

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

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

Keywords Bioenergy · IFBB · Roadside verge · Urban biomass · Contamination · Trace elements

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Abbreviations

DM	Dry matter
FM	Fresh matter
ICP-	Inductively coupled plasma optical emission
OES	spectrometry
IFBB	Integrated generation of solid fuel and biogas from biomass
MF	Mass flow
PF	Press fluid
PC	Press cake
RR	Relative reduction
VS	Volatile solids

Introduction

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

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

Next to these technical challenges, municipalities worry about the concentration of contaminants and the unclear legal consequences. A major reason is that, in many European countries, urban grass cuttings are classified as waste, which puts any usage of this biomass into the difficult legal context of the Waste Framework Directive 2008/98/EC, which defines end-of-waste criteria. The outcome of an ongoing discussion in European politics will specify these criteria for biodegradable waste to support waste managers to adhere to the waste hierarchy and ensure that substances are more likely to be put to a useful purpose and are less likely to be disposed (The Commission of the European communities 2014). Once established, these criteria will help to prevent negative effects on environment and human health, which, for example, can arise from inorganic contaminants.

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

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

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

Thus, the aim of this study was to answer the following questions:

- i. What is the elemental composition of grass from roadside verges in a typical German city?
- ii. Is the elemental composition differing between two- and four-cut management and between cut numbers and is it depending on soil element concentration?
- iii. Is the elemental composition of roadside grass limiting its utilisation for energy recovery with special regard on inorganic contaminants?

- iv. Which influence has the IFBB technique on the elemental composition?

Materials and methods

Investigation sites and soil characteristics

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

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

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

Plant sampling and processing

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

required biomass was removed from the plots. Ensiling lasted for 6 weeks minimum.

Silage was processed with IFBB technology as described by Hensgen et al. (2011). Hydrothermal conditioning was conducted with a silage/water ratio of 1:4 and a temperature of 40 °C for 15 min. The material was subsequently dewatered with a screw press (type AV, Anhydro Ltd., Kassel, Germany), which had a pitch of 1:6 and a rotation speed of 6 rpm. The resulting solid fraction (PC) was dried at 65 °C for 48 h minimum and afterwards ground in the same procedure as that of the raw plant material.

Laboratory analysis

Analysis of Cl

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

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

where

- V* is the volume of silver nitrate used during titration
C is the normality of silver nitrate
M_w is the atomic weight of chloride
M_s is the sample mass.

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

For the determination of Ca, K, Mg, Na and P, as well as Al, Cd, Cr, Cu, Mn, Pb and Zn, plant samples were pre-treated by open microwave. Dried plant material (0.25 g) was transferred to a plastic microwave digestion vessel. HNO₃ (3.5 ml) and H₂O₂ (3.5 ml) were added successively under a fume hood, and the mixture was allowed to react at room temperature overnight (minimum 12 h) before microwave digestion. Next,

