Urbanization and the Terrestrial Carbon Cycle

Pools, Processes and Implications for Ecosystem Services in the City of Hamburg

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Abstract

Although urbanization is a global phenomenon and its importance is projected to increase in the future, the role of urban areas in the global carbon cycle has so far not been conclusively studied. The global carbon cycle has gained interest among the scientific community and beyond during the past decades due to CO_2 being the single most important driver of anthropogenic climate change. Cities are considered the main drivers of CO_2 emissions due to the large global urban population globally. Recently however, other roles played by cities in the global carbon cycle have been acknowledged. Studies have demonstrated that cities to store substantial amounts of carbon in trees and soils, though soils remain largely understudied. Another way in which urbanization affects the carbon cycle is through alterations in leaf litter quality and subsequent decomposition processes. So far, only few studies have examined the effects urbanization has on decomposition, either indirectly through leaf litter quality alterations or directly through environmental alterations at the site of decomposition.

To highlight the benefits humanity derives from ecosystems and make these comprehensible for non-ecologists, the concept of ecosystem services has gained popularity in recent years. The global carbon cycle can be considered a regulating service, as it regulates the global climate. The thesis at hand presents a case study of components of the terrestrial carbon cycle in the city of Hamburg. Findings of the case study presented here are interpreted against the background of the ecosystem service concept.

Chapter 1 provides some background information about the global phenomenon of urbanization, presents common characteristics of urban areas, and gives a short overview of the emerging discipline of urban ecology. As findings of the thesis are to be interpreted against the concept of ecosystem services, the concept is introduced with special emphasize on carbon cycling as an ecosystem service, possible monetization of ecosystem services and ecosystem services generated in urban areas.

Chapter 2 explores carbon storage by urban trees and soils in different biotope types in the city of Hamburg. Urban areas have been shown to store substantial amounts of carbon in trees and soils, but organic carbon storage in urban soils is so far

underrepresented in the published literature. To calculate carbon storage by trees, allometric equations were used while soil organic carbon storage was analyzed with soil samples. No correlation was found between carbon storage in trees and soils of the individual biotope types. About 6 Mt of organic carbon are stored in the city of Hamburg, of which 4 Mt are stored in soils and 2 Mt in trees indicating a gross underrepresentation of carbon storage of urban areas in national carbon budgets. Biotopes differed significantly in the amount of stored carbon, with forested biotope types being of special importance for carbon storage in trees, and water-influenced biotope types being of special importance for carbon storage in soils.

Chapter 3 examines the effects of urbanization on leaf litter quality. Leaf litter of five tree species was sampled at tree stands in the city's center and at its periphery. Analyzed leaf litter quality parameters include dust depositions, epicuticular waxes, contents of structural carbohydrates, carbon and nitrogen as well as other elements. Parameters showed significant inter- as well as intraspecific differences depending on the urbanization level of the tree stand. Species' responses to urbanization were not uniform. Results indicate that urbanization has a considerable effect on leaf litter quality, observable even over short urban to periurban gradients. However, species differ in their reaction to urbanization and further research is needed to reliably predict effects of urbanization across a variety of species.

Chapter 4 addresses the influence of urbanization on decomposition processes and whether potential influences are exerted through leaf litter quality alterations or through direct effects of decomposition site's urbanization. Decomposition of the same leaf litter as in chapter 3 was observed through three different methods: a reciprocal litterbag transplant at urban and periurban sites, a common garden litterbag transplant and a climate chamber incubation. While the urbanization of site of decomposition did not show a significant effect, leaf litter of urban origin decomposed faster than litter of periurban origin. Thus, urbanization affects decomposition indirectly even over short gradients.

Chapter 5 addresses questions raised in chapter 1 and synthesizes findings of chapters 2 through 4. It examines the possibilities of extrapolating found results based on how common observations within the case studies are, compared to observations in other cities. While the carbon storage shows specific patterns in the city of Hamburg, transfers based on either biotope type maps or on other urbanization proxies provide possibilities of extrapolating results to other cities. Leaf litter alterations seem to be similar in different cities. The accelerated decomposition of urban originating litter is most likely transferable to most cities, whose heavy metal deposition is not too severe. On the contrary, effects of urbanization of decomposition site do not seem to be easily transferable. Furthermore, findings are discussed against the background of ecosystem services. Especially, options of incorporating decomposition processes into the ecosystem service concept are examined. Possible applications of the ecosystem service concept in general and findings of this thesis in particular for urban planners are discussed. The thesis concludes with an outlook for compelling future studies.

Zusammenfassung

Obwohl Verstädterung ein globales Phänomen ist, dessen Bedeutung in den nächsten Jahren voraussichtlich weiter zunehmen wird, ist die Rolle, die Städte im globalen Kohlenstoffkreislauf spielen, bisher nicht abschließend erforscht. Das Interesse von Wissenschaft und Öffentlichkeit am globalen Kohlenstoffkreislauf hat in den letzten Jahrzehnten aufgrund der Tatsache, dass CO_2 der wichtigste Einflussfaktor im vom Menschen verursachten Klimawandel ist, zugenommen. Städte sind aufgrund ihrer großen Bevölkerungszahl weltweit Hauptemittenten von CO_2. Allerdings emittieren sie nicht nur CO_2, sondern speichern auch signifikante Mengen Kohlenstoff in Bäumen und Böden, wobei Böden in bisherigen Studien selten untersucht wurden. Darüber hinaus beeinflussen Städte den Kohlenstoffkreislauf durch ihren Einfluss auf Zersetzungsprozesse. Es gibt bisher jedoch nur wenige Studien, die sich mit Veränderungen von Zersetzungsprozessen durch Verstädterung, die einerseits indirekt über einen Einfluss auf die Blattchemie, andererseits direkt über Veränderungen am Ort der Zersetzung wirken kann, beschäftigt haben.

In den letzten Jahren hat sich das Konzept der Ökosystemdienstleistungen durchgesetzt, um Vorteile, die Menschen aus Ökosystemen ziehen, deutlicher herausstellen zu können und sie leichter verständlich zu machen. Da der globale Kohlenstoffkreislauf einen regulierenden Effekt auf das Klima hat, kann er als regulierende Ökosystemdienstleistung betrachtet werden. Die vorliegende Arbeit stellt eine Fallstudie einzelner Komponenten des terrestrischen Kohlenstoffkreislaufes in der Stadt Hamburg dar. Ergebnisse der Arbeit werden vor dem Hintergrund des Ökosystemdienstleistungskonzeptes interpretiert.

Im Kapitel 1 wird zunächst das globale Phänomen der Verstädterung vorgestellt, inklusive einiger allgemeiner Charakteristika von Städten. Im Anschluss wird die Disziplin der Stadtökologie umrissen. Da die Ergebnisse der Untersuchung vor dem Hintergrund der Ökosystemdienstleistungen interpretiert werden sollen, wird dieses Konzept eingeführt. Besonderes Augenmerk wird hierbei auf den Kohlenstoffkreislauf als regulierende Ökosystemdienstleistung gelegt, sowie auf Möglichkeiten der Monetarisierung und Ökosystemdienstleistungen, die in Städten generiert werden.

Kapitel 2 untersucht die Kohlenstoffspeicherung in Bäumen und Böden verschiedener Biotoptypen Hamburgs. Besondere Aufmerksamkeit gilt hierbei den in der Literatur bisher unterrepräsentierten Böden. Die Menge an in Bäumen gespeichertem Kohlenstoff wurde mit Hilfe allometrischer Funktionen errechnet. Die Menge an im Boden gespeichertem Kohlenstoff wurde dagegen anhand von Bodenproben bestimmt. Es konnte keine Korrelation zwischen der Menge an gespeichertem Kohlenstoff in Bäumen und Böden einzelner Biotoptypen festgestellt werden. Insgesamt wurden etwa 6 Mt gespeicherter, organischer Kohlenstoff in Hamburg festgestellt, davon 4 Mt in Böden und 2 Mt in Bäumen. Dies weist auf eine deutliche Unterschätzung urbaner Kohlenstoffspeicher in bisherigen nationalen Kohlenstoff-Budgets hin. Die Biotoptypen unterschieden sich untereinander deutlich in der Menge an gespeichertem Kohlenstoff. Bewaldete Biotoptypen waren für die Speicherung von Kohlenstoff in Bäumen von besonderer Bedeutung, während wasserbeeinflusste Biotoptypen von besonderer Bedeutung für die Speicherung im Boden waren.

Kapitel 3 untersucht den Einfluss des Grades der Verstädterung auf die Laubstreu-Qualität. Laubstreu fünf verschiedener Baumarten wurde sowohl an Standorten im Innenstadtbereich sowie am Stadtrand gesammelt. Das Laub wurde auf Staubdepositionen, epikutikuläre Wachse, Gehalt an strukturellen Kohlenhydraten, Kohlenstoff- und Stickstoffgehalt sowie Gehalt an verschiedenen anderen Elementen untersucht. Die untersuchten Parameter zeigten signifikante zwischen- sowie innerartliche Unterschiede je nach Verstädterungsgrad des Baumstandortes. Allerdings waren die Veränderungen durch die Verstädterung nicht einheitlich zwischen den Arten. Die Ergebnisse beweisen, dass der Verstädterungsgrad des Baumstandortes einen messbaren Einfluss auf die Laubstreu-Qualität hat, und dass dieser bereits über kurze Gradienten nachweisbar ist. Dass die Arten sich hinsichtlich ihrer Reaktion auf den Verstädterungsgrad des Baumstandortes unterscheiden, legt nahe, dass weitere Untersuchungen nötig sind, um verlässliche Aussagen über den Einfluss des Faktors „Stadt“ für unterschiedliche Baumarten machen zu können.

Kapitel 4 beschäftigt sich mit den Einflüssen des Grades der Verstädterung auf Zersetzungsprozesse und ob diese entweder indirekt, durch Veränderungen in der Laubstreu-Qualität, oder direkt, durch den Grad der Verstädterung des Zersetzungsortes gesteuert werden. Die Zersetzung des gleichen Laubstreus wie in

Kapitel 3 wird mit Hilfe dreier verschiedener Methoden untersucht: ein reziprokes Litterbag-Experiment an Innenstadt- und Stadtrandstandorten, ein Litterbag-Experiment in einem Versuchsfeld sowie eine Klimakammer-Inkubation. Der Verstädterungsgrad des Zersetzungsortes zeigte keinen Einfluss auf die Zersetzungsgeschwindigkeit. Demgegenüber zersetzte sich Laub von Innenstadtstandorten schneller als Laub von Stadtrandstandorten. Dies zeigt, dass Verstädterung bereits über kurze Distanzen einen messbaren Effekt auf die Zersetzungsgeschwindigkeit von Laub bewirkt.

Kapitel 5 widmet sich erneut den Fragen, die in Kapitel 1 aufgeworfen wurden und fasst die Ergebnisse der Kapitel 2 bis 4 zusammen. Möglichkeiten der Übertragung der Ergebnisse auf andere Städte werden untersucht. Darüber hinaus werden Möglichkeiten zur Einbeziehung der Ergebnisse in das Ökosystemdienstleistungskonzept diskutiert. Mögliche Anwendungen für das Ökosystemdienstleistungskonzept im Allgemeinen sowie der Ergebnisse dieser Arbeit für Stadtplaner werden erläutert. Die Arbeit schließt mit einer Aussicht auf weiterführende, zukünftige Studien ab.

1 Introduction

Urban areas are both regions of intense anthropogenic land-use change with unpredictable influences on ecological processes within them, as well as drivers of global climate change with exceptionally high CO_2 emissions. However, urban areas' ecosystems also have a regulating influence on the global climate through storing carbon in trees and soils, thus generating an ecosystem service. So far, little is known about the influence urbanization has on the affected carbon cycle processes and the role urban ecosystems play in storing carbon.

First a short overview of urban areas globally, their common characteristics and the study of their ecology is given. Next, the concept of ecosystem services is introduced with special emphasize on carbon storage, monetization and ecosystem services generated within urban areas. After a short portrait of the study-site, the city of Hamburg, the thesis' aims and structure are presented.

1.1 Urban Areas

Urbanization as transformation of previously rural landscapes into urban areas is a global phenomenon of growing importance. More than half of the world's population resides in urban areas (3.6 billion people in 2011), thus health and well-being of the majority of people on earth is synonymous with health and well-being of urban inhabitants (Potere & Schneider 2007). The number of urban dwellers is expected to increase to 67 % (6.3 billion) in the year 2050, exceeding global population growth (United Nations 2011). While a high percentage of the developed world already resides in urban areas (78 %), the increase in the percent of urban inhabitants is expected to occur mainly in the developing world, where at the moment 47 % of the population lives in cities (United Nations 2011). The attraction for people to live in urban areas originates in their concentration of economic value, with about 80 % of the world's gross domestic product being generated in them (United Nations 2011).

At present, the areal extent of urban areas globally has not been reliably estimated. Comparisons of six different scientific areal studies yielded values ranging from 0.27 to 3.52 million km^2 due to different techniques used (Potere & Schneider 2007). The

Millennium Ecosystem Assessment (MA) (MA 2005) uses the upper value of 3.6 million km^2, corresponding to 2.4 % of the earth's surface. Estimations of areal extent of urban areas are hindered both by technical difficulties, as well as variable definitions of "urban" (Potere & Schneider 2007). Though urban areas are always defined as human dominated landscapes, the lack of a clear, global definition of "urban" has been pointed out by the United Nations (United Nations 2011). In Germany, urban areas are defined as having at least 500 inhabitants per km^2 and 50 000 inhabitants in total (Federal Statistical Office of Germany 2012).

While from an anthropocentric viewpoint the importance of urban areas is obvious due to the high number of urban inhabitants, the importance of urban areas for other organisms and ecosystems is higher than the areal extent would suggest. Urbanization affects organisms and ecosystems in areas exceeding those explicitly considered "urban" by the aforementioned definition. The influence or "footprint" of urban areas vastly exceeds the areal extent of urban areas (Folke *et al.* 1997, Grimm *et al.* 2008). Not only do urban dwellers import large amounts of food and other goods produced in rural areas, but also export waste, pollutants and CO_2. The role urban areas play in the various global elemental cycles is so far not fully quantified.

1.1.1 Characteristics of Urbanized Landscapes

Urban landscapes have been shown to vary from rural landscapes in numerous aspects. Due to the pronounced alterations in environmental parameters and ecological implications, urbanization has been referred to as a "massive, unplanned experiment" (McDonnell & Pickett 1990).

The urban heat island (UHI) effect leads to increased mean temperatures in cities compared to their rural surroundings (Oke 1973). The UHI has been attributed to three major causes (Oke 1973): Most importantly, building material (mostly concrete) has a higher heat storage capacity than most natural land covers, resulting in the collection and dissipation of heat from solar radiation. The lack of evapotranspirating surfaces in highly sealed and built-up city environments leads to a higher conversion of latent to sensible heat compared to unsealed surfaces. Additionally, the height of buildings alters wind patterns, resulting in a decreased exchange of the heated air masses from urban areas with rural hinterlands. The UHI has been cited as usually elevating temperature in urban areas by about 3 to 4 °C compared to rural surroundings (Solecki & Marcotullio 2013), but can reach values up to 11 °C in small, particular areas (Aniello *et al.* 1995). In addition to temperature, precipitation is increased in and downwind of cities due mainly to increased emissions providing condensation nuclei for the formation of rain drops, but possible explanations also include increased turbulence stemming from building heights and other effects (Schlünzen *et al.* 2010, Solecki & Marcotullio 2013).

One of the main products of combustion processes is CO_2 and urban areas have been labeled “hotspots” for its release (Grimm *et al.* 2008). The high amount of released CO_2 together with mesoclimatic conditions often result in the formation of a so-called “CO_2 dome” over a city, with increased contents of CO_2 in the urban atmosphere (e.g., Idso *et al.* 2001, George *et al.* 2007). The intensity of the CO_2 dome varies, but differences of up to 100 ppm between urban and rural sites have been observed (Idso *et al.* 2001). However, CO_2 concentrations in urban and rural areas are complex. The difference between urban and rural CO_2 concentration has been observed to be less on weekends (possibly due to less automotive traffic) (Idso *et al.* 2001). And the increase in CO_2 concentration in urban areas can be inversed especially during summer nights, when the respiration of CO_2 by plants in rural areas exceeds the amount of CO_2 released by combustion processes in the city (Berry & Colls 1990).

In addition to CO_2, combustion processes release various other pollutants. N deposition can be as high as 30 to 90 kg ha^{-1} $year^{-1}$ downwind of urban areas, compared to 1 to 4 kg ha^{-1} $year^{-1}$ in rural surroundings (Fenn *et al.* 2003). Release of SO_2 by vehicle combustion has been markedly reduced in Europe since the introduction of lead-free petrol, but emissions are still heightened in urban areas (Alfani *et al.* 2000). The release of precursors (e.g., nitrogen oxides) can lead to increased O_3 concentrations in and especially downwind of cities (Sieghardt *et al.* 2005). Metal and heavy metal pollution is increased in urban areas as well, either from combustion processes or other sources, e.g., Zn and Cu originating from brake and tire abrasion (Loranger *et al.* 1996). Additionally, hydrocarbons and polycyclic hydrocarbons are emitted, well known for adversely affecting human health (Seinfeld 1999). Pollutants can be gaseous (e.g., NO) or particulate (e.g., NH_4HSO_4) and can change between both states through processes such as photochemistry (Seinfeld

1999). Urbanization is often coupled with an increased dust deposition of various origins (e.g., traffic and construction work) (Farmer 1993).

Soils in most urban areas are extremely heterogeneous (Sieghardt *et al.* 2005). Urban soils are often characterized by incorporation of high amounts of man-made material. In the German classification, urban soils with building material layers can be differentiated according to their lime content (often they are Pararendzinen (calcareous) or Regosole (calcareous free) (Wittig & Sukopp 1998, AG Boden 2005)). The international classification WRB would classify them as technosol (WRB 2006), highlighting their anthropogenic origin. Due to the often high amount of incorporated calcareous building material, urban areas in the temperate zone have been called "lime islands" (Wittig *et al.* 1998). Urban soils have been shown to be highly compacted (Erz & Klausnitzer 1998) and contain high amounts of de-icing salts and heavy metals (Erz & Klausnitzer 1998). Generally, contamination of soils in urban areas can be severe.

Urbanization not only affects abiotic environmental parameters, but also organisms and thus biodiversity. Urban areas have been shown to generally have a reduced faunal diversity compared to their rural surroundings (e.g., Weller & Ganzhorn 2004), while on the contrary, vascular plant diversity has been shown to be increased (e.g., Pyšek 1993). Additionally, urban areas often show a high portion of non-native species (e.g., Steinberg *et al.* 1997). The similarity in urban habitats leads to a "global homogenization", with synanthropic species adapted to the altered environments being found in cities around the world and species assemblages being more similar to other cities than to their respective surroundings (McKinney 2006). For a detailed review of urban biodiversity patterns, please refer to Kowarik 2011.

Following the model of a concentric city, with a heavily urbanized inner city and a gradually decreasing level of urbanization towards the city's fringes (Wittig *et al.* 1998), distance to city center can be used as an approximation of level of urbanization. Still, urban areas are complex systems, and general trends can show high variations. The UHI for example has been observed to show both temporal and spatial variations. Temporarily, the UHI shows a distinct diurnal pattern with increased minimum temperatures during nighttime, while maximum temperatures during the day can actually be slightly decreased compared to rural surroundings (Moreno-Garcia 1994). Spatially, Schlünzen *et al.* 2010 has shown the UHI to be decreased by up to 50 % over unsealed compared to sealed surfaces and Wiesner *et al.* submitted has shown this effect to be influenced by soil water content.

The aforementioned alterations are common in urban areas around the globe. Still, differences between cities can be pronounced. Most studies of urbanization induced alterations assess only a single parameter for an individual city. So far, assembling published data for various alterations in a study city and combining it with newly measured data has rarely been done. These data can be a valuable support in addressing ecological questions of urban areas.

1.1.2 Urban Ecology

As urbanization globally gains importance and general trends in alterations of urban environment become better known, more and more ecologists turn towards ecological questions in the realm of urban areas. Historically, urban areas have been seen as lacking ecology (Elmqvist *et al.* 2013). The emergence of urban ecology as a discipline is hard to pinpoint, but first advances in the field can be found in floral works on the rubble fields of World War II (Kowarik 1992). The discipline further developed in the 1970s with, for example, the UNESCO program “Man and the Biosphere” (McDonnell 2011). By now, urban ecology has advanced into an ecological field in its own right, with many individual case studies being published and exceptional interdisciplinary projects. For example, the groundbreaking ten year study of forests in and near New York City (see McDonnell *et al.* 1997 and references within), which has spawned further research of examined phenomena in other cities around the globe (Pavao-Zuckerman & Coleman 2005, Nikula *et al.* 2010). Additionally, both the International Network Urban Biodiversity & Design (URBIO) and the Cities and Biodiversity Outlook (CBO) project, both connected to the UN Convention on Biological Diversity, should be mentioned. Two of the 26 worldwide Long Term Ecological Research Network (LTER) stations are set in urban areas (Phoenix and Baltimore) (Grimm *et al.* 2000). With the funding of the Society for Urban Ecology (SURE) in 2009, the field or urban ecology received their first international research association (Breuste & Qureshi 2011).

While the field of urban ecology advances, the definition of “urban ecology” differs between scientists. Wittig & Sukopp 1998 focus their definition of urban ecology on communities of plants and animals that are specific for the urban environment and do not occur elsewhere. The importance of these communities is stressed by Kowarik 1992. While he does not give a clear definition of “urban ecology”, his model of “nature in cities” is more inclusive, incorporating remnants of pre-urbanized vegetation, remnants of cultural landscapes and planned gardens within the political boundaries of cities. Both authors’ concepts deal with what can be called “ecology in cities” (Grimm *et al.* 2000). Newer studies argue for broadening the definition of urban ecology and incorporating humans and their respective values, stakeholders and so forth as part of the ecosystem “city”, resulting in an “ecology of cities” (Grimm *et al.* 2000, McDonnell 2011).

Despite the advances in the field of urban ecology, most research is done on detached processes or organisms. Studies working towards an integrated view of urban influenced biogeochemical cycles are rare.

1.2 Ecosystem Services

Humans rely on nature for survival. While ecologists have acknowledged the value of ecosystems for a long time, the direct dependence of humanity on the services provided by ecosystems proved difficult to convey. Historically, the limited understanding of the importance of ecosystems on behalf of stakeholders led to a lack of valuation. Through drastically reducing ecosystems to an anthropocentric viewpoint, communicating the value of ecosystems to stakeholders has been simplified (Costanza *et al.* 1997, Gómez-Baggethun *et al.* 2010). To make this thesis’ results more comprehensible, the concept of ecosystem services is a valuable background.

