

Article

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

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

Keywords: bioenergy; municipal; contamination; leaves; polycyclic aromatic hydrocarbons

1. Introduction

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

Contamination with pollutants is a potential problem for public acceptance of biomass conversion plants fed with urban leaf litter. Up until now, there is little known about the concentration of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in leaf litter from urban roads. Heavy metals pose a serious threat to human health [4]. Past literature has reported heavy metal concentrations in soil [5,6] and the distribution of concentrations in soil within cities, with higher values for Cd and Pb for roadside areas compared to urban park areas [7]. Plant availability and uptake of heavy metals, including the possibility of phytoremediation of soils (e.g., [8]), as well as concentrations of heavy metals in urban water (e.g., [9]) and in plants grown in urban areas (e.g., [10]) have also been determined. The general behavior of heavy metals in combustion depends on the volatility of the element in question [11]. The more volatile heavy metals (e.g., Pb, Zn, Hg) have a tendency to vaporize in combustion and condense on fine particles and, therefore, are found in cyclone or filter fly ash or escape with the flue dust into the atmosphere. However, if the combustion unit is fitted with an efficient particulate removal

system, the amount of heavy metals escaping the combustion system with the exhaust is minimal [12]. Less volatile heavy metals on the other hand, such as As, Cr, Cu and Ni remain in the bottom ash of the furnace to a large extent [13]. Concentrations in the various ash fractions must be considered, as they may restrict the potential uses of the ashes and may require disposal if the concentration in the ash fraction is higher than is legally allowed for application as a fertilizer and liming agent on agricultural fields or in forests [12]. To our knowledge, there is no scientific investigation on the degree of heavy metal contamination in street leaf litter designated for combustion. Potential sources of contaminants are motor vehicle emissions, tire wear and asphalt road surfaces, as well as domestic fire emissions, gasworks and commercial incinerators [14]. Research on the concentration of inorganic, as well as organic contaminants in urban biomass has focused on detecting suitable plants as bio-indicators for pollution (e.g., metals in moss [15], grass [16], *Quercus ilex* [17] as well as in *Taraxacum officinale*, *Pinus sylvestris*, and in *Tilia cordata* [18]) and ensuring healthy food production in urban environments (e.g., [19]). Two British practical trials investigating the contamination of street leaf sweepings found that the pollution with PAHs was too high for composting purposes [20,21].

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

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

Thus, the aims of this study were:

- I. To investigate the concentrations of PAHs and heavy metals in urban leaf litter from street sweepings;
- II. To determine the effect of provenience and collection technique on the concentration of PAHs and heavy metals in urban leaf litter from street sweepings;
- III. To investigate the effect of washing and dehydration through the IFBB system on the heavy metal concentration;

- IV. To develop a linear regression model to predict the heavy metal concentration in urban leaf litter.

2. Materials and Methods

2.1. Collection of Leaf Litter

Leaf litter was collected from the city of Kassel, which is located in central Germany and has about 200,000 inhabitants within 107 km². Sampling was conducted in collaboration with the local cleansing department, who provided leaf litter in accordance with their routine work. Therefore, we were able to distinguish among various proveniences ((i) main road (MR); (ii) residential area (RA) and (iii) city center (CC)) and between different collection techniques ((i) vacuum technique (VT) and (ii) sweeping technique (ST)). The three proveniences had different cleaning cycles: main roads were cleaned weekly, residential areas biweekly and the city center was cleaned every second day. The vacuum technique is appropriate for sites which cannot be swept (e.g., parks and small greens along sideways) and where leaf litter is initially gathered with leaf blowers and subsequently picked up by a suction unit. The sweeping technique is usually applied on compacted surfaces and leaf litter is picked up with a rotating brush after moisturizing. Leaf litter collection took place after litter fall in calendar weeks 41, 43, 45 and 47 in 2014, resulting in 24 samples (4 dates × 3 proveniences × 2 collection techniques). For conservation, samples were ensiled in 60 L airtight polyethylene barrels for a minimum of 12 weeks.

2.2. Washing Facility and Washing of Leaf Litter

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

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

2.3. Chemical Analysis

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

atomic spectrometry. In this study, the term “heavy metals” refers to the elements As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Tl and Zn.

