NEW INDEXES FOR THE CONTAMINATION OF WOOD CHIPS WITH MINERAL SOIL

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ABSTRACT: Critical elements such as chloride (Cl), potassium (K), silicon (Si) or heavy metals might determine high temperature corrosion, emission behavior and slagging of solid biofuels during combustion. Using the fact that plant material contains distinctly less iron (Fe) than mineral soils and vice versa manganese (Mn) in plant tissue is significant higher than in soil material and that the Al-content of plant biomass is limited, indexes could be created to classify wood chips into "contaminated with soil" and uncontaminated "biomass" by building ratios of Fe/Mn and Al/200 Thus, "biomass fuel indexes for the contamination with mineral soil" (BFICS) were developed. Plausibility checks were carried out, using tree biomass of various species und soil datasets from other research projects. They showed that for *Pinus sylvestris* an adapted Al-index is necessary. 2.7 % of the tree samples, *Pinus sylvestris* excluded, exceed the threshold value of 1 for the Fe/Mn-index and only 3.3 % exceed 1 for Al/200. The newly developed BFICS are useful to determine the source of critical elements for combustion, for aerosol formation, to detect high shares of non-combustible material and to prove the effectivity of pre-treatments like screening.
Keywords: wood chip quality, chemical elements, fuel contamination indexes

1 INTRODUCTION

Fuel quality of wood chips is critical for failure-free combustion. Wood chips might become contaminated with mineral soil during production processes. Thus, fuels could be enriched in combustion critical elements. Especially small scale furnaces < 100 kW require homogeneous and high quality fuels to avoid boiler disturbances such as clogging of screw conveyors or slagging but also to minimize gaseous and particular emissions. Critical elements such as chloride (Cl), potassium (K), silicon (Si) or heavy metals such as zinc (Zn) or lead (Pb) might determine combustion risks such as high temperature corrosion, emission behavior and slagging in furnaces using solid biofuels. The source of a high concentration of these elements in fuels is not always obvious. For instance, they may derive from green biomass such as leaves and needles or result from contamination by other sources such as soil material. Soils, for example, contain high amounts of Si and K. The shares of soil material in biofuels can be high depending on the origin of the raw material. For instance, material from cuttings along roadside, urban forestry or gardening may include root stock and therefore also a substantial quantity of soil material.

For small boilers, international standards such as ISO 17225-4 [1] for graded wood chips define fuel specifications that include threshold values for some critical elements (N, Cl, S and selected heavy metals) while other elements such as K or Na are usually not limited. However, there is usually no evidence where these elements come from. If the come from the soil a careful production process or a pre-treatment before combustion can help to reduce the contamination and the negative effects. To improve quality assurance during wood chip production, good indicators are required to determine the source of high concentrations of critical elements. Therefore two contaminations indexes were developed.

2 MATERIALS & METHODS

2.1 Raw materials

In total, 97 samples of wood chips (n = 80), of unchipped material (n = 11) and of twigs and needles (n = 6) were collected. Samples derived from forest residues and "energy round wood" (i. e. small-sized delimbed stem wood) of different tree species, from short rotation coppice (SRC), from cuttings along roadsides and from urban forestry.

2.2 Chemical analyses of wood chips

All wood chip samples were analyzed for elemental composition (As, Ca, Cd, Cr, Cu, K, Mg, N, Na, Ni, Pb, S, Si, Zn) based on European standards [2], [3]. Analysis of N was done according to EN 15104 [2] using an elementary analyzer. For all other elements, samples were analyzed according to EN 15290 [3]. To ensure whole sample digestion including mineral soils and waste, HF digestion was used for both major and minor elements. In addition, Cl was analyzed using X-ray fluorescence analysis (XRF) and Hg was analyzed using a mercury analyzer.

2.3 Contamination indexes

The newly developed indexes utilize the fact that plant biomass contains distinctly less iron (Fe) than mineral soils. Vice versa manganese (Mn) in plant tissue is significant higher than in mineral soil material. Therefore the Fe/Mn-ratio can be used to distinguish between biomass and soil material. In addition, the Al-content can be used to separate biomass from soils. The aluminum (Al) content of soils is about 7 %. Plant material normally contains 0.02 % Al [4]. Using element concentrations in plants and soils from literature and own investigations, biomass fuel indexes for the contamination (BFICS) with mineral soil (Fe/Mn-ratio, Al/200-ratio) were developed.