The idea of ecosystems providing “services” to humans can be traced back at least to the 19th century, but the beginning of the concept of ecosystem services are usually traced back into the 1970s with first widely acknowledged publications (Westman 1977, Daily 1997, Gómez-Baggethun *et al.* 2010). Through the publication of the MA (MA 2005) and five years later The Economics of Ecosystems and Biodiversity study (TEEB) (TEEB 2010), the concept of ecosystem services gained worldwide recognition and was implemented not only into science, but also widely into policy making and administration and the use of the ecosystem service concept is mainly to be seen in the interaction between science and politics (Haber 2014). Please refer to

Gómez-Baggethun *et al.* 2010 for a detailed introduction into the history of ecosystem services.

The MA was compiled on behalf of the United Nations by over two thousand scientists and stakeholders to assess the state of global ecosystems and foster their sustainable use with regard to anthropogenic changes and threats. The TEEB was initiated by Germany and the European Commission, building on knowledge established in the MA and focusing on the economic dimension of ecosystem services. Ecosystem services are divided into largely similar classes by both studies. Since the TEEB is based on the classifications in the MA, only the latter classification is presented here.

Ecosystem services are divided into the four classes: provisioning, regulating, cultural and supporting (MA 2005). The provisioning services include food, water and other materials (in a broad sense) of direct use for humans. The regulating services are somewhat more abstract as they are not directly consumed but rather create an environment fit for humans, including the regulation of climate and diseases. Cultural services are all those services that are used by humans for aesthetic, recreational or spiritual reasons. Lastly, supporting service, assist ecosystems in the provisioning of the other services, such as soil formation and nutrient cycling (Figure 1.1).

Despite the undeniable value of the ecosystem service concept, it was and is subject of controversy. The radical anthropocentric viewpoint raises objection as it excludes moral obligations and intrinsic value of nature (Costanza *et al.* 1997). As not all ecosystem functions connected to the provision of ecosystem services are understood, valuation is difficult (Bateman *et al.* 2011). An additional point of critique is the implied notion of being able to completely assess all (or at least all important) ecosystem services of an ecosystem. Though extremely difficult, this might be operable for the current situation, but it is impossible to foresee future potential services. For example, a century ago nobody would have valued carbon storage as an important ecosystem service, since the problem of anthropogenic climate change was not foreseen at the time. To illustrate the difficulty of valuation of ecosystem services even from an anthropocentric viewpoint, Westman 1977 gives the example of a poet inspired by a flower. How does one measure the value of this inspiration, of the poem or of inspirations the poems offered following generations? While the TEEB

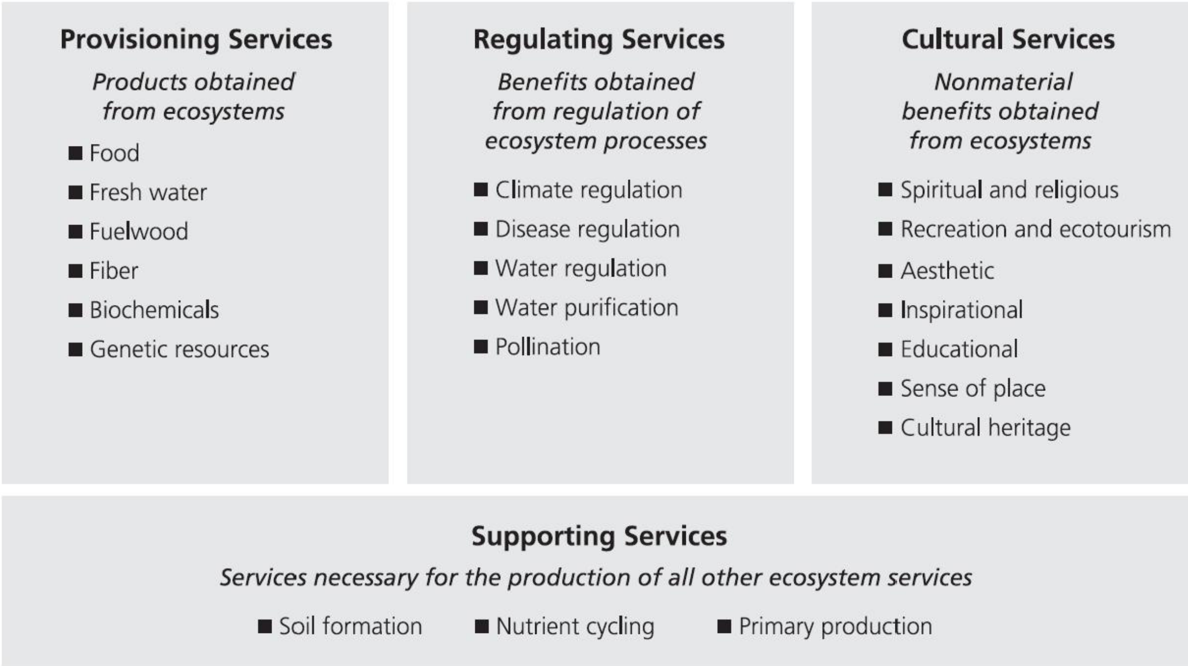

Figure 1.1 The four categories of ecosystem services: provisioning, regulating, cultural and supporting services with examples. The alignment highlights the fundamental function of supporting services for the other three (from MA 2003).

means well in “making a business case for […] ecosystem services”, the approach might undervalue intrinsic and hard to measure values and foster their destruction through a false sense of complete assessment.

With this criticism in mind, the ecosystem service concept should be understood as a helpful addition to moral and scientific standards, and not be used detached of these valuations (Costanza *et al.* 1997, Fisher *et al.* 2008). In Germany, the concept of ecosystem services has been implemented in the national strategy for biodiversity (Bundeministerium für Umwelt 2007) and many corporations and their associated unions as well as NGOs from conservational backgrounds largely support the implementation of the ecosystem service concept, though this support is not without objection (Hansjürgens 2014).

1.2.1 Carbon Cycling as an Ecosystem Service

Since CO_2 is the single most important driver of anthropogenic climate change (IPCC 2007), carbon storage and sequestration as regulating ecosystem services have gained interest among the scientific community in recent years. On a global scale, about 550 Pg C ($550 * 10^{15}$ g C) are stored in higher land plants and about

1 500 Pg C in soils (Siegenthaler & Sarmiento 1993). Both MA and TEEB focus on carbon storage as an ecosystem service, though mentioning the processes of carbon sequestration through forests. For the regulating service of the global climate however, the complete carbon cycle is relevant. A good overview of the carbon cycle can be found in Gurevitch *et al.* 2002: In short, as autotrophs, plants reduce the carbon in CO_2 through photosynthesis, storing carbon in various (organic) molecules for energy storage, structural components, proteins and other purposes. Oxidizing the reduced organic carbon releases energy. Plants either use stored energy through respiration or the carbon passes through the food chain, respectively is respired along the way. Eventually, all organisms die and the stored energy is used by decomposer communities. Globally, about 25 Pg C aboveground litterfall are produced in terrestrial ecosystems (Raich & Schlesinger 1992) and falling leaves constitute about 70 % of this litterfall (O'Neill & DeAngelis 1981). As certain cell structures and chemical components of organisms prohibit a fast or even complete respiration of carbon (e.g., N concentration), a portion is stored as long-lived soil organic carbon (Berg *et al.* 2001).

The speed of decomposition of leaf litter has been shown to be influenced by leaf litter quality. Following is a short overview based on (Berg & McClaugherty 2008): For a long time, lignin content of leaves has been associated with retarded decomposition. Lignin is not a distinct chemical, but rather a group of macromolecules based on phenols with similar structural functions in plants and recalcitrance against chemical disintegration. It decomposes much slower than cellulose and hemicellulose and actually shields them partly against decomposition (lignification). Contrary to lignin, N content of litter has been associated with rapid and complete decomposition in the past, as the nutrient promotes growth of decomposer communities in the early stages of decomposition (when unshielded cellulose or hemicellulose are present). This relationship is reversed in later stages of decomposition, when non-lignified cellulose and hemicellulose have been decomposed and lignin decomposition is the rate determining process. Here, a high N content inhibits ligninase (the enzyme responsible for lignin decomposition) and can form hard to decompose chelates with lignin molecules, thus retarding or inhibiting decay.

So far, the representation of the carbon cycle within the ecosystem service concept is incomplete. While carbon storage has been acknowledged as an ecosystem service, decomposition processes are not considered in most ecosystem service assessments. Possibilities to incorporate them have so far not been examined in detail. Additionally, the effect urbanization has on leaf litter quality and on decomposition has rarely been studied.

1.2.2 Monetization of Ecosystem Services

Both the MA and the TEEB emphasize stakeholders from business and administration to be part of their target audience and propose monetization as a means to reach these audiences. Monetization means expressing the value of an ecosystem service in monetary terms, or to put it colloquially "putting a price tag on nature". Natural ecosystems' goods are rarely traded and this drives their transformation into human-dominated ecosystems, as these have an economic value conveyed in monetary terms (Daily 1997). For example, the service of a natural landscape cleaning water is not traded, while the transformation of said landscape for agriculture leads to marketable products at the potential loss of water cleaning. In their seminal study, Costanza *et al.* 1997 estimated the entire biosphere to yield an average of US$ 33 trillion per year. In the past, recognition of ecosystem services was often fostered by the costs of their replacements, e.g., pesticides after the extinction of pest enemies (Daily 1997). Monetization seeks to estimate costs associated with loss of an ecosystem service in foresight, lessening pressure on ecosystems through value awareness. One means of monetization is creating markets for previously "free" goods, the best known example probably being the global carbon market with a total value of 126 billion € in 2011 (Kossoy & Guigon 2012).

Monetization should be used as an addition to quantitative and qualitative measures (e.g., value of beauty, moral obligations towards non-human organisms) (TEEB 2010). And some case studies point toward an increased support for conservation through monetization (TEEB 2010, Gómez-Baggethun *et al.* 2010). However, the points of criticism raised for the ecosystem service concept of course hold true for their subsequent monetization. Additionally, valuation of ecosystem services in monetary terms may seem absurd for some ecologists and an obvious difference exists between value and price (Bateman *et al.* 2011). Monetization might increase the risk of moral obligations and intrinsic values not being adequately considered. Even excluding the moral dimension, monetization of ecosystem services is flawed, as ecosystem's value in total is infinite (Costanza *et al.* 1997). Pricing might change, e.g., over time (Costanza *et al.* 1997), and accurate monetization of some ecosystem services is simply impossible at the moment (Bateman *et al.* 2011). Subsequently, if precise monetization is not possible, it might be better to abstain from bringing inaccurate numbers into political decision processes (Hampicke 1998). Some fear, that monetization poses the threat of a counterproductive re-focusing from ethical obligation to economic self-interest, which could lead to a shift from conservation to a "cashing in" mentality (Gómez-Baggethun *et al.* 2010). All criticism taken into consideration, it should be noted that ecosystems (or parts thereof) are valuated every time decisions about interferences in them are made (Costanza *et al.* 1997).

Monetization of carbon storage is well established with an administratively organized carbon market. However, the incorporation of the entire carbon cycle provided by ecosystems has not been discussed; especially decomposition processes have rarely been considered.

1.2.3 Urban Ecosystem Services

Urban areas utilize services generated by ecosystems outside their city limits (Folke *et al.* 1997), but ecosystems within cities also generate considerable amounts of services. The importance of urban ecosystems and the services they provide have been recently acknowledged (MA 2005, McGranahan *et al.* 2005) and further assessment of urban ecosystem services have been requested by the secretaries of the environment of the G8 countries (TEEB 2010). Despite the growing body of literature (Gómez-Baggethun *et al.* 2013), many aspects of urban ecosystem services have not been studied conclusively and empirical evidence is still scarce (Pataki *et al.* 2011). While improvement of ecosystem service provision through urban management is being discussed (Gaston *et al.* 2013), these knowledge gaps need to be filled to advise urban policy stakeholders and properly steer ecological sustainable development (Pickett *et al.* 2008).

Bolund & Hunhammar 1999's highly cited paper about ecosystem services generated within cities focuses on direct and local services, listing air filtration, microclimate regulation, noise reduction, rainwater drainage, sewage treatment as well as recreational and cultural values. The concept was later broadened as all ecosystem services are produced to a certain extent in urban areas and inclusion of ecosystem disservices (like the release of ozone forming volatile organic compounds by some trees) was suggested (Escobedo *et al.* 2011, Gómez-Baggethun *et al.* 2013, Gómez-Baggethun & Barton 2013). As urban areas are human dominated, the focus for urban generated ecosystem services is placed on health and cultural values in most assessments (Simon & Fritsche 1998, Tyrväinen *et al.* 2005, Niemelä *et al.* 2010).

Employing the concept of ecosystem services in urban areas aims to inform urban planners through “recognizing, demonstrating and capturing value” of urban ecosystems (Gómez-Baggethun *et al.* 2013). As ecosystems in urban areas often consist of small patches of unsealed surface with a high density of human population surrounding it, the demand for and number of demanded ecosystem services is likely high (Gómez-Baggethun *et al.* 2013). Here, the concept of ecosystem services can aid in urban planning (Niemelä *et al.* 2010) aiming at ecosystems creating multiple services synergistically and sustainably.

Urban areas are “hotspots” for the release of CO_2 (Grimm *et al.* 2008). Yet, ecosystems in urban areas also generate the service of carbon storage (Churkina *et al.* 2010), though some scientists assess the amount of sequestered carbon to be negligible compared to emissions (Pataki *et al.* 2011). While not all scientists acknowledge urban areas to store and sequester carbon at all (Costanza *et al.* 1997, Bolund & Hunhammar 1999, Janssens *et al.* 2005), some emphasize the carbon storage and sequestration potential of urban trees (Nowak & Crane 2002, Niemelä *et al.* 2010, Gómez-Baggethun *et al.* 2013) and soils (Pouyat *et al.* 2006).

The generation of ecosystem services within cities has so far not been studied conclusively, especially processes of the carbon cycle. For example, no study focusing on decomposition processes has been conducted in a German city and just a handful across Europe. Studies of carbon storage in urban trees and soils have been conducted mostly in recent years with a strong bias towards cities in the USA. However, most do not include processes. While first attempts have been made to broaden the concept of ecosystem services to include for example disservices (e.g., release of CO_2 by ecosystems), the few studies examining alterations in decomposition processes have so far not been conducted against the background of ecosystem services.

1.3 Study-Site Hamburg

Hamburg is a metropolis in northern Germany (53°38'N, 10°0'O), with about 1.8 million inhabitants (Statistisches Amt für Hamburg und Schleswig-Holstein 2013a). In addition to built-up areas of housing and industry, the city's political boundaries include agricultural, grassland, leisure, ruderal, transportation and wetland areas. About 8 % of the city's 755 km^2 are protected as nature reserve. About 61 km^2 are water bodies, of which the rivers Elbe (flowing from east to west) and Alster (flowing from the north into the Elbe) are the most prominent ones. Another 6 km^2 are islands located in the North Sea. Hamburg has a temperate oceanic climate with 749 mm of precipitation annually and an average annual temperature of 8.8 °C (Hoffmann & Schlünzen 2010). An UHI effect of about 1.1 K and a 5-20% decreased precipitation compared to areas 43 km downwind of the urban center have been observed (Schlünzen *et al.* 2010).

Hamburg takes pride in its large green areas, water bodies and numerous trees, calling itself a "green city" (e.g., Behörde für Stadtentwicklung und Umwelt 2013). Inhabitants value the green aspects of their city highly. A survey of 3 500 people found the willingness to pay for the recreational use of forests at Hamburg's fringes to be 42 € $year^{-1}$ $person^{-1}$ (Elsasser 1996) and about 70 % of inhabitants visited nearby forests at least once a month in 1994 (Elsasser 1994).

Soils in Hamburg were formed from parent material of both the Saale and the Weichsel ice age as well as fluvial and marine sediments deposited in the Elbe glacial valley, leading to an heterogeneous basis for soil formation and urban imprint (Miehlich 2010). Soils typical for rural areas lacking characteristics of urban imprint like the incorporation of anthropogenic material can be found predominantly on the city's fringes and in near-natural areas within the city. Soils over large areas in the city of Hamburg, especially close to industry like the former Norddeutsche Affinerie are contaminated (or restored after contamination) with e.g., arsenic and cadmium (e.g., Der Spiegel 1985).

1.4 Aim and Structure of Thesis

A review of the available literature revealed that remarkable scientific advances have been made in the interface of carbon cycling, urban ecology and ecosystem services. However, knowledge at this point is still far from being reliable and complete. This thesis is motivated by the goal of highlighting ecosystem services provided by urban ecosystems. It aims at assessing parts of the terrestrial carbon cycle within the city of Hamburg. It explores the generation of the ecosystem service of carbon storage in Hamburg and connects it to basic urban ecological questions of effects of urbanization on decomposition processes. In detail, organic carbon storage in trees and soils was quantified (chapter 2). Leaf litter quality alterations due to urbanization were examined (chapter 3) and subsequently the influence of urbanization on decomposition processes (directly and indirectly) (chapter 4). Findings are discussed against the background of ecosystem services and possible applications for urban planners are assessed.

Chapter 2 presents the quantification of organic carbon stored in trees and soils of Hamburg. To assess the ecosystem service of carbon storage within the city of Hamburg, allometric equations were used to calculate carbon stored in trees, and soil samples were analyzed for organic carbon content in the lab. This was done for a hundred sample plots in the city and results were extrapolated according to biotope type and city area. Results are discussed and compared to results from cities around the globe.

Chapter 3 analyzes the alterations in leaf litter quality due to urbanization of tree stands. Leaf litter quality is examined by employing various laboratory methods. Observed alterations between samples originating from the urban and periurban stands are interpreted with the aid of published values of environmental alterations between the urban and periurban tree stands.

Chapter 4 addresses the urban ecological question of what effects urbanization has on decomposition processes. Three different methods are employed to assess whether urbanization of a) tree stand from which the litter originates or b) site of decomposition has an influence on the mass loss rate. Results are interpreted incorporating findings of chapter 3, measured data and findings in other cities.

Chapter 5 presents key findings of the case studies, and the possibilities of extrapolating results from the case studies towards urban areas globally are discussed. Further examinations are dedicated to the possibilities of incorporating findings of the case studies into the concept of ecosystem services and their subsequent application. To conclude, ideas for future studies are presented.

2 Quantification of Organic Carbon Storage in Trees and Soils

2.1 Introduction

Carbon storage by urban forest trees has been quantified in various urban areas, mainly in US cities (e.g., Rowntree & Nowak 1991, Nowak & Crane 2002, Hutyra *et al.* 2011), but also around the globe including in the UK (Davies *et al.* 2011), Germany (Strohbach & Haase 2012), China (Liu & Li 2012) and Australia (Brack 2002). Soil organic carbon (SOC) is often neglected in urban carbon storage studies (e.g., Davies *et al.* 2011), despite studies indicating more organic carbon being stored in urban soils than in urban vegetation (Churkina *et al.* 2010). So far, only few studies have quantified the amount of organic carbon stored in urban soils (e.g., Pouyat *et al.* 2002, Lorenz & Lal 2012), producing an unbalanced level of knowledge about carbon storage in urban trees and soils. First steps have been made to jointly quantify the amount of carbon stored in trees and soil (e.g., Jo & McPherson 1995), but so far only two studies have used a city-wide sampling regime (Pouyat *et al.* 2002, Edmondson *et al.* 2012). However, to consider the heterogeneity of urban land uses, a finer spatial resolution is required than employed in the aforementioned studies.

As cities differ in many aspects, the amount of carbon stored in trees (Nowak *et al.* 2013) and soils (Pouyat *et al.* 2006) differs strongly between them. Studies are needed to complement previous findings with additional carbon storage values to result in realistic estimates and improve accuracy of global carbon storage models. Up to now, no study has quantified the amount of organic carbon stored in urban forest trees and urban soils in a large European metropolis. This study aims at quantifying organic carbon stored in urban trees and soils of Hamburg (Germany), resulting in a city-wide carbon storage budget of both compartments autonomously. It will consider spatial heterogeneity and examine patterns of carbon storage based on land use and vegetation maps, enabling direct comparison of carbon storage in trees with organic carbon storage in soils. This study will highlight both areas between which the amount of stored organic carbon differs between these compartments as will be areas of special importance for this ecosystem service. Findings offer information to regional planners as well as stakeholders interested in global carbon cycle modeling.

This study examines whether urban trees or soils are more important for carbon storage and whether the relational importance is mirrored in previously published studies. Additionally, it examines how proxies used in national carbon budgets represent urban areas and how carbon storage values from Hamburg compare to cities around the globe. The study determined areas of special importance for regional planners seeking to preserve the ecosystem service of carbon storage.

2.2 Material and Methods

Establishment of study plots and field measurements

To create a stratified random survey of organic carbon stored in trees and soil, the biotope type cadaster of Hamburg was used. The cadaster is based on previously existing maps, aerial photography and ground surveys. It is continuously updated, yielding a comprehensive data set of varying resolution. It is consulted for a variety of legal purposes, including the habitat directive of the European Union (92/43/EEC 1992). It is compiled on the authority of the Behörde für Stadtentwicklung und Umwelt (Office for Urban Planning and Environment) and hierarchically classifies vegetation and landscape utilization units into biotope types, capturing natural conditions as well as accounting for the human component in landscape units as called for by Grimm *et al.* 2000. For this study, the cadaster's units were combined to ten biotope types primarily based on higher hierarchical classes: agriculture, densely built-up, scattered built-up, industry and administration built-up, dry forest, wet forest, grassland, leisure area (e.g., parks, allotment gardens and cemeteries), ruderal (e.g., dry grasslands, brownfields and landfills), transportation (e.g., streets, harbor and airport) and wetland (Figure 2.1). Both water bodies and islands were excluded from this study.