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

2.4. Statistical Analysis

Figures 1 and 2 were generated with SigmaPlot, Version 12.3 (Systat Software, San Jose, CA, USA) and Figure 3 was generated with R, Version 3.0.2 (R Foundation for Statistical Computing, Vienna, Austria). R software was also used to detect differences in element concentrations between or among proveniences, collection techniques and degree of materials processing by applying either Wilcoxon’s rank-sum test for differences between two independent groups or the Kruskal-Wallis test for differences among more than two independent groups with the post-hoc function “kruscalmc”. In the case of degree of materials processing, groups were not independent, so significant results should be interpreted against this background. The dendrogram was based on Euclidean distances, which were hierarchically clustered with Ward’s method. Regression analysis was conducted with R software by applying the “lm” function. Residuals were normally distributed except for Ni, Fe and Cu. Homoscedasticity was verified visually, which revealed Cu to be the only heteroscedastic element.

3. Results and Discussion

3.1. Heavy Metals

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

3.1.1. Heavy Metals in Urban Leaf Litter

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

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

closely monitored, if urban biomass is used for energetic purposes. Cu concentration was in the range of formerly observed concentrations in urban leaf litter.

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

Element	Urban Leaf Litter from Roads	Forest Leaf Litter ¹	Urban Leaf Litter ²	Urban Leaf Litter from Roadside Verges ³	Deciduous Wood ⁴	Standard for Pellets from Non-Woody Materials ⁵
As	0.56 \pm 0.08	0.07	-	-	<0.1	\leq 1.0
Cd	0.13 \pm 0.02	0.14	1.7	0.33	0.1	\leq 0.5
Cr ⁶	6.04 \pm 1.02	0.68	7.6	4.9	1.0	\leq 50.0
Cu	11.84 \pm 1.04	6.3	9.2	29	2.0	\leq 20.0
Fe	7 154.46 \pm 1271.02	110.0	1 461.0	-	25.0	-
Mn	204.99 \pm 24.47	1 850.0	550.0	-	83.0	-
Ni ⁶	7.20 \pm 1.33	1.12	7.2	1.8	0.5	\leq 10.0
Pb	4.14 \pm 0.63	1.3	28.4	20	2.0	\leq 10.0
Zn	61.04 \pm 6.95	36.0	81.0	89	10.0	\leq 100.0

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

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

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

Figures 1a and 2a show the concentration of heavy metals ($\text{mg}\cdot\text{kg}^{-1}$ DM) in leaf litter of urban street trees from various proveniences within the city of Kassel (main roads—MR, residential areas—RA, city center—CC). Arsenic concentration differed between proveniences. Concentration in leaf litter from the CC was considerably lower than from MR and RA, with the difference between CC and RA being significant. This pattern could also be observed for Cd and Fe. While the Mn concentration of material from the CC was significantly lower than both of the other proveniences, the lower Pb concentration in leaf litter from the city center is only significant in comparison to MR. Concentrations of Cd, Cr, Cu, Ni and Zn did not differ significantly between proveniences; although the mean value of material collected from the CC was lower than the means from MR and RA in all cases. The exact cause for the differences between proveniences is unknown, but traffic characteristics (e.g., number of cars, average speed, traffic lights) and the different contact time of leaf litter with the street (two days in the CC, up to 14 days in MR and RA) might influence its contamination. Results of Charlesworth et al. [36], investigating street dust in Birmingham, also indicate spatial clustering of contaminants potentially due to specific industries and traffic characteristics. To gain further insights into the spatial distribution of heavy metals, further research with high spatial resolution is necessary.

Figures 1b and 2b show the concentration of heavy metals ($\text{mg}\cdot\text{kg}^{-1}$ DM) in leaf litter of urban street trees collected with different techniques within the city of Kassel (vacuum—VT and sweeping technique—ST). Fe, As and Pb concentrations were significantly higher when collected with the ST rather than the VT. Cd, Cr, Cu, Mn, Ni and Zn concentrations did not differ significantly between collection techniques, however, a higher concentration of heavy metals in material sampled with the ST was obvious. Theoretically, this technique takes up higher quantities of road debris.