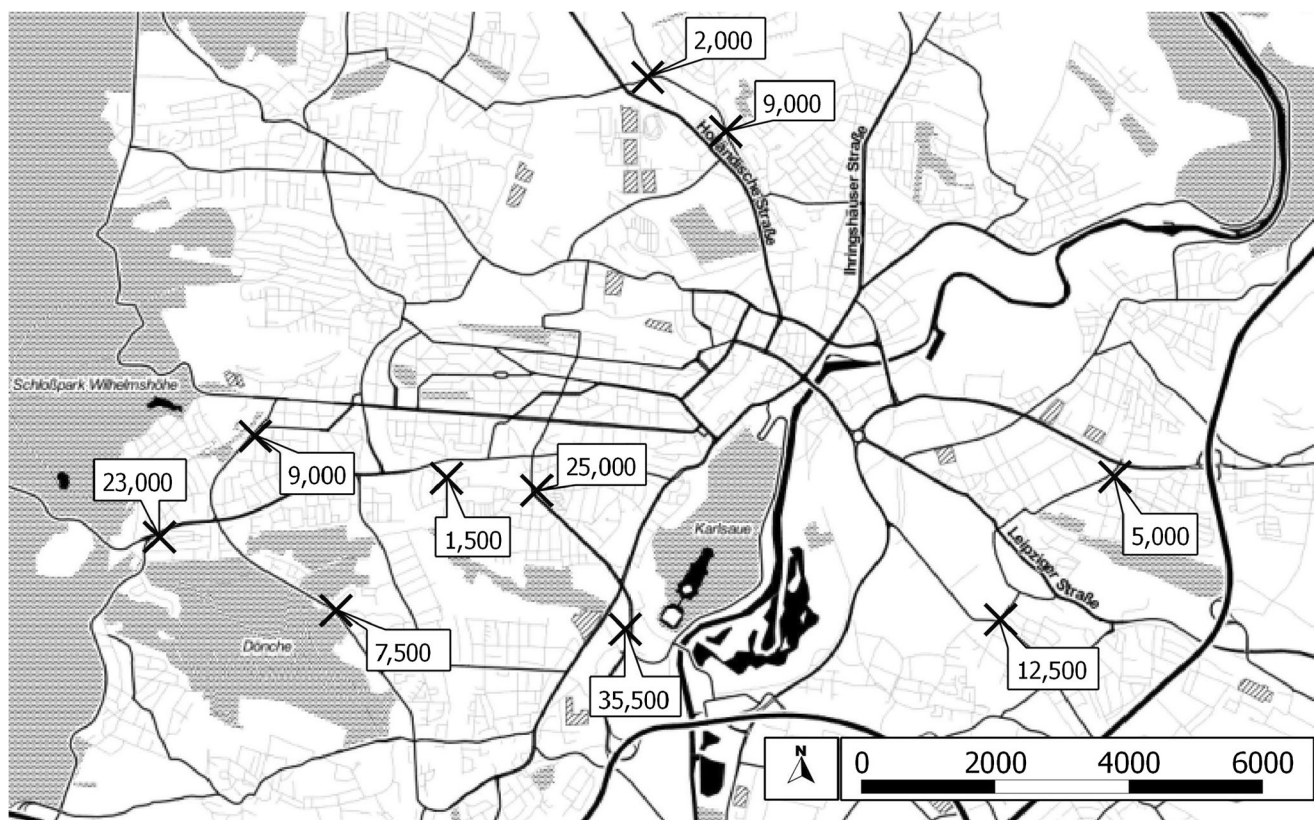


Fig. 1 Locations of the 10 investigation sites within the city of Kassel. Traffic density (cars working day⁻¹) is stated according to the traffic model of the city administration of Kassel, which is calibrated with

traffic censuses. Scale is given in meter. Underlying map: OpenStreetMap contributors (<http://www.openstreetmap.de>)

the samples were diluted until 25 ml and filtered on an acid-resistant filter into a 50-ml volumetric flask. The filtrate (open microwave extract) was analysed for Ca, Mg, Na and K, as well as for Al, Cd, Cr, Cu, Mn, Pb and Zn with inductively

coupled plasma–optical emission spectrometry (ICP-OES: Varian vista MPX, Varian, Palo Alto, CA, USA). For analysis in plant samples, 1 ml of the previously described open microwave extract, 5 ml of water, 1 ml Scheel solution I

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

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

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

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

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

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

Analysis of N, S and Si

N content in soil and plant samples was measured using 150 mg of dried material in an elemental analyser (Vario MAX CHN Elementar Analysensysteme GmbH, Hanau, Germany). S and Si content was measured in plant samples of the two-cut regime only. Samples were prepared with pressure digestion and analysed according to DIN EN ISO 11885 with ICP-OES.