Ten random plots per biotope type, established with the aid of ArcGIS 9.3 (ESRI Inc., Redlands, CA, USA), were sampled from June to October 2012. Digital maps were used to locate and sample determined plots in the field. If access to a plot was impossible or not granted, it was relocated to a nearby location within the same

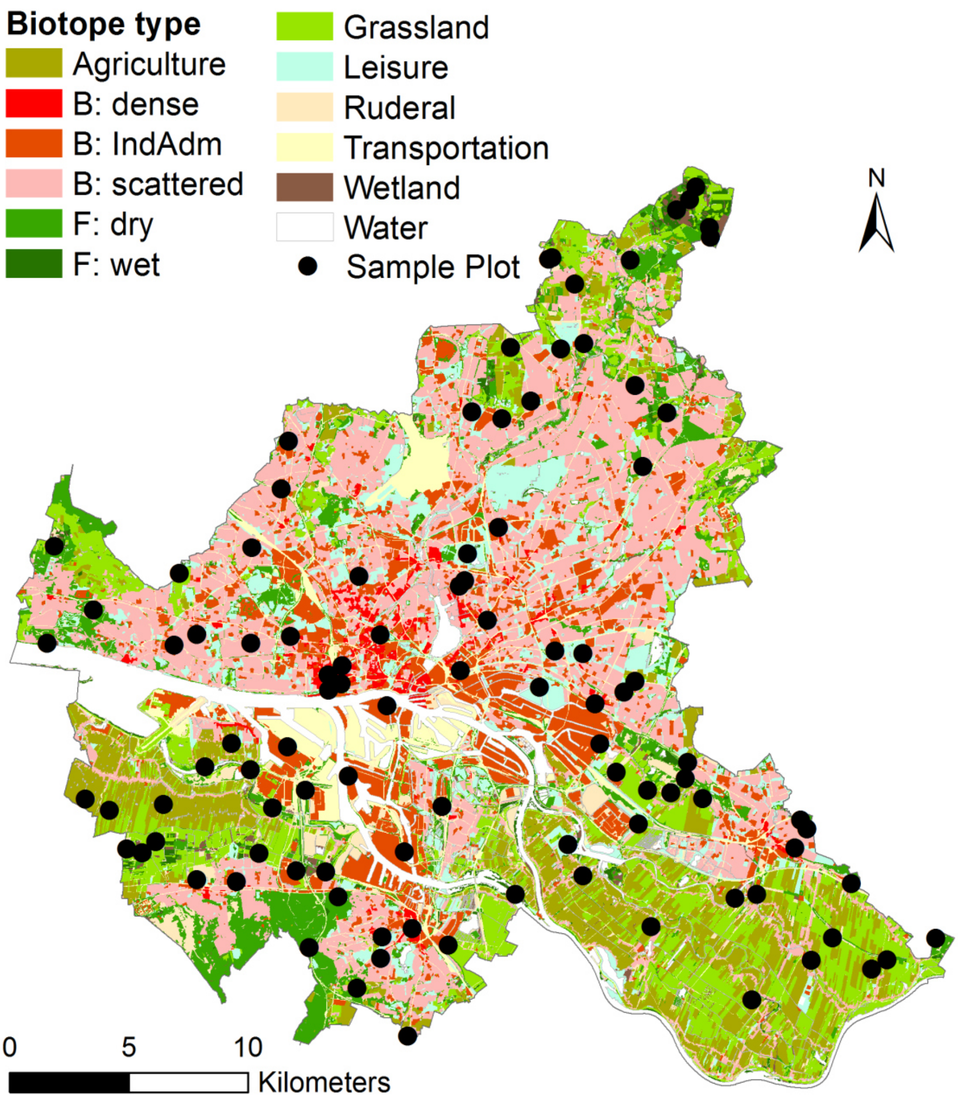

Figure 2.1 The ten biotope types in Hamburg with taken sample plots (B denotes built-up, IndAdm industry and administration, F forest).

biotope type. If this proved to be impossible, the next random plot was used until ten plots per biotope type were sampled. To ensure access to ten sample plots in each biotope type, fifty random plots were created in advance.

Each study plot consisted of a circle with a 15 m radius. To determine tree biomass, diameter at breast height (DBH) of all living trees and branches within the circle exceeding a diameter of 5 cm were measured and species determined. To calculate fine soil mass, soil bulk density and skeleton content were determined according to BKA 2005 (AG Boden 2005), by digging a 30 cm deep hole, noting skeleton content and taking four soil cores of 100 mL: two from 0-10 cm depth and two from 10-30 cm depth. To determine mean SOC content, pooled soil samples of 15 individual drillings per plot were taken from 0-10 and 10-30 cm depth by a soil auger.

Under some circumstances, especially in the built-up areas, the plot design had to be modified. Setting up the plots on unsealed surfaces as close as possible to the originally determined random plots, i.e. on the same property, was aimed at. If properties were too small or offered not enough unsealed surface to set up a representative 15 m radius plot, either a semi-circle was set up or the entire property was sampled. Later, the entire area of the property and the relation of sealed surface were determined using ArcGIS maps. These data were used to calculate the relative proportion of sampled trees and soil to a 15 m radius plot. In total, 25 plots had to be modified (see Figure 2.1 for sample plots across Hamburg.

Carbon storage in trees

To calculate biomass of trees, allometric equations by Jenkins *et al.* 2003 were used, which are based on a thorough literature search, creating a large set of pseudodata to create new equations. Jenkins *et al.* 2003 established ten comprehensive species groups, with biomass equations based on species identity and diameter at breast height for long-lived tree components (woody aboveground biomass and coarse roots), referred to as “tree” in this study. Accordingly, leaf biomass was calculated using formulas by Jenkins *et al.* 2003. If a sampled species could not be found in one of Jenkins *et al.* 2003 groups, it was assigned based on genus, specific wood gravity or habit. Jenkins *et al.* 2003 equations were favored over European allometric equations (e.g., Zianis *et al.* 2005) since they are based on a large data set with multiple equations, which has been shown to produce more reliable results than regional equations based on limited data sets (McHale *et al.* 2009). Some authors suggest a reduction of biomass values calculated for urban trees with allometric equations derived from urban stands (Nowak 1994). However, since other studies found no clear reduction trend in biomass of urban grown trees compared to forest grown (McHale *et al.* 2009, Aguaron & McPherson 2012), and a substantial portion of trees in Hamburg grow in forest-like areas, biomass values were used as calculated by the original allometric equations. To calculate the amount of carbon from biomass values, a conversion factor of 0.5 was applied (Hutyra *et al.* 2011). Carbon storage in trees per plot was summed and means of kg carbon stored in trees per square meter for each biotope type were calculated by integrating the plot area.

For modified plots, a way of calculating the ratio of measured trees to trees that would have been measured on a representative study plot was established. It was distinguished between plots set deliberately on unsealed surface and plots at which entire properties were sampled. If plots were set deliberately on unsealed areas, more trees were measured than would have been on the originally determined, representative sample plot. To avoid overestimation, the amount of carbon stored in trees was reduced proportionally by the proportion of sealed surface of the property. If entire properties were sampled, the area of sampled trees was either larger or smaller than a standard sample plot. Consequently, the amount of carbon stored in trees was multiplied by the area of standard sample plot and subsequently divided by the actual sampled area.

Organic carbon storage in soils

To determine bulk density, the two 100 mL soil cores per layer per plot were oven-dried at 105 °C for 24 h, weighted and means calculated. To determine organic carbon content of the soil, the pooled samples were air-dried and sieved to 2 mm. Subsequently, the samples were ground using a swing mill. Total carbon content of the ground samples was determined using a CN-Analyzer (Vario MAX CNS elementar, Elementar Analysensysteme GmbH, Hanau, Germany). Since samples with a pH of above 6 potentially contain inorganic carbon, pH of sieved samples was measured. If pH exceeded 6, inorganic carbon content was determined using a second CN-Analyzer (Vario MAX cube, Elementar Analysensysteme GmbH, Hanau, Germany). Organic carbon content per sample was calculated by subtracting the amount of inorganic carbon from the amount of total carbon if necessary. To calculate mass of fine soil in the soil layer per plot, determined bulk density was multiplied by soil volume per layer per plot and skeleton content subtracted. The calculated mass of fine soil was multiplied by the determined organic carbon content to yield organic carbon mass per layer per plot. All analyses were conducted separately for 0-10 and 10-30 cm layers and the amounts were summed subsequently. Divided by plot area, this value yielded SOC in kg per m^2. As for carbon stored in trees, means for SOC were calculated for each biotope type.

Since only soils in areas with unsealed surfaces were sampled, SOC would be overestimated on modified plots if the sample mean would be used as plot mean. Sealed soils were assumed to not take part in active carbon processing and assigned to contain no organic carbon. To correct for sealed surfaces, SOC values were reduced proportionally by the ratio of sealed surface of the property. Additionally, the number of individual drillings for the pooled soil sample was reduced proportionally if the sampled area was reduced due to sealing (from 15 for the 15 m radius to a minimum of 8).

Transportation biotope type

Since the study design is not applicable in the transportation biotope type due to traffic and accessibility, two other datasets were used for calculation of carbon stored in street trees and SOC. For tree carbon storage, the street tree inventory in which all 222 000 street trees of Hamburg are registered with species and DBH was used (courtesy of Office for Urban Planning and Environment) with the same allometric equations as above. Trees having a DBH smaller than 5 cm or unrealistic large values for shrub species (indicating crown diameter having been noted as stem diameter) were excluded from the calculation. The calculated amount of stored carbon was summed and divided by the areal extent of the transportation biotope type, yielding mean kg carbon per m^2. For SOC storage, mean carbon content was calculated from mass percent SOC data of 40 tree beds (J. Ehrhardt, *unpublished data*). These values were multiplied by the mean bulk density determined for Hamburg in this study and estimated mean volume of tree bases with 2 m^2 area and 30 cm depth. This value was multiplied by the number of street trees and divided by the area of transportation biotope type yielding mean kg carbon per m^2. Calculated values are conservative estimates. Trees growing in the transportation biotope type, but not close to streets (e.g., along railways) were not considered. Additionally, unsealed areas within the transportation biotope type without street trees (e.g., airport) were not considered for SOC.

Further analyses

Using the biotope type cadaster and the calculated mean values of organic carbon storage for each biotope type, the spatial distribution of organic carbon storage in trees and soils across Hamburg was visualized with the aid of ArcGIS. Absolute values of organic carbon storage for Hamburg were calculated by multiplying the spatial extent of each biotope type with the mean organic carbon storage per square meter.

To test whether and which biotope types differ in their mean amounts of stored organic carbon, non-parametric Kruskal-Wallis tests with subsequent post-hoc tests were used. To test whether the amount of organic carbon stored in trees and soil differ within the biotope types, Wilcoxon test for paired samples was used. All sampled organic carbon storage values were visualized in a scatterplot and checked for correlation. All statistical analyses were conducted in Statistica 9.1 (StatSoft Inc., Tulsa, OK, USA).

2.3 Results

A total of 2145 tree stems were measured, belonging to at least 66 tree species. Of these, 15 were determined on genus level only. Most species per plot were found in dry forest (over 16, including *Crataegus* sp. and *Prunus* sp.). *Salix* sp. was the most abundant genus with 382 stems measured. The largest stem surveyed belonged to a *Quercus robur* L. with a diameter at breast height of 118 cm, standing in a leisure area plot. Mean number of stems per plot was 21. On 40 plots, no trees were found. Overall, wet and dry forest store the highest mean amount of carbon in trees with 12.64 and 12.32 kg C m^{-2}, respectively, followed by leisure area with 5.98 kg C m^{-2}. No trees were found in grassland and only scattered trees in ruderal area and agriculture (0.57 and 0.46 kg C m^{-2}, respectively). Mean carbon storage in trees including street trees in the transportation biotope type in the city of Hamburg was 2.74 kg C m^{-2} (Table 2.1). Kruskal-Wallis test and post-hoc tests revealed highly significant ($p<0.001$) differences in organic carbon storage between biotope types (Table 2.1).

The highest SOC content per square meter was determined in a wet forest plot (42.51 kg C m^{-2}), followed by a wetland plot (39.14 kg C m^{-2}). In total, ten plots were completely sealed: six belonging to the biotope type industry and administration built-up and four to dense built-up. Overall, the highest mean SOC content was sampled in wet forest and wetland (14.43 and 14.16 kg C m^{-2}, respectively), followed by grassland (9.72 kg C m^{-2}). The lowest mean amount was found in the three built-up biotope types: industry and administration, dense and scattered (1.31, 1.56 and 5.81 kg C m^{-2}, respectively). Overall-mean SOC storage of the determined biotope types including transportation areas in the city of Hamburg was 6.30 kg C m^{-2} (Table 2.1). As with tree carbon storage, Kruskal-Wallis test and post-hoc tests revealed highly significant ($p<0.001$) differences in organic carbon storage in soils between biotope types (Table 2.1).

Regarding transportation areas, the most abundant genus was *Tilia* with about 53 000 individual trees. In total, street trees stored about 142 000 tonnes organic C and about 4 000 tonnes organic C in soil, resulting in a mean value of 2.84 kg C m^{-2} for transportation area (Table 2.1, Table 2.2).

Adding the amount of organic carbon stored in trees to the amount stored in soil, wet and dry forest as well as wetland were the biotope types with the highest mean values (27.07, 19.90 and 15.38 kg C m^{-2}, respectively). The three biotope types with the smallest amount of organic carbon stored were the three built-up types: industry and administration, dense and scattered (2.43, 3.87, 7.34 kg C m^{-2}, respectively) (Table 2.1).

No correlation was found between organic carbon stored in trees and soils (Figure 2.2) and Wilcoxon test for paired samples revealed a significant difference between the amounts of organic carbon stored in trees and in soils within the biotope types agriculture, scattered built-up, grassland, ruderal and wetland (Table 2.1). Exclusion of plots without trees did not yield a correlation either (*data not shown*).

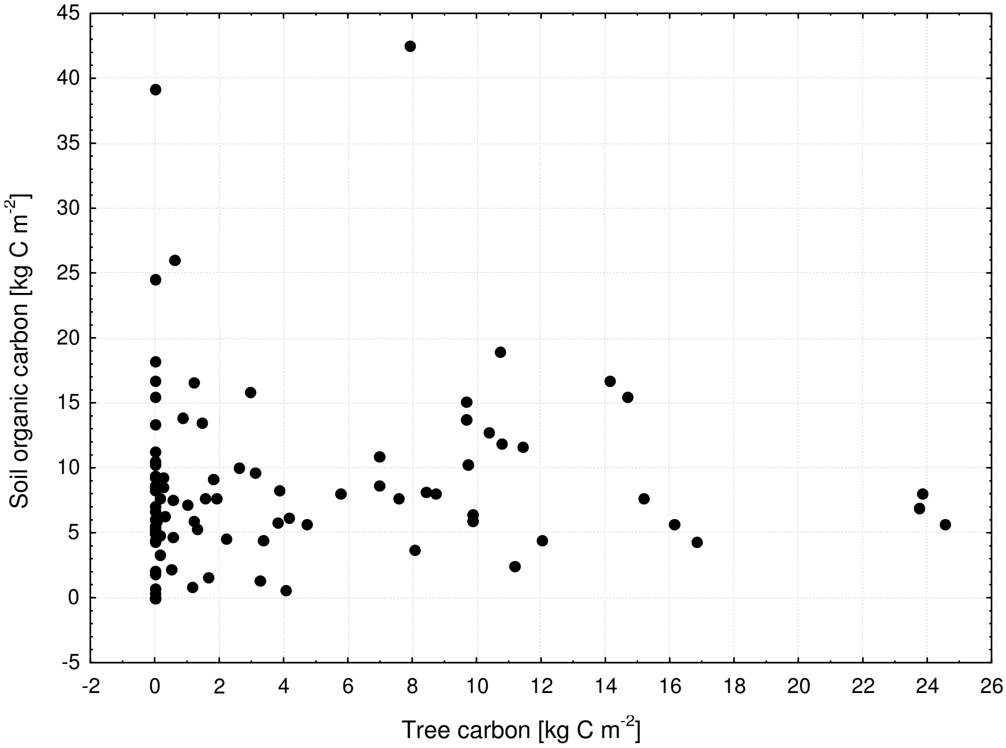

Figure 2.2 Scatterplot of organic carbon stored in trees versus in soil. No correlation could be found (P=0.2417 and r^2=0.0140).

Spatial distribution of organic carbon storage across Hamburg was linked to the distribution of biotope types (Figure 2.1). Carbon storage in trees was especially high in the south and north-west, with areas in the west and south-east storing small amounts (Figure 2.3a). Organic carbon storage in soils was especially high in the north, south-west and south-east (Figure 2.3b). Organic carbon by trees and soil was stored across the city with areas of especially high values located on the cities fringes: the south-west, the north-west and the north (Figure 2.3c).

Table 2.1 Minimum, maximum and mean values of organic carbon storage in trees, soil and the respective sum for the ten biotope types in the city of Hamburg (n= 10, except for transportation; “B:” built-up, “F:” forest, “IndAdm” industry and administration, “n.d”. not determined). Standard errors for estimates are given in parentheses where calculation was possible. Totals incorporate spatial extent of biotope types across Hamburg (including transportation areas but excluding water bodies and islands). Superscript letters indicate post-hoc test results of significantly differing biotope types (Kruskal-Wallis test with P<0.001). P-values of Wilcoxon tests for differences between amount of carbon stored in both compartments of each biotope type (significant values in bold).

Biotope type	Carbon stored in trees [kg C m^{-2}]			Organic carbon stored in soil [kg C m^{-2}]			Sum of carbon stored in trees and soil [kg C m^{-2}]			Difference
	Mean (SE)	Min	Max	Mean (SE)	Min	Max	Mean (SE)	Min	Max	P-value
Agriculture	0.46 (0.23)^{ab}	0.00	1.83	7.41 (0.87)^{ab}	4.44	13.45	7.87 (1.00)	4.44	14.92	**0.005**
B: dense	2.32 (1.13)^{ab}	0.00	9.87	1.56 (0.63)^{a}	0.00	6.42	3.87 (1.70)	0.00	16.30	0.249
B: IndAdm	1.12 (0.59)^{ab}	0.00	5.78	1.31 (0.75)^{a}	0.00	7.98	2.43 (1.30)	0.00	13.76	0.715
B: scattered	1.53 (0.47)^{abc}	0.00	4.16	5.81 (0.57)^{ab}	3.31	9.98	7.34 (0.86)	3.46	12.62	**0.005**
F: dry	12.32 (2.13)^{c}	3.13	24.53	7.57 (0.88)^{ab}	2.40	11.95	19.90 (2.14)	10.34	30.74	0.169
F: wet	12.64 (1.50)^{c}	6.97	23.83	14.43 (3.33)^{b}	4.28	42.51	27.07 (3.06)	15.60	50.41	0.646
Grassland	0.00 (0.00)^{b}	0.00	0.00	9.72 (1.02)^{b}	5.33	16.69	9.72 (1.02)	5.33	16.69	**0.005**
Leisure	5.98 (1.47)^{ac}	0.00	16.14	9.37 (0.90)^{b}	5.63	15.80	15.35 (1.55)	9.24	23.13	0.093
Ruderal	0.57 (0.31)^{ab}	0.00	3.36	9.26 (2.47)^{ab}	0.40	26.02	9.83 (2.43)	0.40	26.60	**0.005**
Transportation	2.77$^{n.d.}$	n.d.	n.d.	0.07$^{n.d.}$	n.d	n.d	2.84	n.d	n.d	n.d.
Wetland	1.22 (0.90)^{ab}	0.00	9.68	14.16 (3.19)^{b}	5.05	39.14	15.38 (3.31)	5.05	39.13	**0.005**
Total	2.74 (0.62)			6.30 (0.84)			9.04 (1.19)			

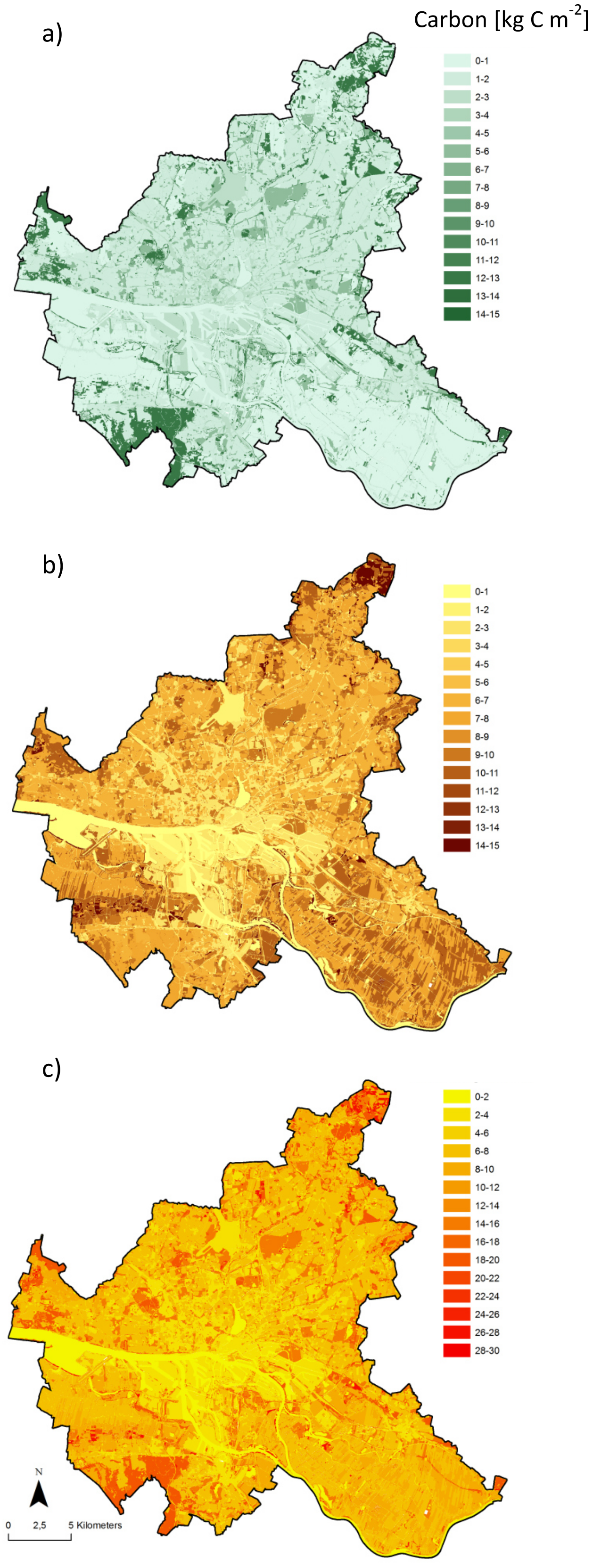

Figure 2.3 Mean amount of organic carbon stored across Hamburg in (a) trees, (b) soil and (c) the sum thereof.

Calculation of total organic carbon amounts stored across the various biotope types revealed that not necessarily the biotope types covering the largest area in Hamburg stored the highest total amounts of organic carbon. Dry forests and leisure areas stored the highest amounts in trees (about 789 000 and 364 000 tonnes, at 64 and 61 km^2, respectively). The third highest amount of carbon in trees (about 306 000 tonnes) and the highest amount of organic carbon in soil (about 1 158 000 tonnes) were stored by the largest biotope type, scattered building (199 km^2). Grassland and agriculture stored the second and third highest amount of organic carbon in soil (about 923 000 and 590 000 tonnes, at 95 and 80 km^2, respectively) (Table 2.2). Foliage over the entire city stored about 43 000 tonnes of organic carbon and the three built-up classes stored about 10 000 tonnes (Table 2.3).

Table 2.2 Area and total values of organic carbon storage in trees, soil and the respective sum for the eleven biotope types in the city of Hamburg ("B:" building, "F:" forest, "IndAdm" industry and administration) including standard errors (where possible).

Biotope type	Area [km^2]	Total carbon stored in trees [t]	Total organic carbon stored in soil [t]	Total sum of carbon stored in trees and soil [t]
Agriculture	79.59	36 636 (±17 953)	589 802 (±69 102)	626 438 (±79 301)
B: dense	11.35	26 323 (±12 776)	17 657 (±7 140)	43 979 (±19 238)
B: IndAdm	82.78	92 599 (±48 600)	108 238 (±61 805)	200 837 (±107 641)
B: scattered	199.32	305 674 (±93 797)	1 157 884 (±112 813)	1 463 558 (±170 648)
F: dry	64.01	788 819 (±136 503)	484 781 (±56 374)	1 273 600 (±137 236)
F: wet	7.88	99608 (±11 835)	113 730 (±26 260)	213 337 (±24 089)
Grassland	94.93	0 (±0)	922 697 (±97 072)	922 697 (±97 072)
Leisure	60.96	364 456 (±89 898)	571 071 (±54 738)	935 527 (±94 263)
Ruderal	26.97	15 245 (±8 344)	249 781 (±66 508)	265 026 (±65 898)
Transportation	51.25	142 148	3 573	145 721
Wetland	7.06	8 583 (±6 358)	100 004 (±22 554)	108 587 (±23 359)
Total	686.10	1 880 090 (±426 063)	4 319 218 (±574 368)	6 199 308 (±818 745)

Table 2.3 Biotope types of Hamburg with their respective area, total carbon stored in foliage, mean, minimum and maximum of foliage carbon per sample plot (standard errors given in parenthesis where possible).

