactive with regard to toxic effects. Consequently the calculated environmental impacts are likely a conservative (rather high) estimate. USEtox characterization factors for metals have been reported to be very uncertain (USEtox, 2015) and have even been labelled as insufficient to model the actual behavior of metals in the environment (Diamond et al., 2010; Henderson et al., 2011). Note that the uncertainty of characterization factors was not included in the uncertainty analysis as no realistic estimate of their variation was available. Including the uncertainty of characterization factors would increase the total model output uncertainty.

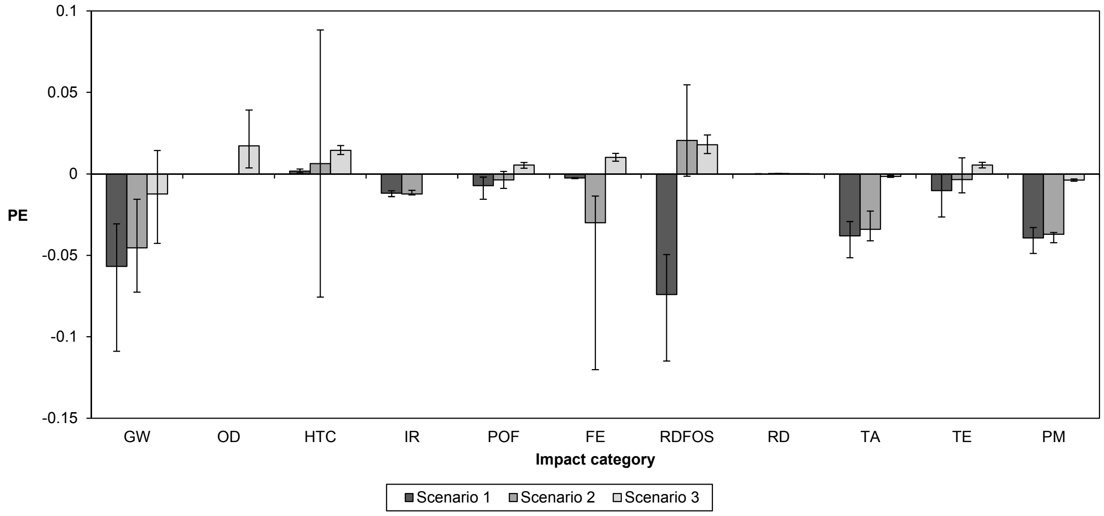

Figure 11: Normalized impact scores for scenario 1-3 (without the impact categories HTNC, ME and ET); error bars represent the 5th and the 9th percentiles of the distributions of the model output uncertainty (Bisinella et al. **VI**)