Statistics and calculations

Statistical analyses was conducted with R 2.15.3 (R Core Team 2013) concerning descriptive statistics, and Mann–Whitney *U* test was used to detect differences in element concentrations between regimes and effects of IFBB procedure. For further inferential statistics, SAS 9.2 was applied using the mixed model procedure MIXED due to repeated measurements with harvest dates nested within sites as repeated measures factor. The type of covariance structure was set as AR(1), which is commonly used for low numbers of equally spaced observations, as it assumes the same correlation for all pairs of observation (Littell et al. 2006). REML method was used to estimate the covariance parameters and standard errors, and *F*-statistics of the covariance model was corrected by Satterthwaite approximation. Differences in element concentrations between single harvests within a regime (four- or two-cut) were

calculated using differences of least-square means taking the covariance structure of data into account. Due to Satterthwaite approximation, denominator degrees of freedom are variable, and thus, the conservative studentised maximum modulus method was used to adjust least-square means statistics (SAS Institute 2015).

Relative reduction of elements due to dewatering was calculated as

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

where x is measured element.

Massflow was calculated as

$$MF = \frac{\text{Percentage of DM}_{\text{presscake in mash}} \times \text{DM}_{\text{presscake}} \times \text{Content}_x \text{ in presscake}}{\text{DM}_{\text{mash}} \times \text{Content}_x \text{ in silage}}$$

where x is the measured element.

Results and discussion

Element concentrations compared to reference and limiting values

The concentrations of Ca and P in grass cut in two- or four-cut-regime and of Mg in four-cut regime were higher than in agricultural or conservation grassland (Table 3). However, concentrations were within ranges that were observed in other herbaceous material from roadside verges. There are no limiting values in German legislation for the concentration of those elements; nevertheless, according to the non-industrial standard DIN EN 14961-6:2012 for pellets from non-woody material class B, a total ash concentration of 10 % is limiting (DIN Deutsches Institut für Normung e. V. 2012). This value was met by the measured ash contents. However, in other studies, higher ash contents were detected (Hartmann 2009; Delafield 2006), likely due to the harvesting technique, which highly influences the amount of collected soil particles (Heckman and Kluchinski 1996, for leaf litter). P and N concentrations differed between the two- and the four-cut regime with higher concentrations in the four-cut regime (Table 4). This might be because the material of the four-cut management is less mature in general and, thus, does contain less carbohydrates, whereas minerals, crude protein and crude fat have a relatively higher portion (Prochnow et al. 2009b). N and K concentrations in both cutting regimes exceeded the agricultural reference values and partly those values found in grass from road-side verges. High K values may refer to the extraordinary dry weather conditions of the summer 2013 (precipitation from June to August was about 48 % lower than the last decade’s average value; Deutscher Wetterdienst 2014). This complies with results of Iannucci et al. (2002), who found increased K concentrations in drought-stressed *Trifolium* species. The N concentration in material from the four-cut regime missed the limiting value of the DIN (2 %

narrowly. High N concentrations with values >2 % in urban grass samples are common, as lawns are known to function as N sink (Raciti et al. 2008). During combustion, N can form NOx emissions, which are not desirable regarding climate protection and human health. However, existing technique can reduce NOx emissions: Prochnow et al. (2009a) and Obernberger et al. (2006) list among others steam air recirculation, appropriate air and fuel staging, as well as advanced air supply systems and boiler geometry as appropriate measures. The S concentration measured in this study was lower than the reference values and met exactly the DIN limiting value. For Na, Al, Mn and Si, the prevailing norms give no limiting values, but measured concentrations fell within the range of or in case of Na below the reference values from agricultural or conservation grass, and for Na and Mn also in the range of grass from roadside verges as reported in the literature. Concentrations of Cl are known to be high in herbaceous material (Obernberger et al. 2006). We measured concentrations of about 5 g kg⁻¹, which met the reference values but highly exceeded the limiting value of the prevailing DIN. Obernberger et al. (2006) give a guiding concentration of 1 g kg⁻¹ for an unproblematic combustion. To achieve proper Cl concentrations, a pre-combustion treatment would be necessary (e.g. leaching, Tonn et al. 2011; washing and fractionating, King et al. 2012; IFBB processing, Bühle et al. 2012). Concentrations of Cd and Pb were below the detection limits of 0.4 and 4 mg kg⁻¹, respectively, in 99 % of samples and, thus, below the limiting value of the DIN and the legal limiting value for fertilisers (Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz 2012). Concentrations of Cr, Cu and Zn fell within the range of the reference values and are far from exceeding the limiting values. In summary, biomass from roadside verges from the city of Kassel had a very similar elemental composition in comparison to agricultural or conservation grass. Especially, concerns about