	Area [km^2]	Total C in foliage [t]	Mean foliage [kg C m^2]	Min foliage [kg C m^2]	Max foliage [kg C m^2]
Agriculture	79.59	1041 (±536)	0.01 (±0.01)	0.00	0.06
B: dense	11.35	450 (±222)	0.04 (±0.02)	0.00	0.18
B: IndAdm	82.78	1564 (±838)	0.02 (±0.01)	0.00	0.10
B: scattered	199.32	8278 (±3034)	0.04 (±0.02)	0.00	0.16
F: dry	64.01	21273 (±4021)	0.33 (±0.06)	0.10	0.62
F: wet	7.88	1809 (±167)	0.23 (±0.02)	0.16	0.39
Grassland	94.93	0 (±0)	0.00 (±0.00)	0.00	0.00
Leisure	60.96	6229 (±1400)	0.10 (±0.02)	0.00	0.25
Ruderal	26.97	367 (±188)	0.01 (±0.01)	0.00	0.07
Transportation	51.25	2328	0.05		
Wetland	7.06	152 (±99)	0.02 (±0.01)	0.00	0.15
Overall	686.1	43491 (±1819)	0.08 (±0.03)	0.00	0.62

2.4 Discussion

This study is the first to quantify the ecosystem service of carbon storage in trees jointly with carbon stored in soil for a European metropolis. Germany accepted the legal obligation of reporting greenhouse gas sources and sinks through the Kyoto Protocols (Federal Environment Agency 2013). But despite the discussion of including urban forest carbon credits in the international carbon market (Stoffberg *et al.* 2010, Poudyal *et al.* 2011), carbon budgets for sinks in the category “settlements” are so far not based on specifically collected data but derived from other land-uses (“grassland” and “woody grassland”) (Federal Environment Agency 2013). Findings suggest that carbon storage in settlements is underestimated by up to a hundred percent in national carbon storage budgets, with 1.34 kg C m^{-2} for biomass C and 5.87 kg C m^{-2} for mineral soil C (Federal Environment Agency 2013) compared to 2.74 kg C m^{-2} and 6.30 kg C m^{-2} found in this study. An even more pronounced mismatch has been observed for UK inventories, where national carbon budgets have been shown to undervalue urban area’s carbon storage by up to an order of magnitude (Davies *et al.* 2011).

Results of total organic carbon storage in Hamburg contradict previous suggestions of only minor carbon storage in urban areas (Kaye *et al.* 2006, Pataki *et al.* 2011). With total organic carbon storage in trees and soil of about 1.9 Mt (1.9 $*10^{12}$ g C) and 4.3 Mt, compared to 1 081 Mt and 2 249 Mt in the whole of Germany (Dieter & Elsasser 2002), Hamburg stores around the same amount of carbon on a per area basis as the rest of Germany (0.2 % of Germany's total carbon in trees and soil on about 0.2 % of the country's area). While carbon is stored across the city, areas of special interest for carbon storage are mostly located on the city's fringes, congruent mainly with forest biotope types and wetlands (Figure 2.3). A definition of "urban" not following political boundaries and excluding the cities fringes would have substantially lowered these values. A clear definition of "urban" and spatial boundaries is thus substantial when evaluating urban carbon storage (Raciti *et al.* 2012b). While the amount of carbon stored within the political boundaries on a per area basis is equivalent to the amount stored in the whole of Germany, the conclusion that urbanization does not affect carbon storage would be misleading. A definition of urban based solely on the three built-up classes, despite considerable amounts of carbon would still be stored due to the large areal extent, would have indicated a much lower per area storage than the average of Germany.

With 2.74 kg C m^{-2} Hamburg's mean carbon storage in trees is almost similar to mean values for US cities, ranging from 0.5 to 4.7 kg C m^{-2} (Nowak & Crane 2002) with overall means from 2.51 kg C m^{-2} (Nowak & Crane 2002) to 2.97 kg C m^{-2} (Rowntree & Nowak 1991). In Europe, mean carbon storage in trees for urban areas range from 1.12 kg m^{-2} in Barcelona, Spain (Chaparro & Terradas 2009) to 3.16 kg C m^{-2} in Leicester, United Kingdom (Davies *et al.* 2011) to 3.23 kg C m^{-2} in Karlsruhe, Germany (Kändler *et al.* 2011). When comparing findings of different studies it is important to keep in mind that not only climate, geology and historical backgrounds of cities differ, but also methodologies (Davies *et al.* 2013), e.g., kind of allometric equations used (McHale *et al.* 2009). Only a published study of Leipzig allows for direct comparisons between carbon stored in trees in the different biotope types, being from the same climate zone, using a similar map of vegetation and utilization for stratification and also defining urban as being congruent with the political boundaries of the city (Strohbach & Haase 2012). In contrast to this study, root biomass, which can be estimated at 25 % of above-ground biomass (Jo & McPherson 1995), was not calculated and biomass values for human dominated land covers were reduced by 20 % following Nowak 1994 as well as slight differences between biotope units exist (Strohbach & Haase 2012). Overall, Hamburg shows higher mean carbon storage in trees in most comparable biotope types than Leipzig, e.g., 2.32 kg C m^{-2} in dense built-up areas of Hamburg compared to 0.51 and 0.42 kg C m^{-2} in tenement blocks and terraced houses and multi-story houses of Leipzig, respectively, resulting in an overall value of 1.18 kg C m^{-2} for Leipzig. This reinforces Hamburg's claim of being a green city, as built-up classes show a high amount of stored carbon in trees.

Quantification of SOC storage in the city of Hamburg revealed that the biotope types wet forest and wetland store the highest amounts (14.43 and 14.16 kg C m^{-2}, respectively). In addition to the aforementioned difficulties in direct comparisons of studies from different cities, SOC studies differ in sampling depth. For example, park soils in Ohio, USA showed carbon storage values from 16.3 to 21.1 kg C m^{-2} at 100 cm depth (Lorenz & Lal 2012) compared to a mean SOC storage of 9.37 kg C m^{-2} at 30 cm depth in leisure biotope types of Hamburg. For this study, sealed surfaces were considered to contain no carbon, since it is unlikely that these carbon pools still take part in carbon cycling (Raciti *et al.* 2012a) and potential amount of carbon stored is highly uncertain: studies have used averages of 3.3 kg C m^{-2} at 1 m depth determined for clean fill as a proxy (Pouyat *et al.* 2006), determined a 66 % reduction of carbon stored under impervious surfaces (Raciti *et al.* 2012a) or found no significant differences between amounts of carbon stored under impervious and pervious surfaces (Edmondson *et al.* 2012). Not reducing SOC values due to sealed surfaces or coarse soil fragments, SOC contents of 5 kg C m^{-2} at 15 cm depth in forest areas of Baltimore, USA (Pouyat *et al.* 2002) were measured, compared to 14.43 and 7.57 kg C m^{-2} in wet and dry forest areas of Hamburg, respectively. Overall, the mean SOC value of 6.30 kg C m^{-2} at 30 cm depth in Hamburg is roughly in the same range as internationally published results, despite the mentioned difficulties in comparison. Combined data from Baltimore and New York City resulted in a mean of 8.2 kg C m^{-2} at 1 m depth (Pouyat *et al.* 2002), while a later study of six US cities resulted in a mean value of 6.3 kg m^{-2} at 1 m depth for SOC storage (Pouyat *et al.* 2006).

Areas in Hamburg with especially high carbon storage values in trees are mainly areas in the south-west and in smaller areas in the north and north-west (Figure 2.3), congruent with the occurrence of forests (Figure 2.1). Additionally, widespread areas of built-up land throughout the city show moderately high tree carbon storage (Figure 2.3a). Areas of special interest for carbon storage in soils are influenced by water or wet soil conditions and are mainly located in the north and north-west, and along an approximately ten kilometers wide corridor along the river Elbe (Elbe valley) flowing from east to west through central Hamburg (Figure 2.3b). In the north, wetlands are predominant which are either fed by the river Alster originating north of Hamburg or are remnants of glacial lakes of the Saale-Ice Age (Engelschall 2010). The Elbe valley is a relic of previous water influence by meandering of the river, as well as of tidal flooding forming bogs, fens and tidal marshes along the valley's fringes close to the river until embankment in the 12. to 16. century and continuous drainage due to agriculture and farmland use (Miehlich 2010).

Previous studies have emphasized the disproportionate importance of SOC storage against carbon storage in trees in urban areas. Found ratios range from 1.2 in Chuncheon, Korea (Jo 2002) to 14.7 for Wyoming, USA (Pouyat *et al.* 2006). This study supports previous findings, with an overall ratio of 2.3, closer to the mean of 2.8 found for US cities (Pouyat *et al.* 2006) than to the ratio of 4.6 found in the only other European study to quantify both organic carbon stored in trees and soil (Edmondson *et al.* 2012). Despite these ratios, the focus of most urban carbon storage quantification studies has been biased towards carbon storage in trees, with carbon storage in soils being neglected (e.g., Hutyra *et al.* 2011). This study's results should encourage consideration of urban SOC studies by stakeholders striving to preserve the ecosystem service of carbon storage.

No correlation between organic carbon storage in trees and soil and a significant difference between carbon storage in both compartments in the agriculture, scattered built-up, grassland, ruderal and wetland biotope types was found in this study (Figure 2.3, Table 2.1). This emphasizes the need for quantification of both compartments, and it refutes previous suggestions implying (possibly through careless wording) the use of aerial tree cover photographs as an indicator for total urban carbon storage (Whitford *et al.* 2001). Extrapolation of total organic carbon storage from aerial photographs would imply a correlation of soil organic carbon storage to tree cover or a similar proxy. Stratification based on biotope types enables a very detailed comparison of particular areas and analysis of differences for the ecosystem service of carbon storage. This approach enables regional stakeholders to locate areas of special interest and additionally indicates whether the amount of organic carbon stored in both compartment differs significantly and needs to be examined separately.

Stakeholders employing the ecosystem service concept need to consider possible trade-offs and synergies (Smith *et al.* 2013), as urban dwellers, in particular, might value cultural ecosystem services more highly than climate regulating ones (Niemelä *et al.* 2010). However, this study not only addresses regional stakeholders, but results should be incorporated in national and global carbon cycle models. Biogeochemical models that exist for rural areas cannot be directly transferred to urban areas (Kaye *et al.* 2006) and first studies to explicitly model carbon sequestration in residential landscapes have been made (Zirkle *et al.* 2012). These models need to be based on an array of empirical data from different cities and collected with differing methods around the globe to be reliable and thus applicable on a global scale.

To conclude, Hamburg stores significant amounts of organic carbon in its political boundaries and carbon storage in urban areas is so far underrepresented in national carbon budgets. Carbon is not stored evenly across the city; on the contrary areas of special interest for regional planners can be localized. Despite the over proportional importance of carbon storage in soils versus trees, soils are underrepresented in published studies and assumptions made by extrapolating terrestrial carbon storage from tree carbon storage need to be dismissed. Future research is needed to investigate the possibility of a study design stratified based on soil properties to capture the spatial heterogeneity of SOC across cities.

3 Alterations in Leaf Litter Quality Due to Urbanization

3.1 Introduction

The numerous aspects of urbanization (especially environmental alterations and enhanced pollution) have been shown to affect tree leaf litter quality (e.g., Alfani *et al.* 2000). Though direct causality is impossible to determine in the complex urban system, changes in leaf litter quality can be interpreted by incorporating results from previous studies performing single parameter manipulations. Higher N depositions might lead to higher litter N contents, however elevated atmospheric CO_2 concentrations have been found to potentially decrease leaf litter N content (Cotrufo *et al.* 1998, Norby *et al.* 2001). Increased CO_2 concentrations can lead to increased lignin contents (Norby *et al.* 2001), but this effect has not been confirmed in all studies (Cotrufo *et al.* 2005). Increased O_3 has also been shown to increase lignin content in some tree species (Boerner & Rebbeck 1995). Increased O_3 exposition as well as drought stress can lead to increased amounts of epicuticular waxes (Bengtson *et al.* 1978, Karnosky *et al.* 2002). Dust can have numerous effects on leaf litter, depending largely on its composition and source (Farmer 1993). Washing of urban leaves has been shown to significantly reduce metal concentrations, suggesting a high portion of found metals are deposited on the leaf surface, stemming from atmospheric deposition rather than uptake via roots (Gratani *et al.* 2000). Urban, periurban or roadside originating leaf samples tend to contain higher amounts of trace elements (e.g., Peachey *et al.* 2009), and concentrations can exceed values negatively affecting plant growth (Scheffer *et al.* 2010). Only a few studies to date have analyzed the effects of the complex alterations of environmental parameters along the urban-periurban gradient on leaf litter quality. Especially interactions between altered parameters might result in unforeseen changes in leaf litter quality.

Extrapolation of leaf litter alterations due to urbanization from previous studies is challenging, as they have been conducted on single species (e.g., Carreiro *et al.*

1999, Nikula *et al.* 2010). However, plant species and their respective litter do not react uniformly to even single parameter alterations, making extrapolations from single-species studies uncertain. For example, different variants of even the same species have shown differing leaf litter reactions to urban sulfur deposition in Córdoba, Argentina (Carreras *et al.* 1996). Extrapolating the results from previous studies to draw general conclusions about litter alterations in cities is further hindered by the high variability of city structures and dwellers' habits around the globe. To create reliable foundations for predictions of leaf litter alterations due to urbanization, further research on various species as well as on similar species in various cities is needed.

Studies analyzing the effects of urbanization on leaf litter quality often employ long gradients reaching far into the rural hinterlands (e.g., about 130 km in Carreiro *et al.* 1999 and 30 km in Nikula *et al.* 2010). While urban air pollution has been known for a while to drop steeply from a city's center to its periphery (Lovett *et al.* 2000), alterations occurring along short urban to periurban gradients have not been studied conclusively.

Environmental parameters and pollution regimes are expected to be altered in the northern temperate city of Hamburg, Germany compared to less urbanized landscapes. Alterations are hypothesized to significantly affect tree leaf litter quality. Further, alterations are expected to drop steeply at the city's fringes, about 11 km from the city's center, resulting in significant differences in leaf litter quality between urban and periurban originating leaf litter. In addition, species are expected to react differently to urbanization and to show significant differences in their leaf litter quality alterations.

3.2 Material and Methods

Study Site

To characterize the urban to periurban gradient in this study, temperature and precipitation data were obtained as GIS shapes from the German Meteorological Service (DWD) with spatially interpolated climatic values (2010). Additionally, mean values of SO_2, NO, NO_2, O_3 and PM_{10} of the study year 2011 measured and published by Freie und Hansestadt Hamburg 2012 were used. Measurements were conducted by permanent stations in the city's center (station Sternschanze), at a station in a rural area on the city's fringe (station Tatenberg) and at a station at the city's fringes, close to a motorway (station Billstedt) (Freie und Hansestadt Hamburg 2012). However, not all stations track all mentioned parameters (Table 3.1). Human population densities were obtained on district level (Statistisches Amt für Hamburg und Schleswig-Holstein 2012).

Selection of Trees

Five tree species were selected for this study. Selected species are *Acer platanoides, Alnus glutinosa, Populus tremula, Quercus rubra* and *Robinia pseudoacacia*, all of which are common in Bertram *et al.* 2010, but not necessarily native to the study area. *Quercus* and *Robinia* both are native to North America, but were widely planted in Europe as park trees. Of the selected species, *Alnus* as well as *Robinia* live in symbiosis with N-fixing bacteria. Individual trees were selected with the objective of growing in open sites in parks or green strips and not in small roadside tree-planting spaces enclosed by a high degree of sealing. They were selected with the aid of a tree cadaster provided by the Office for Urban Planning and Environment Hamburg. For each species ten urban and ten periurban individual trees were sampled, with urban trees growing in the cities center (mean distance of about 3 km to the city hall) and periurban growing close to the cities political border (mean distance 11 km downwind of city hall; distance between sites was 10 to 17 km) (Figure 3.1). Thus, this thesis conducts studies on a contrast rather than a gradient. To clarify the thematic connection to previous studies, however, the term gradient is used here and in the following chapters.

Collection and Analyzes of Leaves

For analysis of epicuticular waxes and dust deposition, green leaves were collected from each tree in 2 to 6 m height in September 2011 and frozen at -75 °C. Leaves of each tree were thawed and a subsample of about 5 g submersed and swung in chloroform for about 30 seconds. Solutions were filtered with weighed glass microfibre filters (GF/C, Whatman International Ltd., Maidstone, England) into weighed petri dishes. Mass of dust deposition and epicuticular waxes relative to fresh weight of leaves was determined by weight differences of filters and petri dishes after complete evaporation of chloroform.

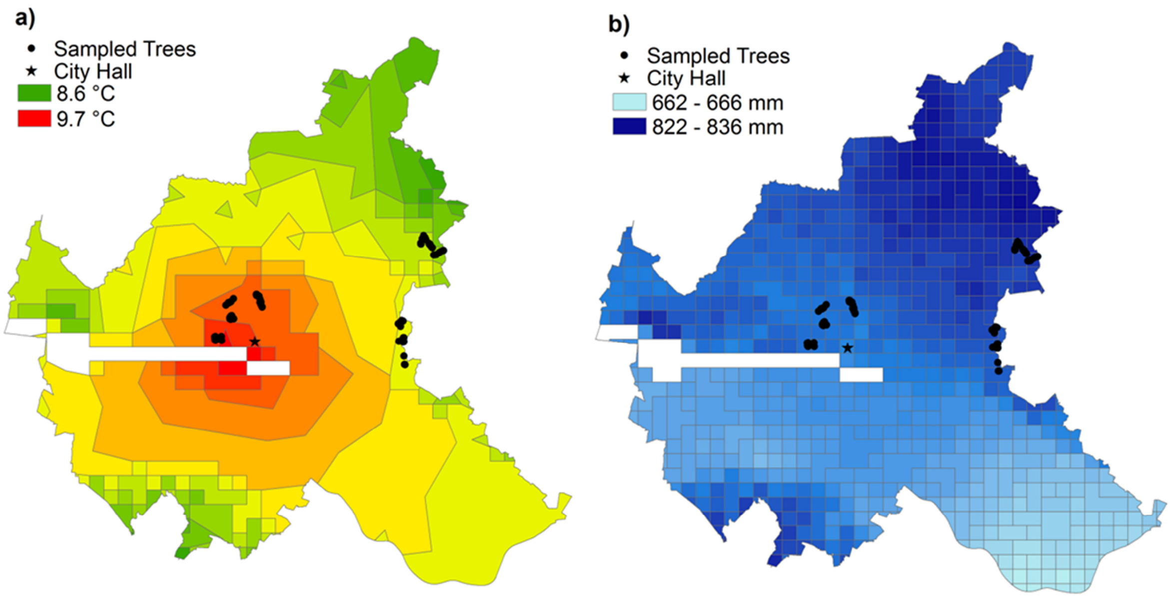

Figure 3.1 Indicating the location of individual trees, city hall and the respective mean a) temperature and b) precipitation [from…to…] in the city of Hamburg (white fields indicate western parts of the river Elbe).

All remaining analyzes were performed on air dried, senescent leaf litter collected off the ground in October 2011. Content of chemical elements was determined via inductively coupled plasma optical emission spectrometry (iCAP 6300 duo, Thermo Fisher Scientific, Schwerte, Germany), except for carbon and N whose content was determined via separate CN analyses (vario MAX CNS elementar, Elementar Analysesysteme GmbH, Hanau, Germany). Content of structural carbohydrates was determined in a fiber analyzer (ANKOM 2000, ANKOM technology, Macedon NY, USA) via subsequent digestion in detergent solutions for neutral and acid detergent fiber (NDF consisting mainly of hemicellulose, cellulose and lignin; ADF consisting mainly of cellulose and lignin) as well as acid detergent lignin (ADL) as described by the manufacturer (ANKOM 2014).

Two urban *Acer* and one urban *Populus* tree were identified as different species during analyses and were subsequently excluded from the analysis. Furthermore, despite green leaves having been sampled separately for wax and dust analyses, senesced litter of two urban *Robinia* could not be separated reliably when collected off the ground, thus yielding identical values for the analysis of senescent litter.

Statistical Analyzes

Mean values and standard errors of measured parameters were calculated for litter of urban and periurban origin for all species. Selected parameters were illustrated as figures, while others were depicted in table form due to spatial restrictions. After checking for normal distribution with Shapiro-Wilks tests, intraspecific differences between origins were tested for significance via unpaired *t*-tests. Box-Cox transformations were used where data did not show normal distribution. If transformation did not result in normally distributed data, Kruskal-Wallis tests were used instead of *t*-tests. To test for differences between species, origins and their interaction, two-way ANOVAs were computed with approximated normal distribution through square root, log 10 or Box-Cox transformations. Spearmans-Rank correlations were calculated to evaluate correlation between measured parameters. All statistical analyses were conducted in Statistica 9.1 (StatSoft Inc., Tulsa, OK, USA).

3.3 Results

Urban to Periurban Gradient

Districts of sampled urban tree stands were warmer (mean of 9.5 °C), drier (753 mm annual mean) and had a higher human population density (about 11 000 per km^2) than periurban ones (9.0 °C, 784 mm, about 4 000 people per km^2, respectively) (Figure 3.1). Atmospheric CO_2 concentrations at periurban stands in similar distance to the ones in this study was determined to be raised by about 22 ppm compared to rural stands (J. Ehrhardt, *pers. communication*). The sample year was characterized by a high deposition of PM_{10} due to a long dry period in the spring and little wind in autumn, and deposition was increased at the urban compared to the periurban station (Freie und Hansestadt Hamburg 2012) (Table 3.1). O_3 values were higher at the periurban than at the urban station (Table 3.1). Though no representative stations measured the SO_2 deposition on periurban stands, atmospheric SO_2 concentrations did not exceed critical values at any measurement station across the city and were determined at 4 µg m^{-3} annual mean at the urban station (Table 3.1). For NO and NO_2, measured values varied strongly at the periurban sites. While the periurban site in proximity to a large motorway had values exceeding those of the urban station, the more remote, rural-like periurban site had considerably lower values (Table 3.1).

Table 3.1 Annual means of pollutant depositions in µg m^{-3} in 2011. Data from Freie und Hansestadt Hamburg 2012 by stations Sternschanze (urban), Tatenberg (periurban 1) and Billstedt (periurban 2 close to motorway), with "-" denoting no measurement of respective pollutant at the station.