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

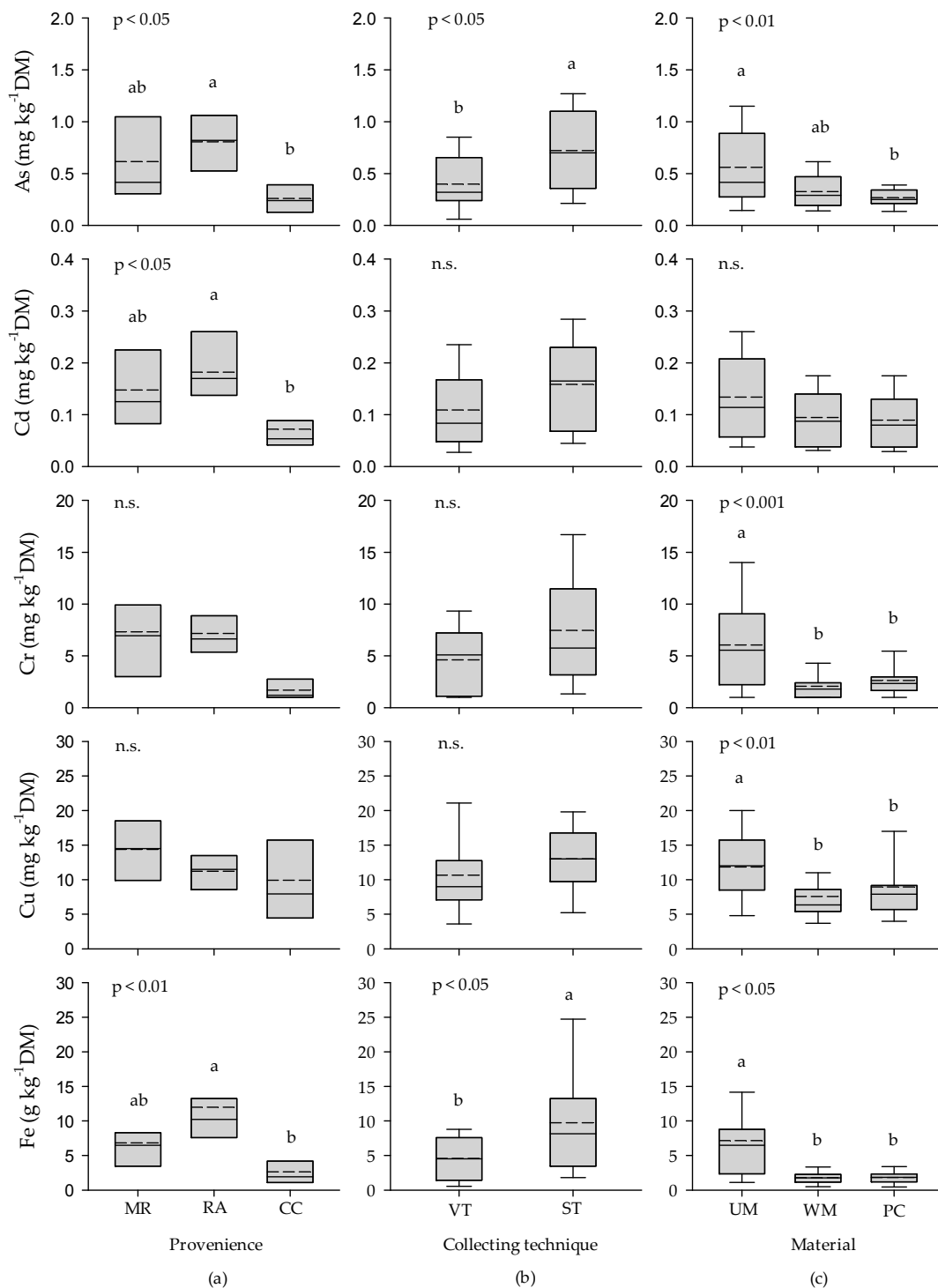


Figure 1. Concentration of heavy metals As, Cd, Cr, Cu and Fe in leaf litter of urban street trees from (a) various provenience (main road—MR, residential area—RA, city center—CC) collected by (b) different technique (vacuum—VT and sweeping technique—ST) and (c) with various degrees of material processing (unwashed material—UM, washed material—WM, press cake—PC). Whiskers indicate the 5th and 95th percentiles. Dashed lines indicate median values. Different letters indicate significant differences; n.s., not significant. Samples with values below the analytical detection limit were included into the dataset, using the detection limit as a conservative estimate of the concentration.