Table 3 Element concentrations (conc.) in biomass harvested on roadside verges in the city of Kassel (Germany)

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

Shown are mean values for the two- and the four-cut regime. Literature values from agricultural or conservation grassland, as well as from grass of roadside verges are given for comparison. Limiting values are presented if applicable

– not determined or available

^aYield weighted mean

^bHartmann (2009)

^cObernberger et al. (2006), grass in general

^dKabata-Pendias (2011), preferable values refer to Germany or similar climate

^eDelafield (2006), values measured in Wales

^fBryson and Barker (2002), values measured in Massachusetts

^gGarcia and Millán (1998), values measured in Spain

^hModlingerová et al. (2012), values measured in *Achillea millefolium* in Czech Republic

ⁱSeling and Fischer (2003)

^jDIN Deutsches Institut für Normung e. V. (2012)

^kBundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz (2012), legislation about fertilising

^lBundesministerium für Umwelt, Naturschutz und Reaktorsicherheit (2012), legislation about using bio-waste on agricultural soil

inorganic contaminants were found not to be valid. In contrast, the inorganic contamination was low in general. This is confirmed by results of Seling and Fischer

(2003), who came to the same conclusion when investigating contaminants in grass cut from roadside verges for compost purpose.

Differences between cuts

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

Effect of the IFBB procedure

The IFBB treatment reduced the content of most elements and total ash. Especially, the high Cl and K concentrations, which are particularly detrimental to combustion processes (Oberberger et al. 2006), could be significantly reduced by more than 80 % on average (Fig. 3, Table 4). To a lesser extent, concentrations of Ca, Mg, Na, N, P and Zn were reduced with mass flows between 19 and 53 % into the PC. These results are similar compared with values achieved with