	SO_2	NO	NO_2	O_3	PM_{10}
Urban station	4	10	30	39	29
Periurban station 1	-	4	16	43	-
Periurban station 2 (close to motorway)	-	14	33	-	24

Nitrogen and Carbon Content

N content varied significantly between species, with *Robinia* and *Alnus* having higher N content than species without N-fixing symbionts (Figure 3.2). No significant difference could be found for origin across all species, but interaction was significant (Table 3.3). Both *Acer* and *Alnus* showed significant differences depending on litter origin when analyzed individually (Figure 3.2). *Acer* showed a significant increase and *Alnus* a significant decrease in litter of urban origin (Figure 3.2).

Carbon content varied significantly between species as well as between origins, with no significant interaction (Table 3.2, Table 3.3). When analyzed individually, both *Populus* and *Robinia* showed a significant decrease in carbon content in litter of urban origin (Table 3.2).

Structural Carbohydrates

Content of all structural carbohydrate fractions differed significantly between species and origins, with NDF and ADL showing significant interactions (Figure 3.2, Table 3.2, Table 3.3). *Quercus* had the highest amount of structural carbohydrates, while *Robinia* had the lowest (Figure 3.2, Table 3.2). When species were analyzed individually, a significant reduction could be found for NDF, ADF and ADL in *Populus* and *Robinia* and for ADF in *Quercus* of urban origin (Figure 3.2, Table 3.2). Contrary, *Alnus* showed a non-significant increase in NDF and ADL of urban origin (Figure 3.2, Table 3.2).

Dust Deposition and Epicuticular Waxes

Species differed significantly in the amount of dust deposited on their leaves and in the amount of epicuticular waxes (Figure 3.2, Table 3.2, Table 3.3). *Alnus* had the highest amount of dust as well as epicuticular waxes. For dust, an almost (p<0.1) significant difference between origins could be found (Table 3.3). While no significant differences could be found for individually analyzed species, there was a trend towards decreased amounts of dust and epicuticular waxes on leaves of urban origin (Figure 3.2, Table 3.2). There was no significant interaction between species and origin (Table 3.3).

Content of Sulfur, Potassium and Phosphor

Contents of sulfur (S), potassium (K) and phosphor (P) varied significantly between species and for S content, a significant difference between origins was found (Figure 3.2, Table 3.2, Table 3.3). All three elements show a significant (S, K) or almost significant (P; p<0.1) interaction between species and origin (Table 3.3).

Other Elements (Al, B, Ca, Cr, Cu, Fe, Mg, Mn, Na, Zn)

All analyzed parameters varied significantly between species and origin, except for Cr, Mg and Zn, which did not show a significant difference depending on origin of leaf litter (Figure 3.2, Table 3.2, Table 3.3). Al, Ca and Zn showed a significant interaction between species and origin (Table 3.3). Some elements showed exceptionally high mean contents in some samples. Mean Cr content of *Acer* litter was 1.40 mg kg^{-1}, of *Alnus* 2.72 mg kg^{-1}, of *Populus* 1.81 mg kg^{-1}, of *Quercus* 1.38 mg kg^{-1} and of *Robinia* 3.46 mg kg^{-1}. Mean Cu content of *Alnus* litter was 23.45 mg kg^{-1}. Mean Zn content of urban *Acer* litter 248.01 mg kg^{-1}, of *Alnus* 208.11 mg kg^{-1} and of *Populus* 924.77 mg kg^{-1}.

Correlations between Analyzed Parameters

We found high correlations between Al, Fe, Cu, Cr and S. All these parameters were negatively or non-significantly correlated to Mn. Mn was positively correlated to C, P and structural carbohydrates (Table 3.4).

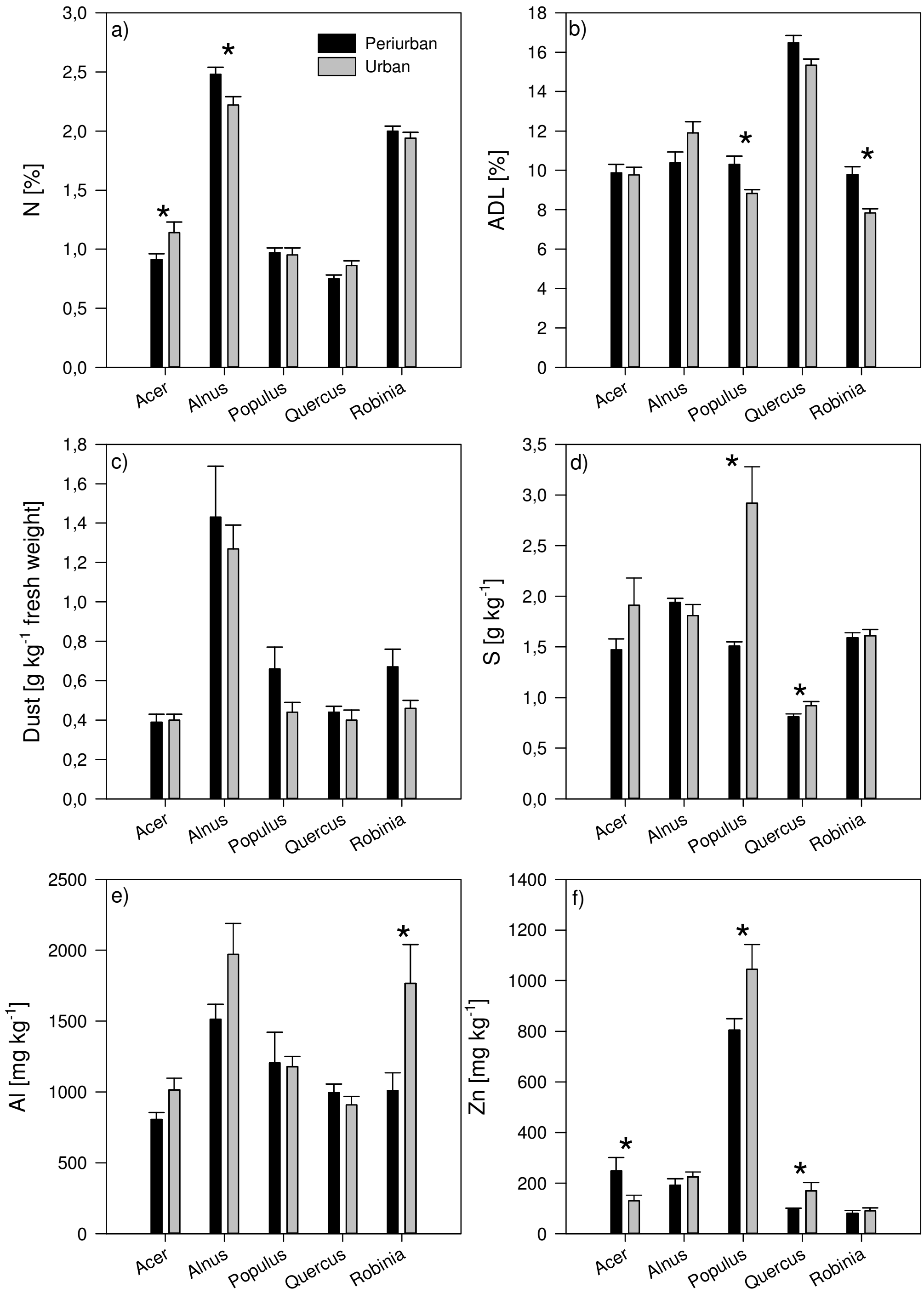

Figure 3.2 Mean values of selected parameters for each species from urban and periurban origin including standard errors: a) nitrogen content of dried litter, b) acid detergent lignin content of dried litter, c) amount of dust on green leaves, d) sulfur content of dried litter, e) aluminum content of dried litter and f) zinc content of dried litter. Asterisks indicate significant intraspecific differences according to *t*-test results.

Table 3.2 Mean values of selected parameters for each species from urban and periurban origin including standard errors. Bold values indicate significant intraspecific differences according to *t*-test results (* denotes analysis after Box-Cox transformation; # Kruskal-Wallis test). All values in relation to dry weight unless stated otherwise ("fw" denotes fresh weight; continued on next page).

Species	Acer				Alnus				Populus			
Origin	Periurban		Urban		Periurban		Urban		Periurban		Urban	
C [%]	44.54	(±0.59)	44.07	(±0.40)	47.63	(±0.15)	47.29	(±0.27)	**46.76**	**(±0.35)**	**45.18**	**(±0.38)**
NDF [%]	55.07	(±2.33)	52.85	(±2.17)	41.60	(±1.44)*	46.01	(±2.40)*	**38.73**	**(±0.77)**	**32.02**	**(±1.18)**
ADF [%]	22.64	(±0.63)	22.86	(±0.93)	21.04	(±0.88)*	20.80	(±2.23)*	**24.98**	**(±0.53)**	**20.90**	**(±0.61)**
B [mg kg^{-1}]	151.34	(±25.89)*	150.55	(±6.46)*	**78.60**	**(±14.99)**	**122.95**	**(±8.36)**	160.38	(±8.18)	181.78	(±18.28)
Ca [g kg^{-1}]	31.97	(±1.78)	28.14	(±1.88)	20.75	(±1.02)	23.32	(±1.75)	**28.03**	**(±1.75)#**	**36.68**	**(±3.24)#**
Cr [mg kg^{-1}]	1.25	(±0.11)	1.54	(±0.18)	**2.04**	**(±0.33)***	**3.40**	**(±0.51)***	1.59	(±0.69)*	2.03	(±0.42)*
Cu [mg kg^{-1}]	12.08	(±1.44)	14.32	(±1.29)	22.36	(±1.34)	24.54	(±1.13)	**12.38**	**(±0.93)#**	**19.68**	**(±0.79)#**
Fe [mg kg^{-1}]	261.87	(±26.32)	331.05	(±21.48)	**386.95**	**(±17.62)***	**489.60**	**(±33.16)***	**298.35**	**(±52.50)**	**442.09**	**(±28.43)**
K [g kg^{-1}]	**6.85**	**(±0.83)**	**10.29**	**(±0.82)**	8.36	(±0.79)	6.11	(±0.75)	7.33	(±0.60)#	7.97	(±0.95)#
Mg [g kg^{-1}]	1.75	(±0.26)	1.88	(±0.15)	1.81	(±0.13)*	2.18	(±0.20)*	1.77	(±0.14)	1.43	(±0.14)
Mn [mg kg^{-1}]	381.65	(±105.92)	352.76	(±75.39)	534.58	(±112.75)*	260.35	(±26.90)*	**309.46**	**(±35.59)**	**137.13**	**(±30.37)**
Na [mg kg^{-1}]	261.89	(±48.91)	360.37	(±30.41)	586.86	(±69.13)*	804.83	(±114.26)*	315.15	(±56.72)	320.12	(±39.94)
P [g kg^{-1}]	1.04	(±0.13)*	1.38	(±0.41)*	**1.07**	**(±0.11)***	**0.77**	**(±0.11)***	1.07	(±0.13)	1.35	(±0.18)
Wax [g kg^{-1} fw]	2.84	(±0.53)	2.62	(±0.32)	7.94	(±1.10)	6.01	(±0.74)	4.45	(±0.62)	3.90	(±0.21)

Table 3.2 continued.

Species	Quercus				Robinia			
Origin	Periurban		Urban		Periurban		Urban	
C [%]	49.10	(±0.20)	48.46	(±0.24)	**46.55**	**(±0.31)**	**44.65**	**(±0.40)**
NDF [%]	57.64	(±1.13)	55.62	(±2.57)	**27.90**	**(±0.47)**	**24.90**	**(±0.45)**
ADF [%]	**30.99**	**(±0.28)**	**29.12**	**(±0.59)**	**18.06**	**(±0.49)#**	**16.21**	**(±0.23)#**
B [mg kg^{-1}]	56.16	(±2.14)*	62.06	(±6.15)*	**93.62**	**(±7.33)**	**140.39**	**(±10.75)**
Ca [g kg^{-1}]	18.72	(±0.97)	20.57	(±2.10)	**37.96**	**(±1.27)**	**48.08**	**(±1.99)**
Cr [mg kg^{-1}]	1.58	(±0.26)	1.18	(±0.28)	3.36	(±1.17)*	3.55	(±0.82)*
Cu [mg kg^{-1}]	9.07	(±0.91)	11.13	(±0.81)	16.59	(±1.03)	19.08	(±1.09)
Fe [mg kg^{-1}]	231.56	(±19.94)	273.52	(±21.65)	**313.62**	**(±18.72)#**	**494.81**	**(±53.12)#**
K [g kg^{-1}]	5.09	(±0.39)	4.62	(±0.63)	**8.04**	**(±0.39)**	**5.86**	**(±0.61)**
Mg [g kg^{-1}]	0.94	(±0.13)	1.21	(±0.11)	1.36	(±0.12)*	1.79	(±0.22)*
Mn [mg kg^{-1}]	572.33	(±59.58)*	680.80	(±124.10)*	101.86	(±14.27)	79.46	(±16.00)
Na [mg kg^{-1}]	382.28	(±45.79)*	541.12	(±89.09)*	448.46	(±93.20)#	600.10	(±171.66)#
P [g kg^{-1}]	2.06	(±0.12)	2.22	(±0.33)	0.75	(±0.03)*	0.92	(±0.08)*
Wax [g kg^{-1} fw]	4.00	(±0.54)*	4.31	(±0.99)*	1.72	(±0.24)	1.44	(±0.29)

Table 3.3 Results of two-way ANOVAs for analyzed leaf litter quality parameters for species, origin and its interaction ("n.s." denotes not significant results, superscript § square root, + log 10 and # Box-Cox transformation).

		N		C		NDF		ADF		ADL§		Dust§		Wax		S§		P#		K	
	df	F	p	F	p	F	p	F	p	F	p	F	p	F	p	F	p	F	p	F	p
Species	4	266.61	***	47.80	***	99.87	***	45.78	***	77.13	***	26.88	***	17.99	***	30.50	***	12.70	***	7.66	***
Origin	1	0.02	n.s.	19.70	***	3.06	(*)	6.26	*	5.38	*	3.10	(*)	1.57	n.s.	13.88	***	0.05	n.s.	0.07	n.s.
Species * Origin	4	4.80	**	1.90	n.s.	2.57	*	1.41	n.s.	5.40	***	0.66	n.s.	0.79	n.s.	7.29	***	2.08	(*)	5.04	**
Error	86																				

		Al§		B		Ca		Cr§		Cu		Fe		Mg		Mn§		Na§		Zn+	
	df	F	p	F	p	F	p	F	p	F	p	F	p	F	p	F	p	F	p	F	p
Species	4	11.67	***	24.64	***	46.95	***	5.27	**	38.56	***	10.52	***	7.91	***	13.40	***	7.78	***	91.54	***
Origin	1	8.15	**	8.82	**	10.52	**	1.50	n.s.	19.20	***	25.42	***	2.28	n.s.	3.64	(*)	5.50	*	0.75	n.s.
Species * Origin	4	2.69	*	1.48	n.s.	3.97	**	1.20	n.s.	1.95	n.s.	1.42	n.s.	1.56	n.s.	1.88	n.s.	0.25	n.s.	5.08	**
Error	86																				

Table 3.4 Spearman rank correlation (ϱ) for analyzed parameters ("n.s." denotes P>0.05).

N [%]	1.00																			
C [%]	n.s.	1.00																		
NDF [%]	-0.43	0.28	1.00																	
ADF [%]	-0.60	0.55	0.75	1.00																
ADL [%]	-0.30	0.70	0.68	0.85	1.00															
Al [mg kg^{-1}]	0.38	n.s.	-0.25	-0.25	n.s.	1.00														
B [mg kg^{-1}]	n.s.	-0.68	-0.29	-0.36	-0.60	n.s.	1.00													
Ca [g kg^{-1}]	n.s.	-0.76	-0.54	-0.61	-0.64	n.s.	0.49	1.00												
Cr [mg kg^{-1}]	0.32	n.s.	-0.21	-0.28	n.s.	0.69	n.s.	n.s.	1.00											
Cu [mg kg^{-1}]	0.63	n.s.	-0.38	-0.46	-0.28	0.71	n.s.	n.s.	0.68	1.00										
Fe [mg kg^{-1}]	0.42	-0.28	-0.35	-0.41	-0.30	0.85	0.24	0.26	0.70	0.85	1.00									
K [g kg^{-1}]	0.34	-0.34	n.s.	-0.26	-0.26	n.s.	0.25	n.s.	n.s.	n.s.	n.s.	1.00								
Mg [g kg^{-1}]	0.28	-0.40	n.s.	-0.25	-0.25	0.30	0.40	n.s.	n.s.	0.27	0.26	n.s.	1.00							
Mn [mg kg^{-1}]	n.s.	0.47	0.62	0.61	0.58	n.s.	-0.48	-0.58	-0.29	-0.27	-0.24	n.s.	n.s.	1.00						
Na [mg kg^{-1}]	0.32	n.s.	n.s.	n.s.	n.s.	0.43	n.s.	n.s.	0.29	0.29	0.36	n.s.	0.26	n.s.	1.00					
P [g kg^{-1}]	-0.36	0.29	0.33	0.38	0.33	-0.36	-0.32	-0.30	-0.30	-0.42	-0.41	n.s.	-0.30	0.35	n.s.	1.00				
S [g kg^{-1}]	0.62	-0.44	-0.43	-0.59	-0.56	0.34	0.42	0.30	0.22	0.63	0.53	0.47	n.s.	-0.33	n.s.	n.s.	1.00			
Zn [mg kg^{-1}]	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.40	n.s.	n.s.	n.s.	n.s.	n.s.	0.30	n.s.	n.s.	n.s.	0.29	1.00		
Wax [g kg^{-1} fw]	n.s.	0.26	0.25	0.30	0.22	0.34	n.s.	-0.39	n.s.	0.22	n.s.	n.s.	n.s.	n.s.	0.21	n.s.	n.s.	0.39	1.00	
Dust [g kg^{-1} fw]	0.44	n.s.	n.s.	n.s.	n.s.	0.39	n.s.	n.s.	0.26	0.47	0.27	n.s.	0.29	n.s.	0.26	-0.33	n.s.	n.s.	0.29	1.00
	N [%]	C [%]	NDF [%]	ADF [%]	ADL [%]	Al [mg kg^{-1}]	B [mg kg^{-1}]	Ca [g kg^{-1}]	Cr [mg kg^{-1}]	Cu [mg kg^{-1}]	Fe [mg kg^{-1}]	K [g kg^{-1}]	Mg [g kg^{-1}]	Mn [mg kg^{-1}]	Na [mg kg^{-1}]	P [g kg^{-1}]	S [g kg^{-1}]	Zn [mg kg^{-1}]	Wax [g kg^{-1} fw]	Dust [g kg^{-1} fw]

3.4 Discussion

The short urban to periurban gradient employed in this study was accompanied by remarkable changes in analyzed environmental parameters. While analyzed environmental parameters show a clear urban to periurban gradient, these results have to be used with caution for interpretation of leaf litter alterations as parameters were not directly measured at tree stands but derived from published sources. For example, some urban trees were sampled close to a water body, which had a cooling effect opposing the observed UHI effect (Schlünzen *et al.* 2010). Some periurban trees were sampled in proximity to heavily used motorways and are most likely exposed to high pollution loads as illustrated by the diverging NO_X values measured at the two periurban stations (Table 3.1). The decreased precipitation at the urban relative to the periurban stand most likely stems from the downwind of the city's center location of the periurban stands (the direction in which possible rain drop condensation nuclei are drifted). Somewhat counter-intuitive was the lowered atmospheric O_3 concentration at the urban stands. This is due to the fact that precursors are emitted mainly in the urban core and (as the rain drop condensation nuclei) subsequently drifted downwind, leading to increased O_3 concentrations in some distance to it (Eikmann 1998).

Found differences along the gradient led to significant intraspecific differences in leaf litter quality between litter of urban and periurban origin. Litter quality varied between species and numerous parameters showed interspecific differences in response to urbanization.

Nitrogen and Carbon

Two factors stand out to potentially alter leaf litter N content in urban environments: N fertilization due to emissions and a decrease in leaf litter N content due to elevated atmospheric CO_2 (Cotrufo *et al.* 1998, King *et al.* 2001, Norby *et al.* 2001). The observed difference in reaction to urbanization between *Acer* and *Alnus* most likely stems from the symbiotic fixation of N in *Alnus*. Since *Alnus* is not N limited, it might not profit from fertilization due to increased N deposition as species without N fixing symbionts do. Here, the increased CO_2 might lead to a reduction in leaf litter N content, while in *Acer* N fertilization due to emissions might override the effect of

CO_2. The differing reaction of *Robinia*, which did not show a significant effect of litter origin, might stem from its symbiosis with other bacteria than *Alnus*. *Robinia* and the other species do not seem to be strongly affected in their litter N content neither by N deposition nor by increased CO_2, or the effects are balancing one another out. While no significant alteration in litter N content due to urbanization in *Populus* was observed, litter of both origins had higher N contents (0.95 % and 0.97 %, respectively) than litter analyzed in Helsinki, Finland. Here, the litter has been observed to increase N content with urbanization (0.74 % compared to 0.58 % in rural litter) (Nikula *et al.* 2010). Possibly, N deposition is not as high in Helsinki with a population of about one third of Hamburg's (600 000 people) or the gradient employed in this study was not long enough to show as pronounced differences.

With decreases across all analyzed species, an identical response of litter C content to urbanization was observed. Comparisons with other studies indicate, however, varying responses. While Alfani *et al.* 2000 also found a decrease in C content of *Quercus ilex* leaves in Rome, Nikula *et al.* 2010 and Balasooriya *et al.* 2009 did not find significant differences in carbon content between urban and rural leaves in *Populus tremula* and *Taraxacum officinalis*, in Helsinki and Gent, Belgium, respectively.

Structural Carbohydrates (NDF, ADF, ADL)

Increases in both CO_2 and O_3 concentration have been linked to an increase in litter lignin content (Norby *et al.* 2001, Boerner & Rebbeck 1995) and leaves of urban origin were exposed to higher CO_2 and lower O_3 concentration compared to leaves of periurban origin. The lowered content of structural carbohydrates in urban litter hints towards an overriding effect of increased O_3 exposure over CO_2 along the gradient. These results are in accordance with previous studies, which found a (non-significant) reduction in Lignin, NDF and ADF for *Quercus rubra* from suburban to urban stands in New York City (Carreiro *et al.* 1999). That O_3 is an important factor of urbanization affecting plants has previously been observed in New York City (Gregg *et al.* 2003).

Dust Deposition and Epicuticular Waxes

Particulate pollution can have numerous negative effects on trees, from leaf surface structure anomalies to death of individual trees (Beckett *et al.* 1998). A high portion of deposited particles on urban forest leaves are organic materials, suggesting green spaces as considerable sources of particulate deposition (Freer-Smith *et al.* 1997). However, the amount of deposited particles decreases with distance to roads (Freer-Smith *et al.* 1997), underlining the importance of vehicular traffic for deposition processes. Periurban stands in this study were generally surrounded by larger portions of green space than urban stands, with some in proximity to large roads, both factors in combination potentially lead to the counterintuitive result of slightly increased deposition of dust on periurban compared to urban leaves.