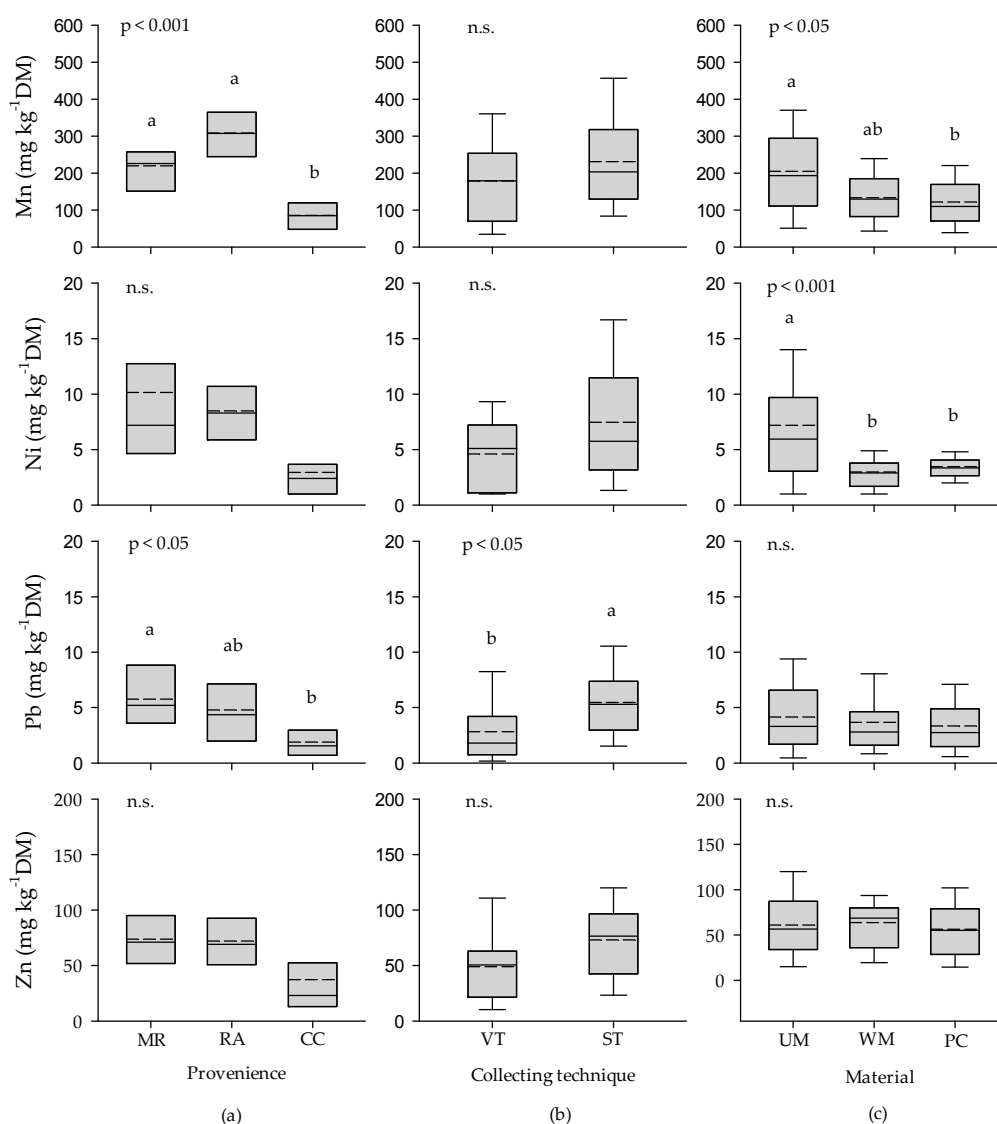


Figure 2. Concentration of heavy metals Mn, Ni, Pb and Zn in leaf litter of urban street trees from (a) various provenience (main road—MR, residential area—RA, city center—CC) collected by (b) different technique (vacuum—VT and sweeping technique—ST) and (c) with various degrees of material processing (unwashed material—UM, washed material—WM, press cake—PC). Whiskers indicate the 5th and 95th percentiles. Dashed lines indicate median values. Different letters indicate significant differences; n.s., not significant. Samples with values below the analytical detection limit were included into the dataset, using the detection limit as a conservative estimate of the concentration.