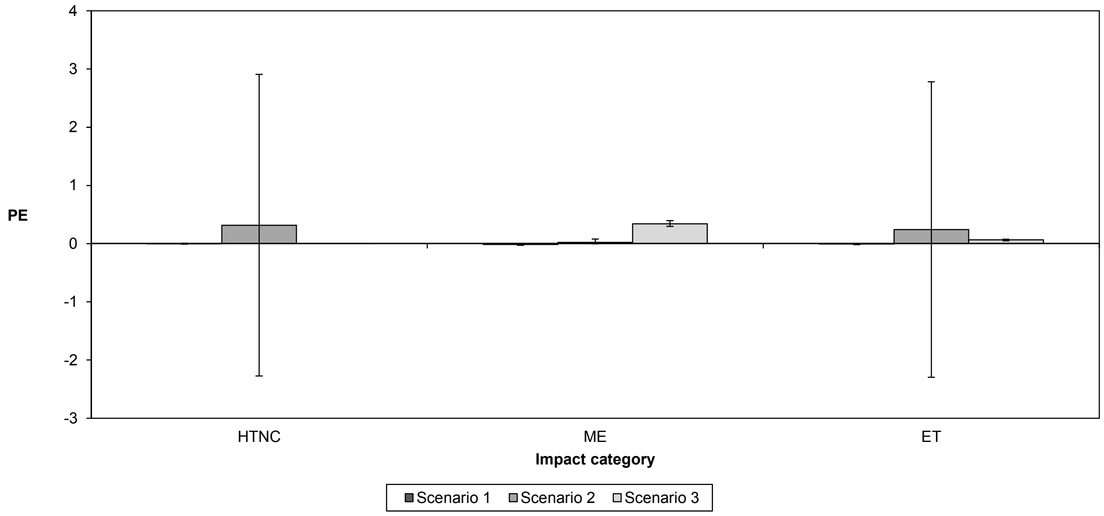

Figure 12: Normalized impact scores for scenario 1-3 for the impact categories HTNC, ME and ET; error bars represent the 5th and the 9th percentiles of the distributions of the model output uncertainty (Bisinella et al. **VI**)

Overall, rather low sensitivity was found for metals. However, when combined with the wide uncertainty ranges for metals very large output uncertainties resulted with considerable potential of shifting the mean values. This clearly demonstrates that sensitivity alone is not an appropriate measure to assess the relevance of physico-chemical waste characteristics which are associated with large variations.

The most relevant physico-chemical waste characteristics for the output uncertainty of scenario 1 were LHV, ash content/VS, fossil carbon content (C_{fossil}), and Hg. In scenario 2 the following additional parameters were identified as most relevant: Cu, Pb, Zn, P, N, and the fraction of biogenic carbon which is anaerobically digestible (C_{bioAnd}). The most relevant physico-chemical waste characteristics for scenario 3 were C_{bio}, C_{bioAnd}.

Of course the uncertainty analysis performed by Bisinella et al. (**VI**) is only valid for the specific process and systems models used for this investigation. As discussed for the landfilling scenario, the relevance of physico-chemical parameters depends crucially on how consistent the individual substances are tracked in the individual process models in the foreground systems. Thus, also other physico-chemical parameters could potentially play an important role and the presented list should not be interpreted as complete. In fact, by improving the understanding of substance-specific dynamics of waste treatment processes better process models considering more substances and more detailed flows can be developed and thereby more nuanced modelling results achieved. Furthermore, the availability of reliable characterization factors for the impact assessment of substances were for this particular investigation - and in general will always be - a LCA-methodological limitation beyond the direct influence of solid waste management experts.

Despite these limitations for generalization and completeness, the results of Bisinella et al. (**VI**) have shown that physico-chemical waste properties crucially influence the reliability of modelling results of waste systems LCAs and thus emphasize that special attention needs to be devoted to high-quality data selection and experimental data generation. As pointed out in the previous chapters of this thesis, many different factors need to be further investigated and current practice adjusted to promote more realistic LCA of waste management systems and more robust decisions on waste management systems.

4.4 Recommendations for selection and application of physico-chemical waste composition data

Based on the results and discussions presented in the previous chapters, this chapter provides recommendations on how to select physico-chemical waste composition data for environmental assessment and related uncertainty analysis. A summary is provided in Table 16.

Table 16: Summary of recommendations for the selection and application of physico-chemical waste composition data for environmental assessment and related uncertainty analysis

<table>
<tr><th>Step</th><th>Situation A:
Primary data available</th><th>Situation B:
No primary data</th></tr>
<tr><td>1. Select relevant waste characterization studies</td><td colspan="2">• Gather data from several studies to obtain intervals instead of single values
• Selection criteria:
- Waste fractions should match the waste management system (e.g. source-segregation and recycling)
- Preferably same location, otherwise similar waste collection and socio-economic aspects as in the geographical scope of the LCA
• Avoid studies which:
- Analyzed samples of simulated mixtures of non-waste materials
- Provide insufficient reporting of characterization methods</td></tr>
<tr><td>2. Check characterization methods</td><td colspan="2">• Check analytical methods in the selected studies for risk of systematic bias with available info (e.g. chapter 2 of this thesis) and consider this in step 3 and 4</td></tr>
<tr><td>3. Choose a preferred value or range for each parameter</td><td>• Use mean of primary values</td><td>• Select the value of the best-fitting study in terms of location, waste collection system and socio-economic aspects</td></tr>
<tr><td>4. Define uncertainty interval for uncertainty analysis</td><td>• Use analytical variation from primary data
+
extend with a wider range from selected literature data for uncertainty propagation to represent uncertainty due to sampling, selection of analytical methods and natural variability</td><td>• Use preferred value(s) and intervals from literature for uncertainty propagation
• e.g. for triangular distributions:
- preferred value = mode
- maximum and minimum = highest and lowest value found in selected literature</td></tr>
</table>