No effect of origin on the amount of epicuticular waxes was observed. Either the O_3 gradient did not suffice in affecting the amount of waxes, or the effect was counterbalanced by the opposing trend of temperature and precipitation. Opposing results of this study, Nikula *et al.* 2010 found increased amount of waxes on urban samples of *Populus tremula* compared to rural ones sampled 24 to 30 km from the city center of Helsinki. However, as they compare a periurban instead of a rural stand to an urban one, the urban stand is expected to be exposed to comparatively higher temperatures and O_3 concentrations due to the formation of O_3 (from urban to periurban) and the subsequent breakup (from periurban to rural) during wind transport (Sieghardt *et al.* 2005).

Content of Sulfur, Phosphor and Potassium

The increased S content of litter of urban origin most likely stems from depositions of combustion processes. S content of leaves has been proposed as a well suited indicator for SO_2 pollution (Carreras *et al.* 1996). However, the highly significant interaction between species and origin challenges this suitability and is in accordance with Hijano *et al.* 2005, who found differing increases of S content in individual urban trees in addition to seasonal variations in Madrid.

K and P content show almost significant interactions between species and origin, and no clear trend can be observed with regard to origin of leaf litter. Soil P content has been found to be poorly predictable by an urban-rural gradient and geological, pedological and human legacy effects seem to mask possible effects of urbanization (Bennett 2003). As for P, the urban-periurban gradient does not seem to be as strong an influence on leaf litter K content.

Other Elements (Al, B, Ca, Cr, Cu, Fe, Mg, Mn, Na, Zn)

Observed increases in elemental content in litter of urban origin most likely stem from deposition of combustion processes and other anthropogenic sources. Contents of Cr, Cu and Zn in some samples exceeded critical values shown to negatively affect plant growth (Scheffer *et al.* 2010). Mean contents of these elements in *Populus* litter were more than twice as high as contents found in litter of the same species grown in Helsinki, Finland (Nikula *et al.* 2010).

As trees of the same origin were subjected to similar pollution regimes, the significant interaction between species and origin in regard to Zn concentrations challenges previous studies, suggesting Zn as a good indicator for pollution from vehicle exhaust (Monaci *et al.* 2000). Previous studies have proposed Al, Mg, Mn and Fe depositions to be of natural origin (Loranger *et al.* 1996, Freer-Smith *et al.* 1997) and Ca, Cu, Na and Zn to stem from anthropogenic sources, e.g., Ca and Na from the use of de-icing salts (Loranger *et al.* 1996).

Correlations between Analyzed Parameters

The high correlations between Al, Cr, Cu, Fe and S suggest that, contrary to previous studies (Freer-Smith *et al.* 1997), Al and Fe were not soil derived, but together with Cu and Cr stemmed from anthropogenic sources. In roadside *Populus tremuloides* litter, correlated, increased metal concentrations (namely Al, Fe, Ni, Zn) have been observed and ascribed to pollution from vehicle exhaustion (Nikula *et al.* 2011). As in this study, Alfani *et al.* 2000 found high correlations between elements and attribute these to similar (anthropogenic) sources and distribution mechanisms. For this study, this would suggest Cr, Cu, Fe and S to stem from common sources. In their study, Alfani *et al.* 2000 found Mn to not correlate with other elements and attribute this to volcanic origin of Mn depositions, contrary to anthropogenic sources. Findings of Mn showing a different pattern of correlation than the other elements were confirmed, however, no volcanic sources can be found in the study area and sources of Mn remain unclear.

Conclusion

This study successfully characterizes changes in environmental and pollution regimes along the urban to periurban gradient in a north-temperate metropolis and analyzed the effects of these alterations on tree leaf litter. Even over short gradients, the influence of urbanization is strong enough to significantly affect tree leaf litter quality, though some parameters (e.g., O_3) might have shown clearer effects if a longer gradient would have been employed. Species' litter varied in its response to urbanization, highlighting the difficulty of extrapolating results of single species studies to general conclusions on leaf litter quality changes due to urbanization. This is of importance for future biomonitoring studies, aiming at extrapolation of pollution regimes of urban areas from a single species. In particular, comparisons between studies employing different species for biomonitoring should be conducted cautiously. The study highlighted the multi-facetted nature of urbanization and the difficulty of estimating implications of urbanization for plants. Observed alterations in litter quality can be expected to have influences reaching far beyond the individual plant. For ecosystems within urban areas, indirect alterations through, e.g., affected decomposition processes, can be expected (chapter 4). Further research is needed to establish reliable predictions of leaf litter responses to urbanization over various species as well as implications for affected ecosystem processes. Future studies should broaden the spectrum of analyzed pollutants and include, for example, organic pollutants like PAH and the reactions of different species to them.

4 Alterations in Leaf Litter Decomposition Due to Urbanization

4.1 Introduction

Cities not only affect the global carbon cycle through anthropogenic release of CO_2 and storage of organic carbon, but have been observed to influence its decomposition (e.g., Fenn & Dunn 1989). As urban areas cover substantial amounts of the earth's land surface (with estimates up to 3.52 million km^2 (Potere & Schneider 2007)), the influence of urban areas on decomposition processes is of interest beyond individual city limits. This is especially true for carbon sequestration modeling in residential landscapes (e.g., Zirkle *et al.* 2012).

Decomposition is a key component in the carbon cycle, as carbon bound in biomass is either released into the atmosphere as CO_2 or stabilized by humification processes into long-lived soil organic matter. The process of decomposition is complex and includes for example ingrowth of microbial biomass and nutrient accumulation in addition to leaching and respiration. Following Berg & McClaugherty 2008, the term decomposition is used here to describe the net mass loss of biomass over time. Decomposition is influenced by abiotic environmental conditions, activity of decomposer communities and the quality of decomposing material. All of these conditions can be altered due to the transformation of landscapes through urbanization with its dense human population, the associated energy consumption and high amount of sealed surfaces (McDonnell & Pickett 1990). Abiotic environmental conditions shown to be influenced by urbanization are raised temperatures (UHI) (Oke 1973) and increased precipitation in and downwind of cities (Schlünzen *et al.* 2010). Decomposer communities have been shown to be influenced by urbanization due to heavy metal deposition (Cotrufo *et al.* 1995) and introduction of non-native earthworms (Steinberg *et al.* 1997). The quality of decomposing material can be altered in numerous chemical parameters known to influence decomposition processes (e.g., N content), with significant interspecific differences in alterations (chapter 3). As some alterations due to urbanization might have an accelerating effect on decomposition, while others might have a decelerating one, predicting the net effect on decomposition is challenging and empirical data is scarce.

Employing gradients from inner city study sites to study sites at a city's fringes or in the rural hinterlands is an important means of studying the ecological impact of urbanization (McDonnell & Pickett 1990). So far, the effect of urbanization on decomposition has only been studied in few cities around the globe and results are contradictory. Environmental and soil alterations at urban sites led to an accelerated mass loss of litter in New York City (Pouyat *et al.* 1997), while a slower decomposition of litter has been found at urban sites in Asheville, NC, USA (Pavao-Zuckerman & Coleman 2005) compared to the respective, corresponding rural sites. Leaf litter alterations in urban originating litter taken from New York City led to a slower decomposition in bioassays compared to litter of rural origin (Carreiro *et al.* 1999). To separate the influence of decomposition site and origin of leaf litter in a joint study design, reciprocal litter transplants at urban and rural sites is a suitable method. Conducting a reciprocal litter transplant, a slower decomposition of urban originating litter especially in soil of urban sites has been found in Naples (Cotrufo *et al.* 1995), while a faster decomposition of urban originating litter and at urban sites has been observed in Helsinki (Nikula *et al.* 2010) compared to their respective rural counterparts. For New York City, nonreciprocal litter decomposition showed no difference in litter mass loss between urban litter at urban sites and rural litter at rural sites, but reciprocal transplants revealed a faster decomposition at urban sites and a counteracting effect of slower decomposition of urban originating litter (Pouyat & Carreiro 2003).

Since results of previous studies are contradictory and cities around the globe differ drastically, e.g., in their structure and pollution regime, more research is needed to detect general trends in the influence of urbanization on decomposition. As Nikula *et al.* 2010 found that the short gradient employed in their Helsinki study (distance of 17 to 27 km between urban and rural sites) significantly affected decomposition processes, this study will examine whether an even shorter urban to periurban gradient (10 to 17 km distance between sites) will still reveal significant alterations.

Individual studies have up to now solely been conducted in individual cities, with leaf litter of a single species and over rather short time periods for decomposition processes (e.g., 6 months in Pouyat *et al.* 1997). As species or even variants of the same species differ in their reaction to urbanization (chapter 3, Carreras *et al.* 1996), potentially leading to differently altered decomposition processes, this study includes leaf litter of five tree species to enable interspecific comparisons. Chosen species are common in the study area and attention was paid to include species with differing ecology, namely symbiosis with N fixing bacteria and native as well as non-native species. To compare results between cities without the confounding influence of interspecific differences, this study includes two species previously studied in other cities (*Populus tremula* in Helsinki and *Quercus rubra* in New York City). To enable observations in different stages of decomposition in a limited amount of time, three different methods were employed: a climate chamber incubation focusing on very early stages of decomposition, a common garden experiment with an accelerated decomposition leading to high mass loss values and a reciprocal litter transplant with intermediate mass loss values.

This study aims to analyze (1) whether origin of tree litter (urban vs. periurban, respective city center vs. city fringe) affects its decomposition. Further (2), it will examine direct influences of decomposition sites (urban vs. periurban) on mass loss by comparing decomposition at urban and periurban sites. Additionally (3), it will evaluate interspecific differences in decomposition between the five chosen species and the respective influences of urbanization.

Results of the three individual experiments were compared to assess differences in methodologies. Further, leaf litter quality and abiotic site conditions of the urban and periurban decomposition sites were measured to identify possible mechanisms underlying changes in mass loss of tree litter caused by urbanization.

4.2 Material and Methods

Collection of Leaf Litter and Analyzed Species

Air-dried, senescent leaf litter samples already used for chapter 3 were used in this study. Petioles of litter were discarded, litter torn into pieces of about 3 cm diameter, and pieces pooled according to species and origin of leaf litter i.e. urban and periurban tree stands, yielding ten pools in total (two urban *Acer* and one urban

Populus were determined to be of another species during this step and their litter excluded).

Litterbag experiments

Litterbags were constructed from PVC-coated fiberglass fly-screen with a mesh-size of 1.2 mm x 1.4 mm by heat welding, allowing access of soil microorganisms to the litter, but excluding macrofauna (Swift *et al.* 1979). Litterbags were quadratic with 15 cm side length and were filled with about 2 g of the pooled, air-dried litter.

Two correction factors were established for mass of initial litter. One was a species specific air-dried to oven-dried correction factor, obtained by dividing the mass of five litter subsamples dried at 105 °C for 48 h per species by their initial air dried weight. The other was a site of decomposition (see below) specific travelbag factor, accounting for litter fragments lost due to handling and transport. Travelbags were constructed in the same way as other litterbags and were transported to and back from the decomposition site with mass loss due to handling determined subsequently. 25 travelbags were constructed in total and culminated in a mean correction factor of 4 % litter mass lost.

Reciprocal Litter Transplant Experiment: Sets of litterbags were deployed in March 2012 at 15 urban and 15 periurban sites and retrieved in August 2012. Each set of litterbags consisted of ten bags: each species (*Acer*, *Alnus*, *Populus*, *Quercus*, *Robinia*) of each origin (urban, periurban). The 30 sites of decomposition were chosen from the 100 tree sites of litter origin (chapter 3). The assessment of a potential "home-field advantage" (e.g., Kagata & Ohgushi 2013) (e.g., *Acer* litter decomposing faster under an *Acer* tree) was beyond the scope of this study. To prevent it from being a confounding factor, three urban and three periurban sites of decomposition per species were chosen, resulting in six sites under an *Acer* tree, six under an *Alnus* tree and so forth. Litterbags were covered by 1-5 cm of soil, to prevent disturbance, e.g., through passersby and were shaded through the nearby tree and its understory.

After retrieval, litterbags were opened and contents washed to separate litter residues from contaminants, e.g., soil and visible fauna. Afterwards, residues were oven dried at 105 °C for 48 h and weighed.

Soil Parameters and Leaf Litter Quality: To determine soil temperatures at urban and periurban decomposition sites during the litterbag experiment, iButtons® (accuracy of ±0.5 °C and resolution of 0.0625 °C; DS1922L-F5#,Maxim Integrated, San Jose, Ca, USA) were placed in plastic zipper bags and placed alongside the buried litterbags (see below) at 0-5 cm depth. To determine differences in water content, pH and salt concentration between urban and periurban decomposition sites, 100 mL soil cores were taken at all decomposition sites at six dates during the course of the litterbag experiment. To detect possible water shortages during dry periods, sampling dates for taking cores were set to be after at least three days without precipitation. The cores were transported in airtight plastic bags and gravimetric water content determined by weight difference before and after drying at 105 °C for 24 h. Dried samples were used to determine pH in $CaCl_2$ and electrical conductivity in H_2O with a pH and conductivity meter (Eijkelkamp 18.28, Giesbeek, Nederland).

All leaf litter quality analyses were conducted on air-dried, ground leaf material similar as in chapter 3. Carbon and N content was determined via CN analyses (vario MAX CNS elementar, Elementar Analysesysteme GmbH, Hanau, Germany), content of main nutrients and some trace elements (Al, B, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P, S, Zn) via inductively coupled plasma optical emission spectrometry (iCAP 6300 duo, Thermo Fisher Scientific, Schwerte, Germany). Furthermore, structural carbohydrate content was determined through subsequent digestion in a fiber analyzer (ANKOM 2000, ANKOM technology, Macedon NY, USA) in detergent solutions for neutral and acid detergent fiber (NDF consisting mainly of hemicellulose, cellulose and lignin; ADF consisting mainly of cellulose and lignin) as well as acid detergent lignin (ADL) as described by the manufacturer (ANKOM 2014).

Common Garden Litter Transplant Experiment: To examine alterations in decomposition based solely on origin of leaf litter and without the influence of site of decomposition, 15 sets of litterbags (see above) were placed in an experimental field at the Biocenter Klein Flottbek, Hamburg. Soil at the experimental site was known to be naturally wet. Further, the soil was covered by a thin, black, water permeable fleece, preventing weed growth and together with sun exposure of the field led to increased soil temperatures.

As for the reciprocal litter transplants, litterbags were deployed in March 2012 and retrieved in August 2012, opened and contents washed to separate litter residues from contaminants. Afterwards, residues were oven dried at 105 °C for 48 h and weighed.

Climate Chamber Incubation

Leaf litter separated by species and origin was incubated under controlled conditions in a dark climate chamber at 21 °C for 14 days in May 2012. Soil was taken from the experimental field, sieved at 2 mm, its water content increased to 60 % water holding capacity and allowed to rest for six days at 6 °C. Adapting a method by Isermeyer 1952, 1 g of pooled litter was mixed with 50 g wet soil in 1 L jars, with four replicates per litter pool. Two types of controls were set up with four replicates each, empty jars as blanks to detect possible error and jars containing soil without leaves to measure basal respiration.

To follow decomposition, CO_2 respired from soil (controls) and soil with litter (samples) respectively was caught in 25 mL of NaOH in open plastic containers set into the airtight jars. Containers were changed every 24 h, 0.5 M $BaCl_2$ as well as a few drops of indicator (phenolphthalein) were added to the NaOH and titrated with HCl until neutralization. Preliminary experiments had shown rapid decomposition rates during the first days of the experiment. Thus, 0.1 M NaOH was used during the first seven days and 0.05 M NaOH the following, adapting the used $BaCl_2$ (10 mL and 5 mL, respectively) as well as the HCl (0.1 M and 0.05 M, respectively). Oxygen supply was given by opening of the jars for changing NaOH containers. Blanks found the error of CO_2 entering the jars during this step to be negligible.

For the climate chamber incubation, decomposition rate was calculated with an adapted formula by Alef & Nannipieri 1995:

$$D_r = \frac{(V_0 - V) \cdot 2.2}{dw \cdot t}$$

Equation 4.1 D_r decomposition rate [mg CO_2 g^{-1} h^{-1}], v_0 amount HCl used for titration in milliliters for soil with litter, v amount HCl used in milliliters for the soil sample (control), *dw* dry weight of soil in grams, *t* incubation time in hours and 2.2 the conversion factor (1 ml 0.1M NaOH equals 1 mg CO_2). A conversion factor of 1.1 was used for the time of the experiment in which 0.05M NaOH was used instead of 0.1M NaOH.

Additionally, the amount of CO_2 released during the incubation time of 14 days of the experiment was calculated with the formula:

$$D_t = \sum(V_0 - V) \cdot 2.2$$

Equation 4.2 D_t total amount of relased CO_2 after 14 days [mg CO_2 g^{-1}], v_0 amount HCl used for titration in milliliters for soil and litter, v amount HCl in milliliters used for the soil sample (control), 2.2 the conversion factor (1 ml 0.1M NaOH equals 1 mg CO_2). A conversion factor of 1.1 was used for the time of the experiment in which 0.05M NaOH was used instead of 0.1M NaOH.

Data Analyses / Statistical Analyses

All statistical analyses were conducted in Statistica 9.1 (StatSoft Inc., Tulsa, OK, USA). Prior to ANOVAs, data was visually checked for normal distribution. If normal distribution could not be obtained through transformation, nonparametric tests were performed.

Reciprocal Litter Transplant Experiment: For litterbags employed at urban and periurban sites, differences in mass loss between species, origin of leaf litter and site of decomposition were analyzed with Kruskal-Wallis tests, and the respective interactions with a three-way ANOVA, despite a lack of normal distribution. To detect interspecific differences, multiple mean rank comparisons were computed. To detect intraspecific differences with regard to origin of litter and site of decomposition, Mann-Whitney tests were performed. Since *Populus* showed a very pronounced contrast in decomposition between urban and periurban originating litter in the climate chamber incubation experiment (see below), a Mann-Whitney test was conducted for differences between mass losses of all litter with regard to origin excluding *Populus* data.

Soil Parameters: Mean temperatures, water contents, pH and electrical conductivities measured at urban and periurban decomposition sites were tested for significant differences via ANOVA.

To test for correlations between mass loss in the reciprocal litter transplant to measured soil parameters and leaf litter chemical properties, linear regressions were computed.

Common Garden Litter Transplant Experiment: For litterbags employed at the experimental field, differences in mass loss between species and origin of leaf litter were analyzed accordingly with Kruskal-Wallis- and Mann-Whitney tests, and the respective interactions with a two-way ANOVA, despite a lack of normal distribution. To detect interspecific differences, multiple mean rank comparisons were computed. To detect intraspecific differences with regard to origin of litter, Mann-Whitney tests were performed.

Climate Chamber Incubation: Decomposition rate was visualized and subsequently tested for differences between species and origin of leaf litter with a repeated measure ANOVA. Additionally, decomposition rate during the time of the experiment with the most rapid decomposition (seven days, beginning after the first 48 h) was tested with a separate repeated measure ANOVA as well. A multifactorial ANOVA was computed to test for differences in the total amount of released CO_2 during the 14 days of incubation. Intraspecific differences due to origin as well as interspecific differences were tested for via Tukey HSD post-hoc test. Since *Populus* showed a stark difference in the amount of released CO_2, a multifactorial ANOVA excluding *Populus* was computed to test whether differences were solely based on this species.

4.3 Results

Litterbag experiments

Reciprocal Litter Transplant Experiment: While origin of leaf litter and species had a significant effect on mass loss ($p \leq 0.05$ and $p \leq 0.001$, respectively), site of decomposition did not ($p \geq 0.1$) (Figure 4.1). Litter of urban origin decomposed faster than litter of periurban origin (61 % and 53 % mass loss, respectively) (Figure 4.1a). Despite the pronounced difference found in the climate chamber incubation for *Populus* with regard to origin (see below), when *Populus* data were excluded from the analysis, the difference between urban and periurban origin was still significant (*data not shown*, $p \leq 0.05$). *Alnus* is the species with the highest (86 %) and *Quercus* the one with the lowest (29 %) mass loss (Figure 4.1c). In a three-way ANOVA, no significant interactions between factors were found. Significant intraspecific differences in mass loss due to origin of litter or site of decomposition were only detected in *Robinia* with urban originating litter decomposing faster (Figure 4.2).

Of the employed 300 litterbags, 16 were lost due to disturbance at urban sites (ten of one site and six individual litterbags).

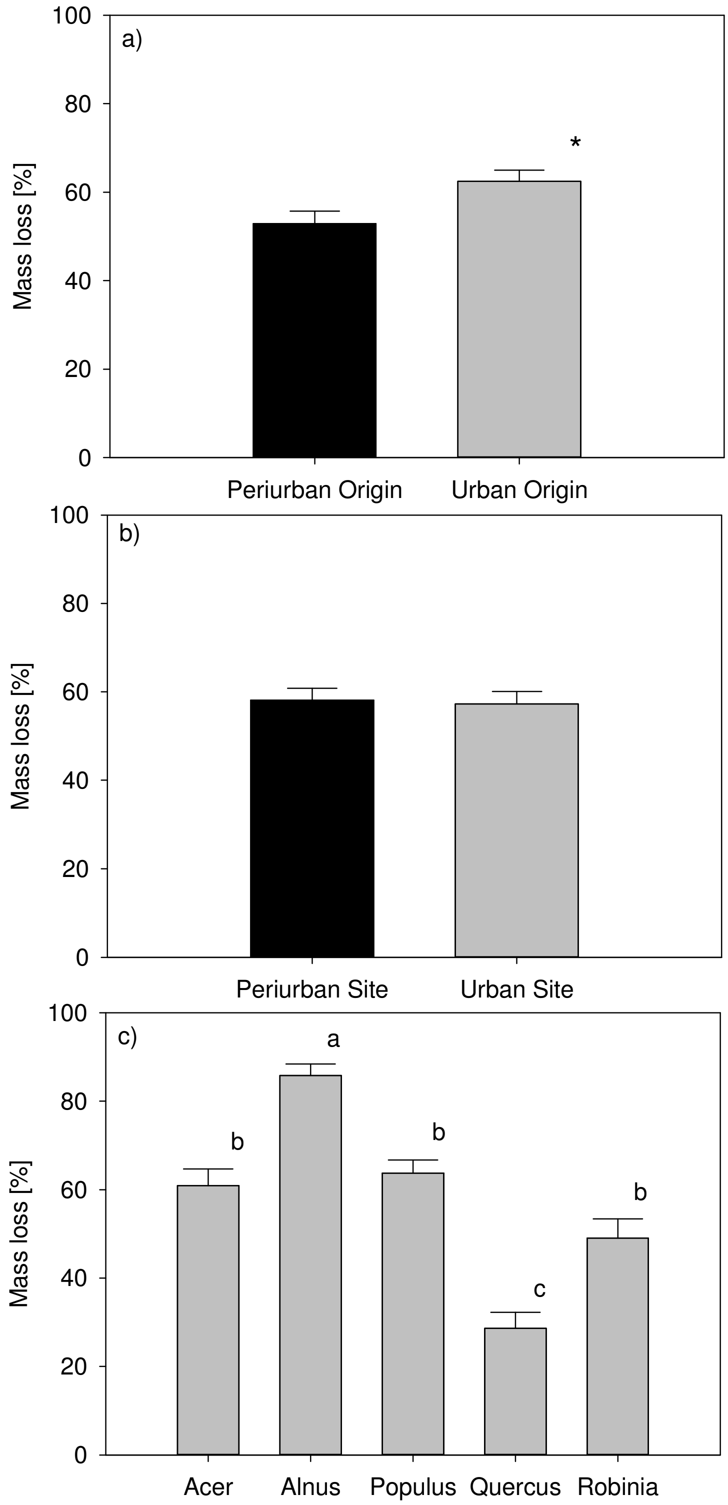

Figure 4.1 Mass loss of reciprocal litter transplant depending on a) origin of litter, b) site of decomposition and c) species. Asterisks indicate significant difference according to Mann-Whitney test, letters indicate groups according to multiple mean rank comparisons of species' means.