Figures 1c and 2c show the effect of washing and the IFBB system on the leaf litter material from the city of Kassel. Washing reduced the concentration of all elements with the exception of Zn. The reduction was not significant for As, Cd, Fe and Mn. The IFBB process, on the other hand, achieved a significant reduction in As, Fe and Mn concentrations compared to the unwashed material. In the case of Cr, Cu and Ni, the concentration was significantly reduced by washing, but no further reduction occurred with the IFBB process. On the contrary, the concentration increased slightly, which was also observed by Piepensneider et al. [30] for urban roadside cut material and can be explained by abrasion of metal within the equipment used for the IFBB system. Nicola et al. [17] also found that washing vital leaves from *Quercus ilex* reduced the concentration of heavy metals (Cr, Cu, Fe, Pb and Zn) significantly.

From a total of 24 samples, Tl and Hg could only be detected in 15 and 10 samples, respectively (Table 2). Thus, the minimum values in Table 2 are below the detection limit of $0.01 \text{ mg}\cdot\text{kg}^{-1} \text{ DM}$. The median concentration of both elements in unwashed material was $0.02 \text{ mg}\cdot\text{kg}^{-1} \text{ DM}$, while maximum values were $0.05 \text{ mg}\cdot\text{kg}^{-1} \text{ DM}$ for Tl and $0.06 \text{ mg}\cdot\text{kg}^{-1} \text{ DM}$ for Hg. Nicola et al. [17] argue that accumulation of particle-bound and gaseous contaminants on the leaf surface is dependent on tree species, since leaf surface properties (morphology, chemistry of waxy components) might affect the accumulation process.

Table 2. Concentrations of Tl and Hg ($\text{mg}\cdot\text{kg}^{-1} \text{ DM}$) in leaf litter of urban street trees. UM, unwashed material; WM, washed material; PC, press cake. Minimum, maximum and median values refer to the full data set of 24 samples.

Element	Material	Number of Samples with Detected Concentrations	Minimum Value	Maximum Value	Median
Tl	UM	15	<0.01	0.05	0.02
	WM	13	<0.01	0.04	0.02
	PC	6	<0.01	0.04	<0.01
Hg	UM	10	<0.01	0.06	0.02
	WM	7	<0.01	0.06	<0.01
	PC	10	<0.01	0.06	<0.01

3.1.2. Ash Content as a Predictor for Heavy Metal Concentration

Linear regression analysis revealed a strong relationship between ash content and heavy metal concentration (Table 3). Linear models were significant for every element, with coefficients of determination between $R^2 = 0.77$ for As and $R^2 = 0.21$ for Cu. Values higher than 0.5 were observed for Fe, Mn, Pb and Zn. Thus, it can be stated that if a leaf litter sample is high in ash content, it is very likely that the material is also contaminated with heavy metals.

Table 3. Results of linear regression analysis determining the relationship between ash content (% DM) and heavy metal concentration ($\text{mg}\cdot\text{kg}^{-1} \text{ DM}$) in leaf litter of urban street trees. Residuals of the models for Ni, Fe and Cu were not normally distributed.

Element	Intercept	Slope	R ²	Significance
As	−0.173	0.031	0.77	***
Cd	0.010	0.005	0.44	***
Cr	−0.237	0.278	0.39	**
Cu	6.629	0.219	0.21	*
Fe	−4606.400	495.620	0.71	***
Mn	8.919	8.263	0.53	***
Ni	0.061	0.317	0.29	*
Pb	−0.947	0.215	0.53	***
Zn	0.785	2.539	0.62	***

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

3.1.3. Relevance of Heavy Metals in Urban Leaf Litter for Combustion

The heavy metal concentration in non-woody biomass measured in this study fell below the European and German standard limits for non-woody fuel pellets [35]. Contaminated biomass types such as demolition timber and plants from phytoremediation areas have been shown to contain significantly higher concentrations of heavy metals [12]. There are two major concerns regarding heavy metals in combustion. One is emissions of heavy metals with the fly dust, which is especially applicable for the more volatile elements, such as Hg, Pb, Zn and Cd. The other concern focuses on the contamination of ash with heavy metals, making it impossible to use the ash on agricultural or forested lands. During combustion in a state of the art combustion unit, three ash fractions are generated: the bottom ash, the coarse fly ash or cyclone fly ash and the fine fly ash or filter fly ash [12,13]. The bottom ash is the largest fraction with 60%–90% of the total ash, the cyclone fly ash is the second largest fraction