The key message is that data selection should aim at intervals instead of single values and that secondary data should be collected and considered even if primary data are available to compensate for the numerous influencing factors, which can hardly be all considered in a single waste characterization study. In the following paragraphs the defined steps are discussed in more detail.

The ***selection of relevant waste characterization studies*** should generally aim at selecting several studies providing information from a similar context, to be able to derive intervals for individual physico-chemical parameters instead of single values. Concrete criteria to be considered for the selection are difficult to define as quantification and ranking of the different influencing factors is pending. However, the wide value ranges in literature (Götze et al. **I**) and variation between materials within a material type (Götze et al. **III**) emphasize the need for detailed waste material fractioning. The fractions should fit the scope of the modelling. For example, if recycling schemes are assessed the analyzed material fractions should reflect the properties of the materials which are diverted during source-segregation and mechanical sorting in the modelled scenario. This is important to in order to consider appropriately the resource quality of individual material flows routed to different remanufacturing processes and the hazardousness of remaining waste and reject flows. The selected studies should also match with the geographical scope of the assessment, however, as previously discussed and presented in Figure 9 and Figure 10, macro regions are not suitable as an exclusive selection criterion. Thus also waste collection systems and socio-economic aspects of the waste characterization studies should fit the scope of the assessment. Regarding simulated waste samples, these data are not suitable to describe the variability and heterogeneity of real waste materials, thus should be avoided. Moreover, studies which insufficiently report analytical characterization methods should be avoided as they do not allow any considerations of possible systematic influences. An exclusion of studies based on specific analytical methods appears to be not realistic at this point due to limited data availability and variety of existing methods; they should, however, be considered as described in the next paragraphs.

A ***check of characterization methods*** in the selected studies should be performed and risk for systematic effects from analytical methods be considered during use of the values and interpretation of results. Generally enhancing consistency within the collected values should be anticipated. For example, the comparability of values obtained with different acid digestion methods could be improved by using the element recoveries provided in Götze et al (**II**) as "correction" factors.

The modeler should ***choose a preferred value or range for each physico-chemical parameter*** to perform the modelling of substance flows used to quantify environmental emissions. If the modelling software allows it, using a preferred range of values should be favored over using a single value. If primary data are available, the preferred value (or range) should refer to the mean of experimental results and/or the upper and lower confidence interval/standard deviation. If only secondary data from literature are available the preferred value (or range) should refer to the study (or studies) matching best with the waste collection system and socio-economic aspects in the geographical scope of the assessment.

Finally, the modeler should ***define the uncertainty interval for the uncertainty analysis*** for each physico-chemical parameter. If primary data are available the uncertainty interval should be extended by the value ranges found in relevant literature because the analytical uncertainty, which is typically derived from the repeated analysis of the same sample, is not suitable to reflect systematic effects of employed methods for mechanical and chemical sample preparation, mass reduction, sampling point, fraction definition and temporal variation. If only secondary data are available the uncertainty interval should be based on the entire value range found in selected literature. Often the value ranges in literature are not normally distributed and "outliers" in high concentration levels are very common especially for metals and trace elements (Götze et al., **I**). Such values should be included in uncertainty intervals as they are likely part of the actual distribution and of significant importance for the decision-making process (Clavreul et al., 2012; Skutan and Brunner, 2012). This finding suggests that assuming normal probability distributions for physico-chemical parameters during uncertainty propagation is very questionable, and log-normal distributions have been reported as more suitable to describe the skewed variability of concentrations in environmental materials and waste (Ahrens, 1954; Rotter, 2002). For LCA modelling typically very few values are used to construct uncertainty distributions and these values may origin from studies using different methods which can affect the results. Thus, simpler distributions such as triangular distributions or fuzzy sets may be more appropriate to propagate the uncertainty in environmental assessment (Clavreul et al., 2013; Klee, 1993). In conclusion, the preferred value selected in step 3 (Table 16) could for example be used as mode, and the highest and lowest value from literature as maximum and minimum of the triangular distribution for uncertainty propagation; for the propagation of fuzzy intervals the entire range of values from relevant literature around the narrower preferred value range (either from primary data or best-fitting literature) could be used.