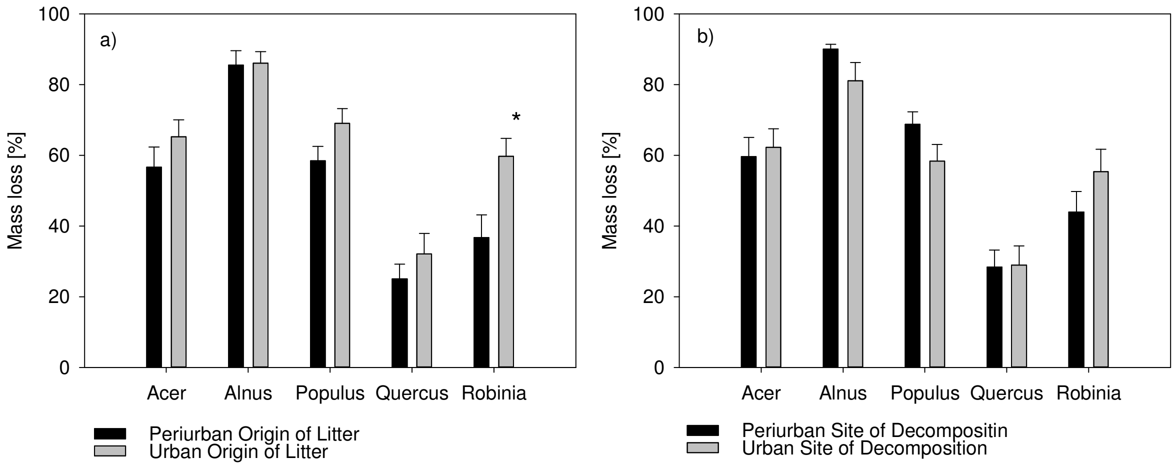

Figure 4.2 Intraspecific differences in mass loss in the reciprocal litter transplant depending on a) origin of litter and b) site of decomposition. Asterisk indicates significant intraspecific difference according to Mann-Whitney test.

Soil Parameters and Leaf Litter Quality: Urban soils were slightly warmer than periurban ones (about 0.3 °C) and contained slightly more water (Table 4.1). Urban soils were slightly less acidic than periurban soils, but this difference was not significant (Table 4.1). However, urban soils had a significantly increased electrical conductivity compared to periurban soils (Table 4.1).

Table 4.1 Mean and SE (min. and max. for pH) of measured soil parameters at the periurban and urban decomposition sites with the respective ANOVA F- and *p*-value ("n.s." not significant).

	Periurban (SE)	Urban (SE)	F-value	*p*-value
Temp. [°C]	13.0 (±0.2)	13.3 (±0.1)	3.020	<0.1
Water content [g g^{-1} soil]	0.17 (±0.01)	0.21 (±0.01)	6.082	<0.05
pH	4.2 (3.4-6.5)	4.5 (3.7-6.2)	0.503	n.s.
EC [µS cm^{-1}]	107 (±5)	165 (±14)	5.814	<0.05

Litter showed inter- as well as intraspecific differences in its chemical composition. For example, *Alnus* and *Robinia* litter had a higher mean N concentration (2.46 % and 1.98 %, respectively, *data not shown*) than species without N-fixing symbionts (Table 4.2).

Table 4.2 Chemical properties of leaf litter pools (all values on a per litter dry weight basis; NDF neutral detergent fiber, ADF acid detergent fiber, ADL acid detergent lignin).

Species	Acer		Alnus		Populus		Quercus		Robinia	
Origin	Periurban	Urban	Periurban	Urban	Periurban	Urban	Periurban	Urban	Periurban	Urban
NDF [%]	50.03	59.44	37.33	36.58	37.19	33.51	58.57	55.79	26.76	25.43
ADF [%]	19.09	22.75	20.50	19.60	23.52	20.52	29.63	28.56	16.48	16.85
ADL [%]	8.27	9.97	10.64	10.23	9.17	8.29	15.84	15.10	9.22	8.99
N [%]	0.98	0.94	2.49	2.42	1.07	0.91	0.77	0.90	2.07	1.90
C [%]	44.69	44.58	48.52	47.40	45.87	45.25	49.26	48.67	46.78	44.42
P [g kg^{-1}]	1.39	0.54	0.53	0.92	0.95	1.23	2.28	2.22	0.75	0.91
S [g kg^{-1}]	1.57	1.54	0.98	2.11	1.75	2.96	0.75	0.95	1.64	1.56
K [g kg^{-1}]	7.61	9.58	3.81	6.66	7.51	7.36	5.16	4.00	7.48	6.98
C:N	45.68	47.32	19.45	19.62	43.05	49.70	63.88	53.86	22.60	23.39
C:P	322.07	819.58	910.18	515.11	484.83	368.17	215.74	219.64	623.43	487.71
ADL:N	8.45	10.59	4.26	4.23	8.61	9.10	20.54	16.71	4.46	4.73
Al [mg kg^{-1}]	699.69	1257.62	727.50	1593.08	2363.85	1693.85	722.38	929.77	1168.62	2773.85
B [mg kg^{-1}]	140.40	165.75	46.58	119.75	176.30	207.30	76.52	77.56	103.10	138.45
Ca [g kg^{-1}]	31.12	31.28	10.18	24.01	29.10	37.61	18.32	20.13	35.57	46.62
Cr [mg kg^{-1}]	1.63	1.16	0.81	1.10	1.62	1.68	3.91	2.94	0.77	2.23
Cu [mg kg^{-1}]	12.25	16.35	10.50	24.34	16.25	28.87	9.64	12.50	17.22	20.16
Fe [mg kg^{-1}]	227.45	392.55	181.80	433.70	517.95	580.65	168.25	266.65	331.95	712.55
Mg [g kg^{-1}]	1.90	1.96	0.87	2.14	1.49	1.42	0.95	1.08	1.32	2.11
Mn [mg kg^{-1}]	230.80	488.55	321.78	248.00	310.80	132.75	512.60	596.30	84.79	69.91
Na [mg kg^{-1}]	253.70	326.10	294.25	789.90	355.05	307.90	383.10	410.15	374.70	465.75
Zn [mg kg^{-1}]	186.70	139.30	73.83	190.25	738.85	1070.00	86.18	163.00	74.14	74.54

Linear regression found no significant correlation ($p \geq 0.1$) between analyzed soil parameters and mass loss of litterbags at the respective sites. Mass loss of litter at urban and periurban sites correlated significantly with leaf litter quality parameters (Table 4.3).

Table 4.3 R^2 of linear regressions between leaf litter quality and mass loss (bold values indicate $p<0.05$; NDF neutral detergent fiber, ADF acid detergent fiber, ADL acid detergent lignin; all on a per litter dry weight basis).

Chemical Parameter	R^2
NDF [%]	-0.36
ADF [%]	-0.51
ADL [%]	-0.59
N [%]	0.55
C [%]	-0.29
P [g kg^{-1}]	**-0.71**
S [g kg^{-1}]	0.46
K [g kg^{-1}]	0.15
C:N	-0.59
C:P	0.61
ADL:N	**-0.71**
Al [mg kg^{-1}]	0.24
B [mg kg^{-1}]	0.23
Ca [mg kg^{-1}]	-0.04
Cr [mg kg^{-1}]	**-0.69**
Cu [mg kg^{-1}]	0.45
Fe [mg kg^{-1}]	0.30
Mg [g kg^{-1}]	0.41
Mn [mg kg^{-1}]	-0.34
Na [mg kg^{-1}]	0.27
Zn [mg kg^{-1}]	0.21

Common Garden Litter Transplant Experiment: Soil at the experimental field site had a higher mean temperature (17.41 °C), contained more water (0.33 g per g dry soil), was less acidic (pH 5.7) and had a lower electrical conductivity (102 µS/ cm) than soils at the urban and periurban sites.

Mass loss at the experimental field site was higher for all species than in the reciprocal litter transplant experiment. As at the urban and periurban decomposition sites, litter of urban origin decomposed faster than litter of periurban origin (94 % and 92 % mass loss, respectively, $p \leq 0.05$) (Figure 4.3a). When differences between origins were tested for species individually, only *Populus* showed a significant difference in mass loss ($p \leq 0.01$) (Figure 4.3c). However, when *Populus* is excluded from the overall analysis of mass loss depending on origin, the difference is still almost significant ($p \leq 0.1$) (*data not shown*). Species differed significantly in their mass loss ($p \leq 0.001$) and post-hoc tests revealed that *Acer*, *Alnus* and *Populus* decomposed faster than *Quercus* and *Robinia* (98 %, 99 %, 99 % and 78 %, 91 %, respectively) (Figure 4.3b). Two-way ANOVA found no interaction between the factors origin of litter and species.

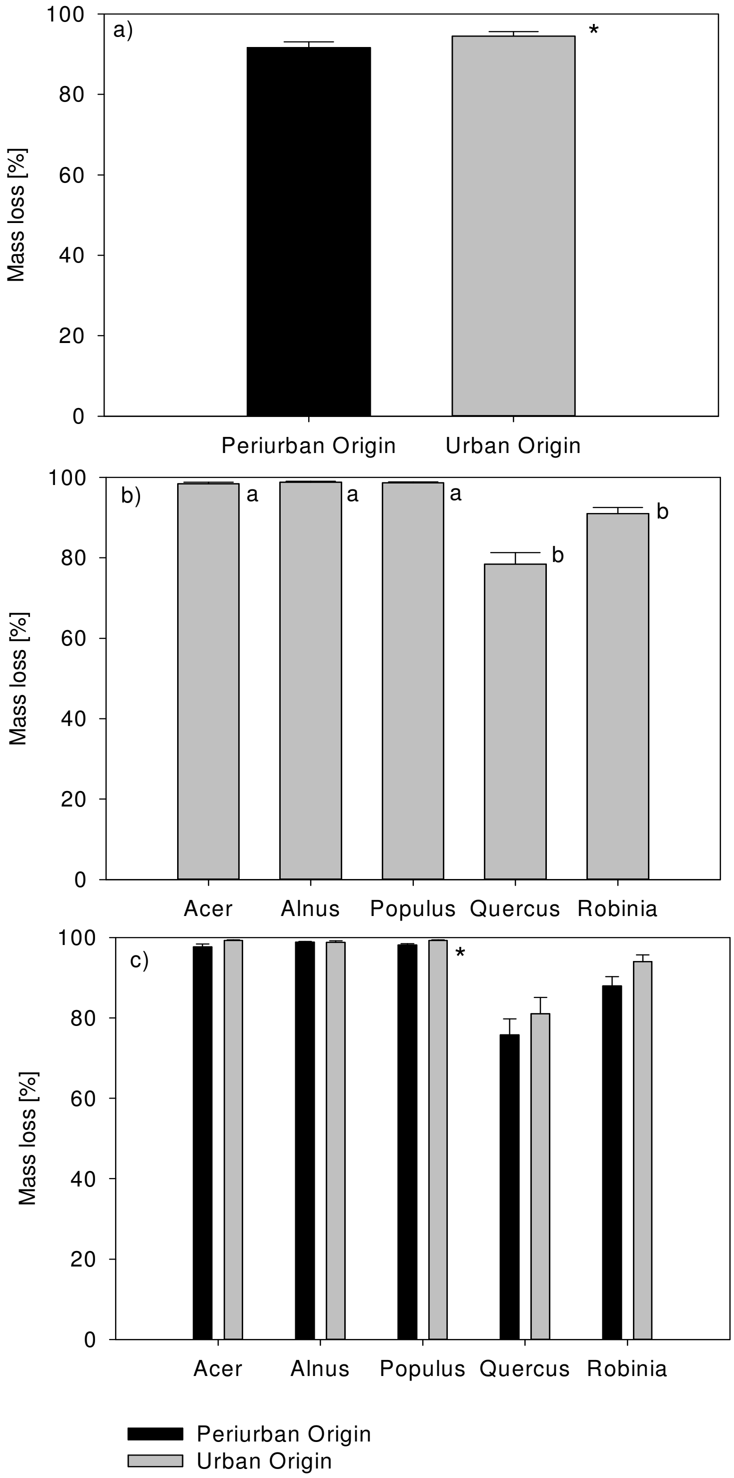

Figure 4.3 Mass loss in the common garden litter transplant depending a) on origin of leaf litter, b) on species and c) showing intraspecific differences. Asterisks indicate significant differences according to Mann-Whitney tests and letters indicate multiple mean rank comparison results for species' means.

Climate Chamber Incubation

Decomposition rate over the entire 14 days of the experiment differed significantly between species ($p \leq 0.001$), origins of leaf litter ($p \leq 0.001$) and time ($p \leq 0.001$) (Table 4.4). Decomposition rate of most species increased during the first 48 h until it gradually decreased (Figure 4.4). If only the seven days with the most rapid decomposition were included, decomposition rate still differed significantly between species ($p \leq 0.001$), origin ($p \leq 0.001$) and time ($p \leq 0.001$) (Table 4.5). The interaction between species and origin was found to be significant, too ($p \leq 0.001$) (Table 4.5). While urban litter tended to decompose faster, *Acer* and *Alnus* of urban origin showed a slightly reduced decomposition rate. The symbiotic N-fixing species *Robinia* and *Alnus* had the highest decomposition rates, while *Quercus* had the lowest.

Table 4.4 Repeated measure ANOVA results for rate of respired CO_2 in the climate chamber experiment for the 14 days of incubation.

	F	*p*
Species	111	<0.001
Origin	20	<0.001
Species x Origin	9	<0.001
Time	1527	<0.001
Time x Species	60	<0.001
Time x Origin	7	<0.001

Table 4.5 Repeated measure ANOVA results for rate of respired CO_2 in the climate chamber experiment for the 7 days of incubation with the highest rate.

	F	*p*
Species	81	<0.001
Origin	26	<0.001
Species x Origin	10	<0.001
Time	760	<0.001
Time x Species	27	<0.001
Time x Origin	8	<0.001

Total amount of released CO_2 after 14 days of incubation differed significantly between species ($p \leq 0.001$) and origin ($p \leq 0.001$). The interaction between species and origin was found to be significant as well ($p \leq 0.001$). In accordance with the decomposition rate, *Robinia* and *Alnus* showed the highest amount of CO_2 and *Quercus* the lowest (Figure 4.5b). Including all species, urban litter released more CO_2 than periurban litter (Figure 4.5a). However, *Acer* and *Alnus* released slightly less CO_2 from urban than from their respective periurban litter (Figure 4.5c). In contrast, *Quercus* and *Robinia* released more CO_2 from litter of urban origin and *Populus* litter of urban origin released almost 40 % more than litter of rural origin (Figure 4.5c).

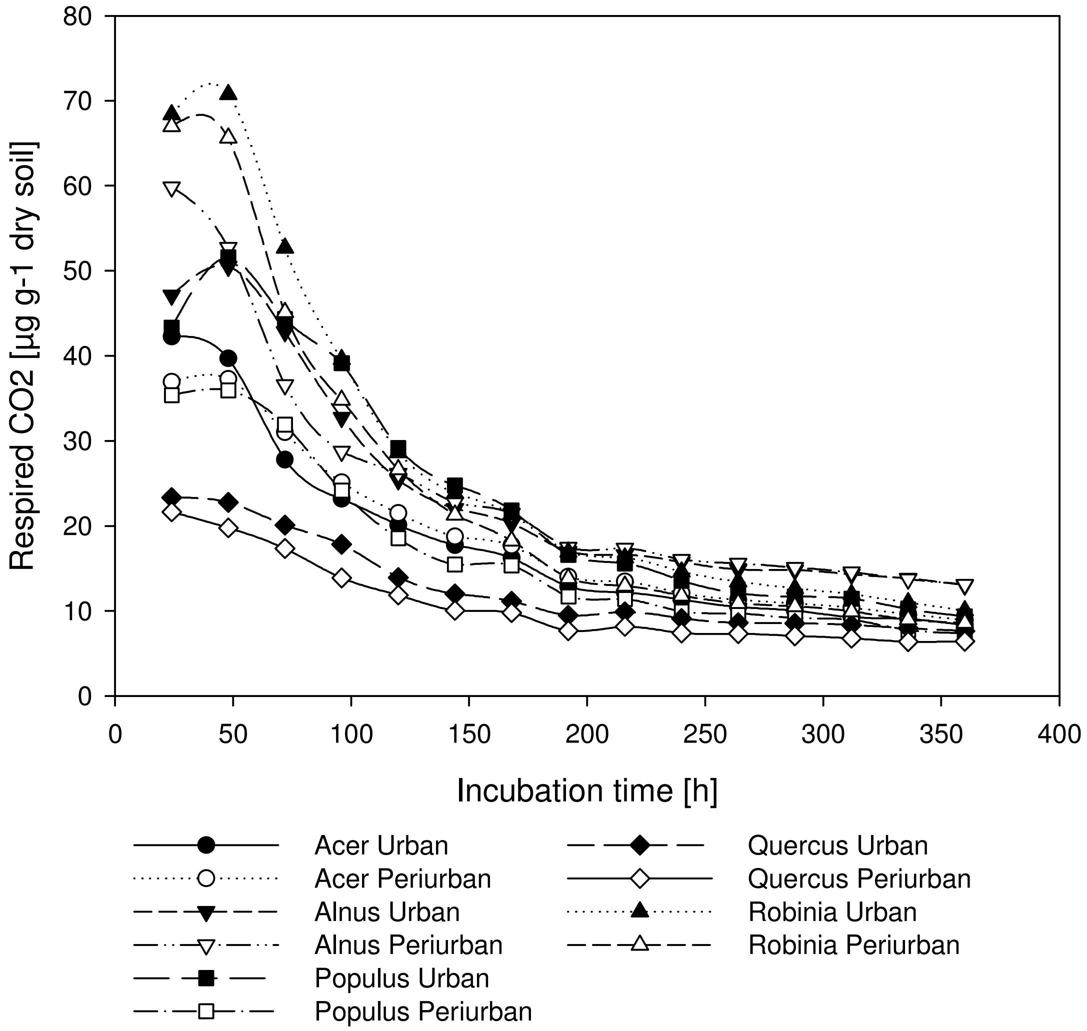

Figure 4.4 Mean respiration rate in CO_2 [mg] per g dry soil amended with litter per hour for all species of both origins.

Despite the pronounced difference found in the climate chamber incubation for *Populus* with regard to origin, when *Populus* was excluded from the analysis, species still differed significantly in the amount of released CO_2 ($p \leq 0.001$). However, while urban litter over the four remaining species still released more CO_2 than periurban litter, this difference was only almost significant ($p \leq 0.1$) with a significant interaction between species and origin ($p \leq 0.05$).

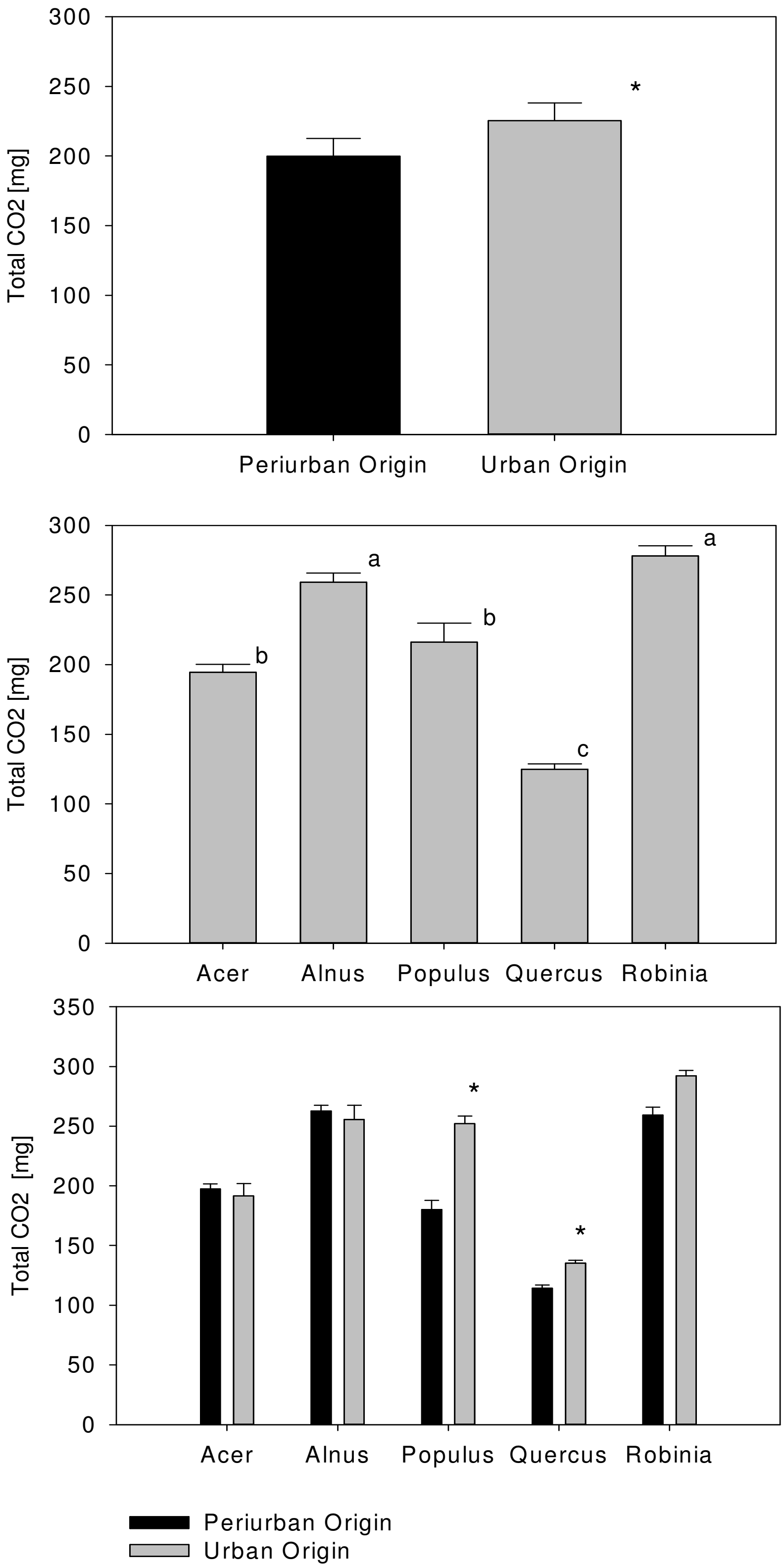

Figure 4.5 Differences in total amount of respired CO_2 in the climate chamber incubation after 14 days with regard to origin of litter. Asterisks indicate significant differences due to origin of litter while letters indicate post-hoc groups for species' means.