10%–35% and the filter fly ash is the smallest fraction (2%–10%). It was found that only between 1% and 21% of the ash escapes with the flue dust, with a mean of 1.6% [13]. Narodoslowsky and Obernberger [13] found that the average distribution of heavy metals for Zn, Pb, Hg and Cd was about 90% in the cyclone and fly ash and only about 10% in the bottom ash. On the other hand, about 50% of Co, Ni, Cr and V were found in the bottom ash with only about 10% of these elements in the filter fly ash. It was concluded that the gaseous emission of heavy metals during combustion is only of minor concern, except for Hg emissions [13]. However, we found Hg only in 10 out of 24 samples for the unwashed leaf litter and concentrations were only marginally higher than in beech wood (0.2 versus 0.12 mg·kg⁻¹ DM, [12]) and much lower than in straw (6 mg·kg⁻¹ DM, [12]) or contaminated biomass samples (2.7–1000 mg·kg⁻¹ DM, [12]). The largest problem is the contaminated fly ash collected by the filters, which is a highly polluted hazardous waste that has to be disposed of [13] or industrially treated [11]. Although this fraction is the smallest, it contains the majority of the Cd and Zn, whereas between 85% and 95% of the plant nutrients are contained in the usable ash fractions [11].

3.2. PAHs

3.2.1. PAHs in Urban Leaf Litter

From the 16 PAHs investigated in this study, 5 (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, and Dibenz(ah)anthracene) could not be detected in any sample (Table 4). The other 11 PAHs occurred in 1 to 13 samples of the total set of 24 samples. The most abundant substance, with the highest single and median value, was Fluoranthene, which is a pollutant originating from low-temperature and inefficient combustion. Pyrene and Benzo(b)fluoranthene were also present in higher amounts and a greater number of samples. According to Harrison et al. [37], these PAHs are especially indicative of incineration and oil combustion. Furthermore, Benzo(k)fluoranthene and Benzo(a)pyrene are indicators of road dust as an emission source. Harrison et al. [37] showed that car traffic was the most important factor influencing the PAHs concentration.

Table 4. Concentration of polycyclic aromatic hydrocarbons (PAHs) (mg·kg⁻¹ DM) in leaf litter of urban street trees in comparison to literature values for *Quercus ilex* leaves from Naples, Italy [17]. Minimum, maximum and median values refer to the full data set of 24 samples.

PAH	Chemical Formula	Number of Samples with Detected Concentration	Minimum	Maximum	Median	Literature Value ^{1,2}
Naphthalene	C ₁₀ H ₈	0	<0.05	<0.05	<0.05	0.102
Acenaphthylene	C ₁₂ H ₈	0	<0.05	<0.05	<0.05	0.052
Acenaphthene	C ₁₂ H ₁₀	0	<0.05	<0.05	<0.05	0.007
Fluorene	C ₁₃ H ₁₀	0	<0.05	<0.05	<0.05	0.038
Phenanthrene	C ₁₄ H ₁₀	12	<0.05	0.360	<0.05	0.262
Anthracene	C ₁₄ H ₁₀	0	<0.05	<0.05	<0.05	0.025
Fluoranthene	C ₁₆ H ₁₀	13	<0.05	0.668	0.174	0.328
Pyrene	C ₁₆ H ₁₀	8	<0.05	0.520	<0.05	0.419
Benz(a)anthracene	C ₁₈ H ₁₂	6	<0.05	0.349	<0.05	0.054
Chrysene	C ₁₈ H ₁₂	6	<0.05	0.282	<0.05	0.205
Benzo(b)fluoranthene	C ₂₀ H ₁₂	9	<0.05	0.520	<0.05	0.127 ^a
Benzo(k)fluoranthene	C ₂₀ H ₁₂	1	<0.05	0.150	<0.05	0.127 ^a
Benzo(a)pyrene	C ₂₀ H ₁₂	5	<0.05	0.282	<0.05	0.047
Indeno(123-cd)pyrene	C ₂₂ H ₁₂	2	<0.05	0.179	<0.05	0.003
Dibenz(ah)anthracene	C ₂₂ H ₁₄	0	<0.05	<0.05	<0.05	0.045
Benzo(ghi)perylene	C ₂₂ H ₁₂	4	<0.05	0.249	<0.05	0.002
Sum	-	-	<0.05	3.053	0.267	2.10 ^b