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

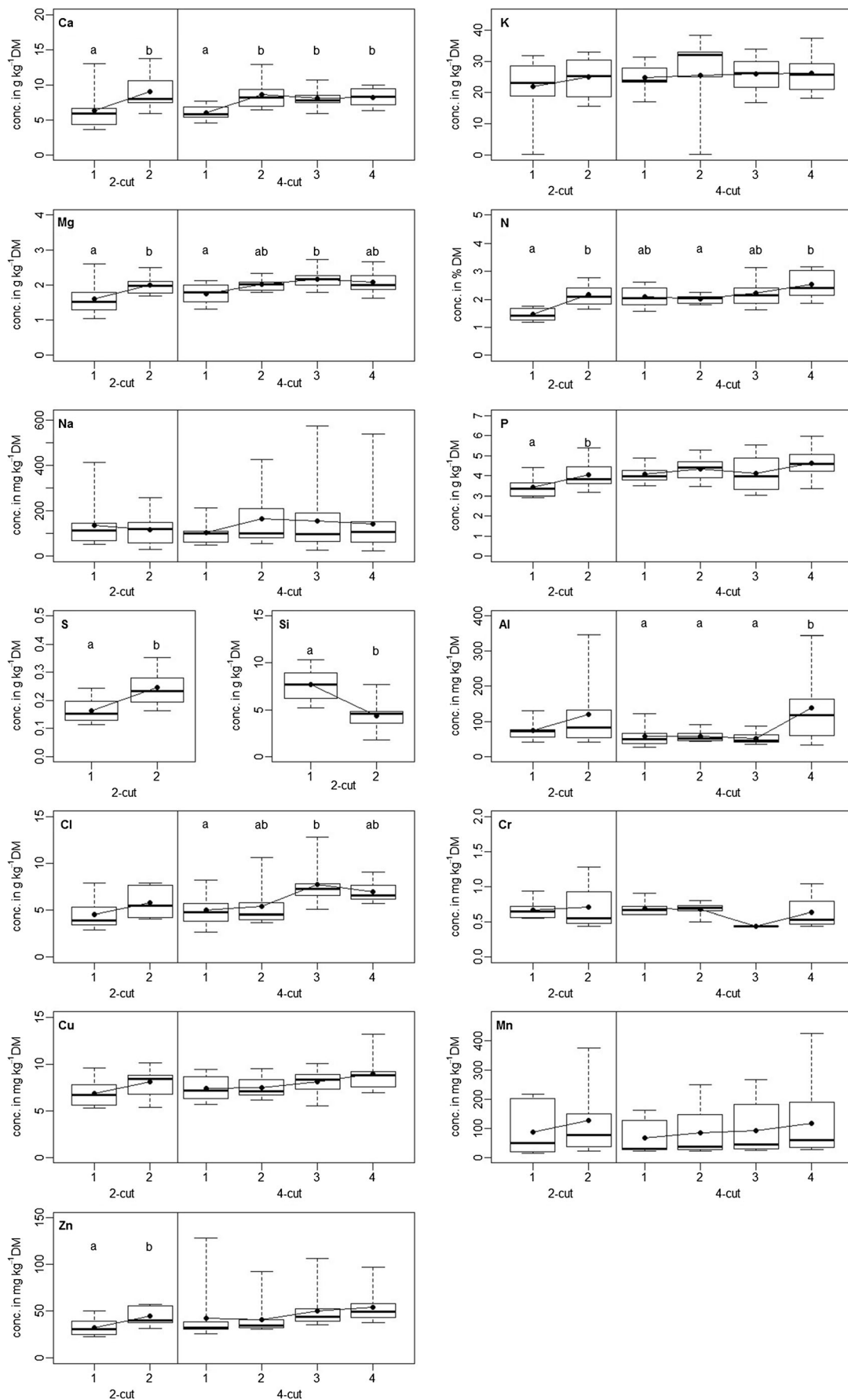
material from semi-natural grasslands (Hensgen et al. 2012), though the element mass flow into the PC was slightly lower in our study for most elements but S. The concentrations of Mn decreased in the PC, but the reduction was not statistically significant, while the concentration of Al did not change by the treatment and Cu and Cr contents even increased. This is probably due to the fact, that we used standard machinery configurations of stainless steel both during mashing and dewatering, which is hardened with Cr and may contain other metals as well. In the operating procedure, abrasion takes place and may increase the concentration of single elements in comparison to the silage. Although we used Cr- and Cu-enriched materials, the limiting values of the DIN were matched in the PC (Table 3).

As organic components escape in gaseous form during combustion, elements are concentrated in the remaining ashes. Cd, Pb and Zn are particularly volatile causing highest concentrations in the fine fly ash fraction compared to bottom or coarse fly ash: 35–65 % of total Cd and 35–55 % of total Zn can be found in this fraction, which has to be disposed. Bottom ash, in contrast, is rich in minerals and least volatile trace elements (e. g. Cr) (Oberberger and Supancic 2009).