4.4 Discussion

The study at hand revealed a faster decomposition of urban originating leaf litter compared to leaf litter of periurban origin. Urbanization of decomposition site did not show significant effects. Species showed interspecific differences in their decomposition, but the general trend of accelerated decomposition of urban originating litter was observed over all species. While the accelerated decomposition might lead to a faster release of CO_2 into the atmosphere in early stages of decomposition (e.g., first year), it is not safe to say that this effect is maintained in later stages of decomposition. It has to be pointed out that the observed accelerated decomposition cannot be taken as synonymous with a reduced accumulation of soil organic matter in litter of urban origin (Berg *et al.* 2001).

Origin of Leaf Litter

Leaf litter origin had a significant influence on decomposition, with litter grown on trees in urban areas exhibiting an accelerated mass loss. Mass loss in litterbags at urban and periurban sites was significantly and negatively correlated to ADL:N ratio, P and Cr content of initial litter. Nikula *et al.* 2010 found similar results in Helsinki and listed the higher N, P, base cation as well as the lower lignin, total phenolics, C:N and lignin:N contents and ratios of urban originating litter as possible reasons for its accelerated decay. In New York City, a slower decomposition of urban over suburban, which, in turn, decomposed slower than rural originating litter, was determined in bioassays, and Lignin and NDF content of initial litter were found to correlate with decay rates (Carreiro *et al.* 1999). A later litterbag study employing leaves of the same tree stands, sampled in a different year, detected slower decomposition of urban originating litter as well, but found no correlations to initial leaf litter quality (Pouyat & Carreiro 2003). In accordance to these studies, a slower decomposition of urban originating leaf litter was observed in Naples and London and attributed to increased heavy metal pollution of leaves (Cotrufo *et al.* 1995, Post & Beeby 1996).

Results suggest that leaf litter quality plays a crucial role in the accelerated decomposition of urban originating litter, and litter quality has been postulated as a dominant factor of decomposition under favorable weather conditions (Coûteaux *et al.* 1995). Alterations in leaf litter due to urbanization seem to either enhance the nutrient supply to decomposer communities or altered leaf lignin structures allows faster access of litter decomposers to the lignified portion of nutrients (Berg & McClaugherty 2008). Surprisingly, though a correlation of decomposition to litter quality parameters was found, these parameters are not altered in a consistent way in the urban originating litter. While the analysis of litter of individual trees found a trend towards decreased structural carbohydrates in urban originating litter (chapter 3), neither ADL:N, P nor Cr show lower values in urban originating litter across all species in this study. This underlines the complex nature of decomposition processes. Not only are correlations between litter quality parameters and mass loss no proof of causality (Prescott 2010), but the individual parameters' predictive value differs between species and stage of decomposition as well (Berg & McClaugherty 2008). Contrary to Cotrufo *et al.* 1995 and Post & Beeby 1996, the contrast in airborne heavy metal loads between urban and periurban tree stands in the city of Hamburg does not seem to be pronounced enough to delay decomposition of urban originating litter.

Influence of Decomposition Site

No significant difference in mass loss at periurban and urban decomposition sites and no significant correlation of mass loss to measured environmental parameters were found. Previous studies that found an acceleration of decomposition in urban areas related it to higher temperatures (Pouyat *et al.* 1997, Pouyat & Carreiro 2003, Nikula *et al.* 2010), non-native earthworms (Pouyat *et al.* 1997, Pouyat & Carreiro 2003) or increased N deposition (Nikula *et al.* 2010). Studies that found a deceleration of decomposition at urban sites linked it to increased heavy metal pollution (Cotrufo *et al.* 1995) or decreased soil moisture (Pavao-Zuckerman & Coleman 2005).

Soil temperature at urban sites had a 0.3 °C higher mean than soils at the periurban sites in about 10 to 17 km distance, while a 2 °C to 3 °C higher temperature at urban stands was cited in New York City litterbag studies (Pouyat *et al.* 1997, Pouyat & Carreiro 2003). Assuming a Q_{10} of two (Raich & Schlesinger 1992), the temperature difference in the New York City litterbag studies explained a 20 to 30 % increased decomposition at the urban sites (Pouyat *et al.* 1997, Pouyat & Carreiro 2003), while the temperature difference in the present study would merely accelerate decomposition by 3 %. Considering the rather green and unsealed character of both urban and periurban study sites, found differences seem to mirror anticipated air temperature differences through the UHI well. While Schlünzen *et al.* 2010 determined a UHI of 1.1 °C at Hamburg's inner city sites compared to sites about 43 km from the city center, they already pointed out a possible reduction of the UHI effect over unsealed surfaces of about 50 %. Wiesner *et al.* submitted, in their in-depth study of evaporable soil moisture minimizing Hamburg's UHI effect, detected a mean annual air temperature difference of about +0.25 °C at suburban sites in similar distance to the city center as the periurban sites of this study. Due to the high number of employed iButtons (n=30), the small detected temperature difference should be a realistic representation of temperature differences. Still, results should be interpreted cautiously as the difference is outside the accuracy of individual iButtons and the range of 0-5 cm depth they were buried in will influence measurements as "noise".

Soils at urban sites of this study contained slightly more water than soils at periurban sites. Opposing findings in Asheville, where urban soils contained less water, leading to a decelerated decomposition (Pavao-Zuckerman & Coleman 2005), no limitation of decomposition through water shortage at urban or periurban sites seem likely.

The higher electrical conductivity at urban sites indicates higher soil salt concentrations and likely stems from higher inputs of de-icing salts in urban areas. Despite being increased, EC values at urban sites were still low, but a direct influence of salt concentration on decomposer organisms cannot be excluded (Czerniawska-Kusza *et al.* 2004). Moreover, increased soil salinity due to de-icing salts has been shown to increase the mobility of soil heavy metals, in addition to their increased deposition in urban areas due to higher traffic loads (Norrström & Jacks 1998, Zehetner *et al.* 2009). Heavy metals are known to adversely influence decomposition (Kandeler *et al.* 1996). While Cotrufo *et al.* 1995 found a decomposition retarding influence of heavy metal polluted soils in Naples, Post & Beeby 1996 found results similar to this study in London with no influence of heavy metals in roadside soils on decomposition rate.

While a high abundance of non-native earthworms were found in New York City (Steinberg *et al.* 1997) and these were considered a main reason for the accelerated decomposition at urban sites, with especially juvenile earthworms being able to access litter through the litterbags' mesh (Pouyat *et al.* 1997, Pouyat & Carreiro 2003), introduction of non-native species does not seem to be as pronounced in

Hamburg. Heidemann 1987 recorded two species native to southern Europe in her analysis of Hamburg's soil fauna, but these were only found on two of the fifteen plots analyzed. At the moment, a relevant influence of non-native earthworms on decomposition processes in the city of Hamburg does not seem likely (Dr. Anneke Beylich, *pers. communication*).

Alterations in environmental and soil parameters between urban and periurban sites of this study were apparently not strong enough to significantly affect decomposition processes. The difference of this study's results to previous studies most likely stem from the very short gradient of about 10 to 17 km employed (compared to, e.g., 130 km between urban and rural sites in Pouyat & Carreiro 2003). Another explanation could be the counteracting effects of accelerating (increased temperature and humidity) and decelerating (increased electrical conductivity) alterations at urban decomposition sites. The rapid decomposition at the common garden experiment with its drastically different environment (higher temperature, higher humidity, lower acidity and lower electrical conductivity) suggests more pronounced environmental alterations would result in a significantly accelerated decomposition.

Differences between Species

No pronounced difference in species' reaction to urbanization was observed. When significant intraspecific differences in the reciprocal litter transplant, the common garden litter transplant and the total amount of respired CO_2 in the climate chamber incubation experiment were determined, urban originating litter decomposed faster than the periurban counterpart. However, the significant interaction in the climate chamber incubation ANOVA between species and origin of litter points towards differences in species' reaction to urbanization, though these are not significant when species are analyzed individually.

In the climate chamber incubation experiment, the symbiotically N fixing species *Alnus* and *Robinia* released most CO_2, while *Quercus*, with its high amount of lignin, released the least. As mass loss values increased, comparing the reciprocal litter transplant and the common garden experiment, mass loss in *Robinia* seems to decelerate relative to the other species, while mass loss in *Alnus* increases similar to the not symbiotically N fixing species. The high N content of *Alnus* and *Robinia* litter was expected to initially accelerate decomposition, but act as a retarding factor as decomposition progresses (Berg & McClaugherty 2008). A possible explanation for the deviating result of high mass loss in *Alnus* in the common garden experiment could be that the chosen mesh size of litterbags is only suitable for early-stage decomposition. Potentially, as decomposition progresses, litter parts that are not truly decomposed (i.e. respired), but rather solely fragmented are lost through the mesh, thus rendering the method unreliable.

Individual species' leaf litter decomposition is affected differently by different cities. Contrary to results from New York City (Carreiro *et al.* 1999, Pouyat & Carreiro 2003), *Quercus rubra* litter decomposed faster in the climate chamber incubation when originating from urban stands. While this difference was only significant in the climate chamber incubation, the same trend was observed in the litterbag studies. *Populus tremula* leaf litter decomposition was affected in similar ways in Helsinki and Hamburg, with urban originating litter showing a faster decomposition (Nikula *et al.* 2010).

The different employed methods yielded similar results, with urban originating litter decomposing faster. However, all methods have specific advantages and disadvantages. While litterbag experiments are time consuming and decomposition site set-ups in urban areas have a high potential for disturbance, they yield valuable insights into decomposition processes *in situ*. However, as seen in the common garden experiment, mass loss of only partly decomposed material from the litterbags can become a problem in later stages of decomposition. If only the effect of litter origin is to be studied, climate chamber incubations could serve as fast alternatives to collect data.

5 Synthesis

5.1 Key findings

This thesis presents a case study of ecosystem services in cities, namely parts of the regulating service of the carbon cycle within Hamburg. The thesis touched upon vastly different scales and concepts, from the global climate to chemical alterations in leaf litter, and from pools to processes within the carbon cycle. Parts of the carbon cycle more closely examined in this thesis were storage of organic carbon in trees and soils, alterations in leaf litter quality due to urbanization and their resulting effect on decomposition, as well as direct effects of urbanization on decomposition.

Specifically, this thesis found:

- Significant amounts of carbon are stored in trees and soils within the political boundaries of Hamburg, with a total amount of about 6 Mt carbon of which 2 Mt are stored in trees and 4 Mt in soils.
- Though wetland soils and trees in forested areas at the city's fringes showed the highest carbon density per square meter, the large built-up classes throughout the city store substantial amounts as well.
- Even over short distances, alterations in leaf litter quality can be observed due to urbanization. For example, when significant intraspecific differences were found, structural carbohydrates were reduced in urban samples compared to periurban ones. However, some observed alterations differed between species.
- The observed alterations in leaf litter quality due to urbanization lead to an accelerated decomposition of leaf litter originating from urban sites.
- While an indirect effect of urbanization on decomposition through leaf litter alterations was observed, no direct effect of urbanization through environmental alterations at the sites of decomposition was detected.

5.2 Extrapolation of Results to Urban Areas in General

The observed patterns and alterations of carbon storage and leaf litter quality as well as leaf litter decomposition yield valuable insights into the carbon cycle in the city of Hamburg. But how valid are extrapolations from the case study Hamburg to other cities?

Extrapolations of organic carbon pools found in Hamburg's trees and soils to pools in cities around the globe have to be conducted with reservations. Chapter 2 discussed the drastic differences between cities' amount of stored carbon in detail, pointing towards Hamburg's storage of carbon in trees and soils being concentrated on the city's fringes. With its high areal percentage of rural and near-natural "green" areas, Hamburg is most likely unique in its carbon storage pattern. Thus, transfer of storage amounts solely on a per area basis to other cities would not yield reliable results. Using carbon storage in individual biotope types of this study and link them to equivalent biotope type cadasters of other cities might yield valuable approximations, but not all cities possess these. Combining easily available data, like population density, tree cover, soil properties (especially water influences) and soil sealing into an urbanization index (Schmidt *et al.* 2013) might yield a proxy for extrapolations of carbon storage to other cities. Extrapolations would have to be interpreted with caution, as they would be connected to a high level of uncertainty due to the heterogeneity of tree stands and especially soils within and between cities.

Extrapolating found alterations in leaf litter quality in Hamburg to other cities seems plausible, considering that environmental parameters seem to be altered in similar ways in other cities. Hamburg exhibits general trends in environmental alterations typical of urban environments around the world, though most of them are not as pronounced as observed in other cities (chapters 3 and 4). Temperature differences between urban and periurban decomposition sites were in ac-cordance with the UHI theory of increased temperatures in urban centers (Oke 1973). CO_2 concentrations were elevated in the city center (Idso *et al.* 2001), as were heavy metal and other pollutant depositions (Post & Beeby 1996, Alfani *et al.* 2000). As in other cities (Sieghardt *et al.* 2005), O_3 was elevated at periurban compared to urban sites. While marked interspecific differences in leaf litter quality alterations were observed depending on urbanization of tree stand, observations of the same species in different cities seemed to yield somewhat similar results (chapter 3, *Quercus rubra* in Carreiro *et al.* 1999, *Populus tremula* in Nikula *et al.* 2010).

The interspecific differences found in leaf litter alterations did not result in marked interspecific differences in the effect of urbanization on decomposition. If a significant intraspecific difference depending on origin of leaf litter was found, all species showed a faster decomposition of urban originating litter (chapter 4). While the result of an accelerated decomposition due to urbanization effects on tree stands and their litter quality is pretty forward in Hamburg, it only partly agrees with findings in other cities. While some studies also found an accelerated decay of urban originating litter (Carreiro *et al.* 1999 and Pouyat & Carreiro 2003 for New York City, Nikula *et al.* 2010 for Helsinki), others found a decelerated one (Cotrufo *et al.* 1995 in Naples, Post & Beeby 1996 in London). The decelerated decomposition was attributed to an increased heavy metal deposition on the leaves. Thus, as long as heavy metal depositions are not too intense, accelerated decomposition of leaf litter grown in urbanized tree stands seems to be a general trend in different cities.

Extrapolating the influence of urbanization effects of decomposition site does not seem to be as straightforward as the influence observed for urbanization effects of leaf litter origin. While no influence of the degree of urbanization of decomposition site on leaf litter decomposition was observed over the short gradient employed in Hamburg, previous studies found an accelerated decomposition in urban areas and linked it to increased temperatures, increased N deposition or non-native earthworms (Pouyat *et al.* 1997, Pouyat & Carreiro 2003, Nikula *et al.* 2010). Other studies report a decrease of decomposition at urban sites and linked this to heavy metal pollution or decreased soil moisture (Cotrufo *et al.* 1995, Pavao-Zuckerman & Coleman 2005). Extrapolating the effects of urbanization of decomposition sites thus requires an assessment of the intensity of urbanization induced environmental alterations.

In conclusion, extrapolations of found results to cities around the globe have to be conducted with caution. Carbon storage shows city specific patterns. However both the biotope type approach used in this study and the use of a general urbanization proxy would be possibilities for spatial extrapolations to other cities. Leaf litter alterations due to urbanization seem to be generally similar, though interspecific differences exist in detail. The effect urbanization has on decomposition due to litter quality changes shows similar trends around the globe, if heavy metal depositions do not show an overriding effect. Extrapolating the effect urbanization of decomposition site has does not seem to be as straightforward, with marked differences between cities.

5.3 Incorporation of Findings into the Ecosystem Service Concept

Hamburg's trees and soils provide a remarkable ecosystem service, with substantial amounts of carbon being stored. Hamburg's trees and soils store about 6 Mt of organic carbon (chapter 2). In contrast, about 3.3 Mt carbon (equal to about 12 Mt of CO_2) were emitted in the year 2010 (Statistisches Amt für Hamburg und Schleswig-Holstein 2013b). Thus, an amount of carbon roughly equivalent to the amount emitted by the inhabitants of Hamburg in two years is stored. This study did not evaluate sequestration values in addition to storage values, but Nowak & Crane 2002 found annual carbon sequestration of all urban forest trees in the USA to be equivalent to USA population's emissions over a five day period. It can thus be concluded that, while carbon storage is significant, emissions are high enough to make sequestration seem minor.

Including the carbon stored in urban trees and soils into the carbon market would be a possible way of monetizing the ecosystem service. The inclusion of forest carbon stocks into the carbon market is discussed as a tool to encourage forest preservation (REDD 2013). So far, carbon pools in forests and soils are not traded in the EU carbon market (COM 645/3 2008). For emissions, on the other hand, market prices of carbon equivalents are highly fluctuant depending on, e.g., quality of offsets (Valatin 2010). It can thus be concluded that carbon stocks in Hamburg's urban trees and soils might be implemented in the carbon market in the future. However, at the moment, a reliable pricing of the detected pools is not possible.

While urban carbon pools are well acknowledged throughout the scientific literature dealing with ecosystem services (e.g., MA, TEEB), fluxes concerning the respiration from decomposition processes are not included in the concept so far. A reason could be the high uncertainty connected to the processes that cause litter carbon to be either respired into the atmosphere or stored in soil organic matter. As an example, some textbooks state that, without disturbance, soils would reach equilibrium, after which respiration and carbon storage are balanced (Aber & Melillo 2001). On the contrary, newer textbooks state that, without disturbance, soils would potentially accumulate carbon infinitely (though stressing disturbance as inevitable even in natural ecosystems) (Berg & McClaugherty 2008). The phenomenon of soil organic matter accumulation through litter decomposition is so far not well understood.

At the moment, reliable predictions about the amount of carbon being stored in soil organic matter depending on the chemical properties of the decomposing litter are not possible. Only few species' litter decomposition has been examined long enough to draw conclusions from litter chemical quality to resulting soil organic matter amount (Berg *et al.* 2001). As the amount of carbon stored in soil organic material as a function of litter quality is not known, neither is the influence of decomposition speed measured in this study. Thus, while observations about decomposition speed are quite forward, reliable predictions about the influence of urbanization on accumulation of soil organic matter cannot be derived from this thesis. In addition to the uncertainty, increments in soil organic matter are small on time scales relevant for planning, while losses in soil organic carbon can be rapid (Berg & McClaugherty 2008).

Without the processes of decomposition and soil organic matter formation, the representation of the carbon cycle as a regulating service is incomplete from a scientific, urban ecologist's viewpoint. The high amount of litter produced in Hamburg (about 10 000 tonnes annually only in the three built-up classes) (Table 2.3), reveals that substantial amounts of carbon are inserted into this process each year. However, from an applied viewpoint, exclusion of this process might increase practicability, particularly for stakeholders without scientific background.

5.4 Relevance of Findings for Urban Planning

Green spaces and their beneficial effects are widely incorporated into city planning (e.g., Behörde für Stadtentwicklung und Umwelt 2013), though this usually does not explicitly include the concept of ecosystem services. Some authors set high hopes on the incorporation of the ecosystem service concept into urban planning, e.g., regarding the reduction of cities' ecological footprint (Gómez-Baggethun *et al.* 2013). By now, the concept is beginning to be implemented, especially in Western European cities (Kronenberg *et al.* 2013). However, incorporation is held back by lack of political will and institutional capacities (Wilkinson *et al.* 2013). Additionally, many stakeholders in urban planning are either not familiar with the concept or find it too complex and abstract for planning (Niemelä *et al.* 2010). In effect, topics other than ecosystem services are often given higher priority, e.g., housing (Wilkinson *et al.* 2013).

Planners aiming at preserving the ecosystem service of carbon storage in the city of Hamburg were shown areas of special importance, and the importance of soils for carbon storage was highlighted (chapter 2). In regard to the rapid advance of soil sealing (about 140 ha annually in Hamburg) (Statistisches Amt für Hamburg und Schleswig-Holstein 2013a) and the connected disturbances of soils, the need for their protection becomes apparent. While the importance of soil organic carbon storage for the overall ecosystem service of carbon storage is evident, implementation into urban planning is hindered through benefits not being locally visible ("global" climate) and a lack of perceivable add-on benefits.

As stated before, the incorporation of decomposition fluxes into the concept of ecosystem services is difficult and their consideration in urban planning unlikely. However, the aim of preserving carbon pools is easy to communicate. And in the case of urban trees, valuable add-on services, e.g., for air purification and recreation, are provided. Implementing urban forests into the carbon market has been proposed and associated with high quality offsets (Poudyal *et al.* 2011). The mentioned difficulties (uncertainty, slow accumulation rate) prohibit the inclusion of decomposition and soil organic carbon sequestration processes in monetization attempts at the moment. While the amount of stored carbon in urban areas can be substantial (chapter 2), it has to be kept in mind that the amount of carbon sequestered is small compared to emissions (e.g., Nowak & Crane 2002), and emission reduction strategies for urban areas are needed (Lebel *et al.* 2007).

5.5 Future Studies

The thesis at hand not only advanced the knowledge of carbon cycling in cities, but connected it to the concept of ecosystem services as well. To assess how general the observed patterns and processes are to the phenomenon of urbanization, similar studies in different cities should be conducted. Studies in cities outside the world's temperate zone are especially needed, as they are currently underrepresented in carbon cycle studies. For future studies assessing alterations in leaf litter quality and litter decomposition, employment of longer gradients further into the rural hinterlands might be useful. Though the employed gradient in this study resulted in observable alterations, trends might have been clearer along a longer gradient (e.g., O_3 gradient). Studies focusing on leaf litter quality alterations will benefit from assessing whether elements or pollutants are taken up via roots, absorbed through leaves or are deposited on leaf surfaces. Found interspecific differences in leaf litter quality alterations due to urbanization indicate the need for studies conducted on larger sets of species. Connecting results from this thesis with studies about carbon sequestration through the urban forest (e.g., Nowak & Crane 2002) and with soil respiration (Pouyat *et al.* 2002) will further advance the field of urban carbon cycling towards a "distinct urban biogeochemistry" as asked for by Kaye *et al.* 2006. To incorporate findings of alterations due to urbanization into models of carbon cycling (Imhoff *et al.* 2004, Trusilova & Churkina 2008), further research of the long-term alterations in decomposition is needed. Especially, whether leaf litter alterations influence the amount of carbon stored into long-lived soil organic matter, or solely the rate of decomposition. Long-term studies should be conducted on a broader set of species (Berg *et al.* 2001), to enlarge the data pool and allow reliable forecasts of soil organic matter accumulation based on litter quality.

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Contributions

The author of this thesis developed, designed and conducted the studies described. He prepared the statistical analyses, graphical presentations and texts. Further, he collected the data, except for the climate chamber incubation described in chapter 3, which was conducted as a Bachelor thesis by Anja Wilken, supervised by him.

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertationsschrift selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.