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

The concentration of 24 PAHs in vital leaves from *Quercus ilex* was found to be 2.1 mg·kg⁻¹ DM [17], whereas Howsam et al. found 0.041 mg·kg⁻¹ DM of 23 PAHs in oak leaves from a woodland area [38]. Concentration of PAHs is dependent on leaves' physiological features. Hairiness, for instance, was found to cause a significantly higher PAH concentration compared to hairless leaves [38]. The maximum concentration of Benzo[a]pyrene was 20.7 mg·kg⁻¹ DM in leaf litter sweepings from

urban roads when collected by a vehicle with a rotary brush and vacuum head [21]. Notably, this was lower than values detected in manually collected leaf litter [21]. The authors hypothesized that PAHs might be removed by water spray on the front of the vehicle prior to collection, but high variation in concentrations did not allow a solidified conclusion to be made. However, the detected minimum value ($0.70 \text{ mg}\cdot\text{kg}^{-1} \text{ DM}$, [21]) was still more than twice as high as the maximum value detected in our study ($0.28 \text{ mg}\cdot\text{kg}^{-1} \text{ DM}$). In contrast, Ellis and Keyse [21] measured less than half of the concentration found by the present study when sampling only fresh leaf litter with the vacuum device of the collection vehicle without using the rotary brush. Therefore, collection technique seems to influence the concentration of Benzo[a]pyrene in leaf litter.

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

3.2.2. Hierarchical Clustering of PAHs in Urban Leaf Litter

Hierarchical clustering of samples based on their PAH concentration revealed three distinguishable clusters (Figure 3). One cluster included all samples without any PAH contamination, a second cluster comprised all samples with a contamination of 1–4 PAHs and the third cluster included the remaining samples with a contamination of 6–7 different PAHs. Interestingly, the highly contaminated group contains no samples from the CC. This area is cleaned in a shorter cycle; leaf litter is taken up every second day. Thus, the time of exposure to street dust and exhausts from cars is shorter, possibly reducing the level of pollution. Considering the time of sampling, the samples from calendar weeks 41 and 43 were found more often in the none or less polluted cluster, whereas samples from later collection dates (calendar weeks 45 and 47) were also found in the more highly polluted group. This could be due to rainfall or other environmental conditions that were not recorded in this study.

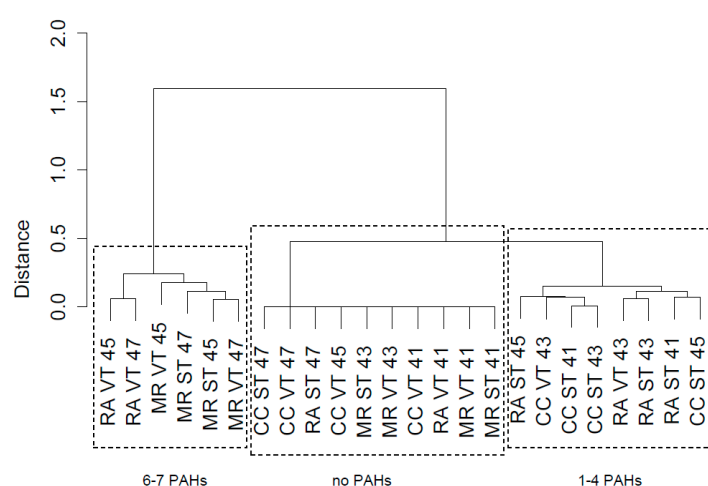


Figure 3. Hierarchical clustering of 24 samples of leaf litter from urban street trees based on their PAH concentration by referring to Euclidean distance. CC, city center; MR, main road; RA, residential area; VT, vacuum technique; ST, suction technique. Numbers indicate calendar weeks during which the sample was taken.

3.2.3. Relevance of PAHs in Urban Leaf Litter for Combustion

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

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

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

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

4. Conclusions

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

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