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

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

ns not significant, – not determined



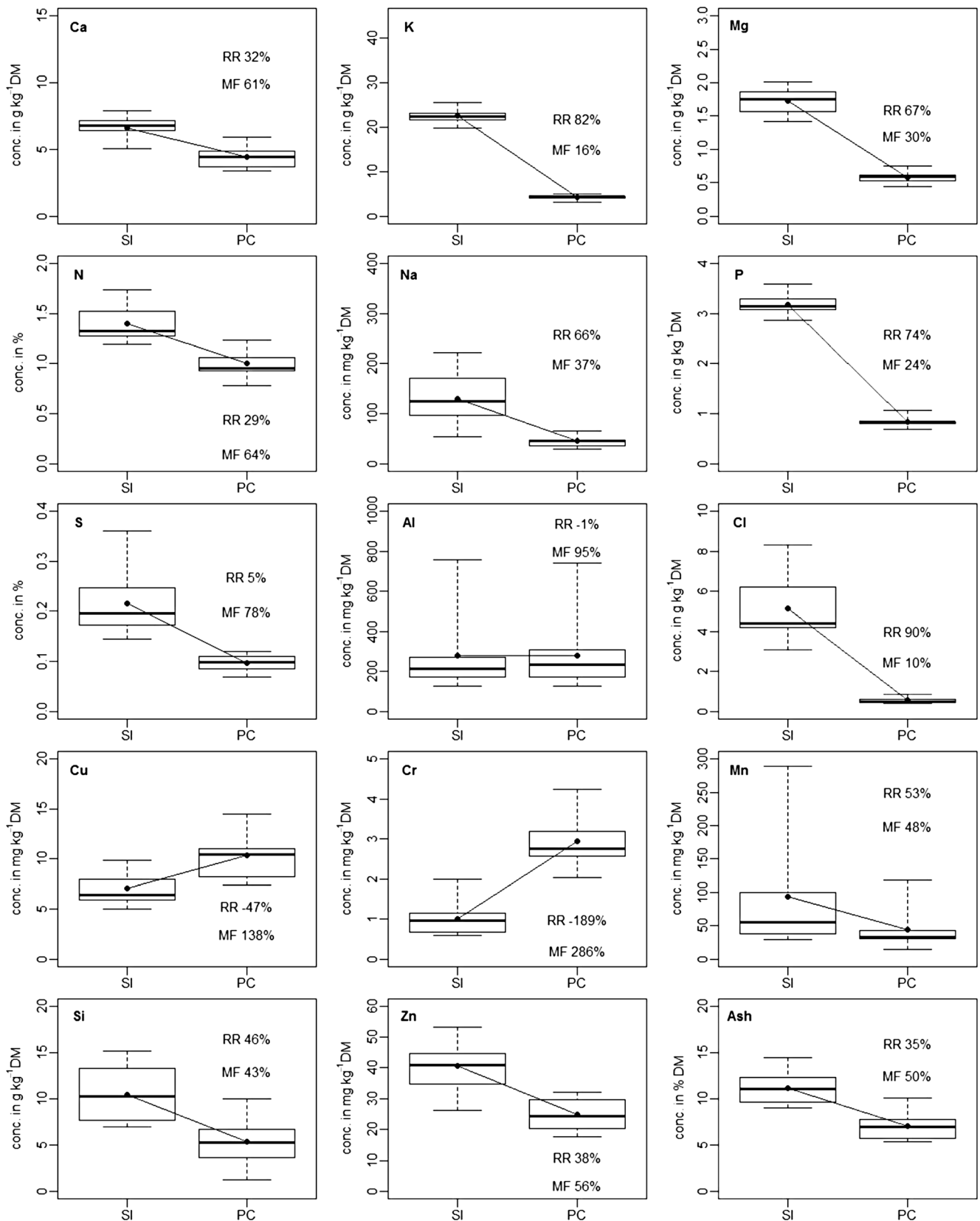


Fig. 3 Element concentrations in silage (SI) and IFBB press cake (PC) produced from biomass harvested on roadside verges in the city of Kassel (Germany). Dots indicate arithmetic means, line in the box indicates

median and whiskers give minimum and maximum values. RR refers to the relative reduction of element concentration through the IFBB process, and MF indicates the actual mass flow of elements into the PC

Although the IFBB process enriched the solid fuel with Cu and Cr, concentrations in the PC were in the range of the agricultural reference values for untreated grass. Corresponding to the decrease in Ca, Mg, Na, N, P and Zn concentrations in the PC, concentrations of these elements increased in the dry matter of PF. During anaerobic digestion of PF, concentrations may further increase due to the conversion of organic matter into biogas. For the PF in this study, we calculated an increase in Zn concentration from 138 to 351 mg kg⁻¹ DM, which is well below the limiting value of the German bio-waste regulation.

Relations to soil element concentration

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

Challenges in urban environments

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

Conclusions

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

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