5 Conclusions

Direct waste analysis was found to be the most frequently used waste characterization approach in literature. Compared to other approaches, direct waste analysis offers high flexibility and additional information on fractional composition for individual material fractions and waste flows. However, there is a clear need for improving direct waste analysis. It was shown that different characterization methods for direct waste analysis exist and that their reliability for total element content analysis is strongly dependent on the material fraction and the specific physico-chemical parameter. Physico-chemical waste characterization should be ideally performed on individual waste material fractions with similar mechanical properties (e.g. density, ductility, hardness) supporting time-efficient and unbiased mechanical sample preparation. The mechanical sample preparation of metal fractions is especially challenging.

Acid digestion methods were found to strongly affect the analytical results for the total element content. Generally, digestion methods involving large amounts of HF performed best but for some specific element-material combinations the overall optimal methods led to significant underestimation of the total element content. A single acid digestion method is thus not equally well-suited for all elements included in multi-element analysis. This needs to be considered by waste characterization and modelling practitioners. Considering material and parameter-specific aspects for the selection of appropriate acid digestion methods is crucial to obtain an accurate total content data of analyzed elements. Furthermore, acid digestion methods should be specified and reported by waste characterization studies.

A consistent dataset for 73 physico-chemical characteristics of household waste fractions from residual and source-segregated collection was obtained and is now available for future LCA modelling of waste management systems. For some waste material fractions differences between residual and source-segregated samples were found. However, the influence from individual factors (such as cross-contamination, different disposed products in the flows, “natural” variation, etc.) could not be quantified. While for parameters associated with organic matter generally higher levels were found in samples from residual flow the results for trace metal content are more complex. Several material fractions were identified where considerable heavy metal amounts were an intrinsic property of recyclables and thus need to be considered as “background concentrations” in non-hazardous waste materials.

Similarly, RRE were quantified in almost all fractions analyzed and especially high concentrations were associated with mineral and soil-like materials. Previously RRE have been typically associated with the presence of electronic/hazardous waste in MSW. The quantified levels for RRE in non-hazardous waste fractions need to be considered as "background concentrations" when concluding on electronic waste as a source and for estimations of related resource efficiency.

It was shown that selection of physico-chemical waste characterization data from literature significantly influences the reliability of the LCA of waste management systems. Based on the wide value ranges reported in literature, physico-chemical parameters contributed to a substantial share of the uncertainty in all scenarios, but especially for scenarios including incineration and digestion combined with application on land. Physico-chemical parameters contributed substantially to the output uncertainty of the LCA modelling results and were in many cases more important than technology and scenario specific parameters when the entire value range found in literature was used. Furthermore, it was shown that the parameter sensitivity in the LCA modeling alone is not a sufficient measure to assess the relevance of physico-chemical parameters. Instead it needs to be combined with realistic uncertainty ranges for each physico-chemical parameter in the input waste.

The selection of secondary waste composition data was shown to be related to several challenges: i) limited data availability, ii) poor data reporting, and iii) confusion about the meaning of total element contents. These issues can only be solved by transparency in data reporting and awareness between data-generating and data-applying research fields. Concluding from the results of the experimental acid digestion method comparison and the literature review, analytical techniques play an important role for accurate physico-chemical waste characterization data. At this point, however, low data availability and a large variety of waste characterization methods in literature limit the quantification and ranking of influencing factors via statistical data analysis. Nevertheless, it was found that the regional context of the data origin appeared to be less or equally important than other potential influencing factors.

Ideally environmental assessment should apply primary physico-chemical waste characterization data because many factors can be better controlled. However, unclear effects of different characterization methods and "natural" variation influence even primary data. Thus, value ranges (as opposed to single values) should be considered always. To compensate for unknown biases, systematic uncertainty analysis and evaluation of data selection compared to literature values should be considered mandatory even if primary data are available. Especially data for trace metal concentrations have been shown to be extremely variable and prone to be affected by sampling, mechanical sample preparation and analytical methods so that the typically reported analytical uncertainty is not meaningful in a context of uncertainty analysis of waste management LCA. The concept of realistic uncertainty ranges and data selection criteria needs to be further investigated for primary as well as for secondary data.

6 Outlook

Based on the findings presented in this thesis and the experience gained during the course of the PhD project future research of the following aspects is suggested:

Fractional and physico-chemical characterization of source-segregated recyclables which take properties relevant for recycling processes into account should be extended to different regions and waste management systems.

To improve direct waste analysis alternative sample preparation and/or analytical methods, for example smelting of specimen and non-destructive analytical methods should be explored. This is especially relevant for metal and plastic fractions for which current milling equipment can lead to de-mixing and particle size reduction is limited.

Systematic comparison of alternative analytical techniques for the individual waste materials and parameter combinations should be performed to quantify systematic differences in measured results and evaluate related advantages and drawbacks.

Experimental investigations should be compared and complemented with large scale data analysis to assess the combined effects of several influencing factors beyond the laboratory dimension. This may require advanced statistical and/or data mining techniques to deal with the several challenges related to the analysis of physico-chemical waste characterization data. These challenges include “missing data”, constraints related to compositional data (not smaller than zero, not higher than 100% etc.), and the fact that the data are typically not normally distributed. But to be able to do so, physico-chemical waste characterization data need to be made available and collected to a much larger extend than it has been done previously.

While the previously mentioned topics may lead to a higher frequency, more accurate waste characterization data and better understanding of influencing factors, the following topics need to be addressed by the waste LCA community to improve the application of waste composition data in environmental assessment. Research on transfer coefficients for material and individual substances in all waste treatment and recycling processes needs to be extended. Such investigations should pay special attention to the quantities, composition, and final disposal of reject flows as they are likely the most contaminated output flows and may dramatically influence recycling efficiencies and off-set emissions. For some processes such as the use on land of organic waste products and in-depth I study of release and partitioning in environmental media is important to complement limitations of current toxicity models used for the calculation of characterization factors.

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8 Papers

I **Götze, R.**, Boldrin, A., Scheutz, C., Astrup, T. F., Physico-chemical characterisation of material fractions in household waste: Overview of data in literature. *Waste Management.* DOI: 10.1016/j.wasman.2016.01.008

II **Götze, R.**, Astrup, T.F., Elemental composition of household waste materials: influence of acid digestion methods on multi-element analysis. Submitted to *International Journal of Environmental Analytical Chemistry*

III **Götze, R.**, Pivnenko, K., Boldrin, A., Scheutz, C., Astrup, T. F., Physico-chemical characterization of material fractions from residual and source-segregated household waste in Denmark. To be submitted to *Waste Management*

IV Edjabou, M. E., Jensen, M. B., **Götze, R.**, Pivnenko, K., Petersen, C., Scheutz, C., Astrup, T. F., Municipal solid waste composition: Sampling methodology, statistical analyses, and case study evaluation. *Waste Management*. DOI: 10.1016/j.wasman.2014.11.009

V Pivnenko, K., Olson, M. E., **Götze, R.**, Erikson, E., Astrup, T. F., Chemicals in the paper and board fractions of municipal solid waste. Submitted to *Waste Management*

VI Bisinella, V., **Götze, R.**, Damgaard, A., Astrup, T. F., Influence of waste characterization data in life cycle assessments of waste management systems. To be submitted to *Journal of Cleaner Production*

In this online version of the thesis, **paper I-VI** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from.

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The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four sections:
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