2.4 Plausibility checks

The new indexes were tested using datasets (n = 5296) from several research projects, i. e. rock and soil data from the periodic soil status report in Bavaria (BZE)

[6] (*n* = 2648), data from Göttlein & Weis (2011) (*n* = 354)[7] and the geochemical atlas of Bavaria (*n* = 88) [8]. The data for biomass samples of various tree species (*Picea abies, Fagus sylvatica*, *Quercus* spp., *Pinus sylvestris*, *Fraxinus excelsior*, *Pseudotsuga menziesii*, *Carpinus betulus)*, also derived from BZE [6] (*n* = 762) and Göttlein & Weis[7] (*n* = 1443). Göttlein & Weis (2011)[7] harvested the biomass by cutting down whole trees. Thereby, contamination of samples with mineral soil is possible. At BZE [6] leaves and needles were sampled by tree climbers or helicopter. Thus, contamination of these samples with mineral soil was not possible. For Biomass samples in these studies, digestion with HNO_3 was used for Soil samples digestion with HNO_3 or HF was used.. Elements were analyzed with ICP and ICP-OES.

3 RESULTS & DISCUSSION

3.1 Fuel indexes for soil contamination

Element concentrations of wood chips indicated a contamination of some samples with mineral soil as concentrations of Si and ash sometimes exceeded typical values for forest residues (see rectangle in Figure 1) with high ash contents of up to 18 w-%. The data also showed that for ash contents above 3.5 w-% Si-concentrations rapidly increased, as well. High Si-concentrations indicate contamination of samples with mineral soil to be the source of the high ash contents.

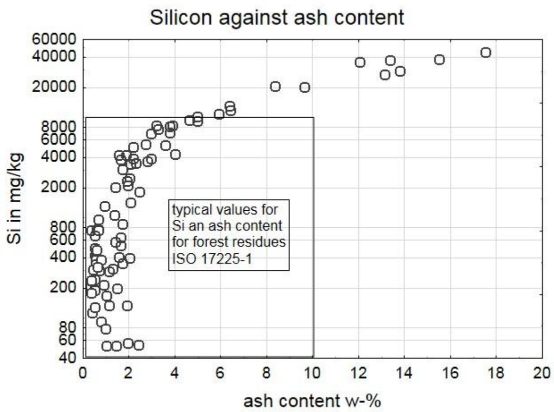

Figure 1: Silicon concentration (Si) in relation to ash content of wood chip samples (*n* = 97). The rectangle shows typical values for forest residues according to ISO 17225-1.

Considering different Fe- und Mn–concentrations in soil and biomass, Mn was plotted against Fe (Figure 2) allowing for the distinction of two different groups of samples. High Fe-contents indicate that samples belong to the group with high soil contamination. On the other hand, high Mn-contents indicate biomass samples without soil contamination. The Fe/Mn-ratio was calculated for all samples. Samples with ratios < 1 were assigned to pure biomass, samples with ratios > 1 were considered to be contaminated with mineral soil. To confirm this classification, a second index was developed. Strong differences in Al-concentration of plants and soils were used as the second biomass fuel index for contamination with soil (BFICS). Average Al-concentration in plants is about 0.02 w-%. High Al-amounts are usually toxic to plant metabolism [9]. However, there are some plant species who can tolerate higher Al-concentrations. Such Al-accumulators are an adaption [10] to high Al-content in soils for example in tropical areas. They can accumulate up to 3 w-% Al in leave tissue. Some pine species such as *Pinus nigra* [10] are also known for being Al-accumulators (up to 1 w-% Al). Data from BZE [6] and Fiedler & Rösler [11] showed Al-concentrations in needles (*Pinus sylvestris*) as high as 0.06–0.07 w-% (average 0.03–0.033). Therefore, two Al-coefficients, i. e. Al/200 and Al/400 were tested and the resulting distribution of the samples to the two groups “biomass” and “contamination with soil” was compared to the classification by the Fe/Mn-index (Figure 3). The best compliance of both indices was regarded to be suitable for the classification of contamination groups.

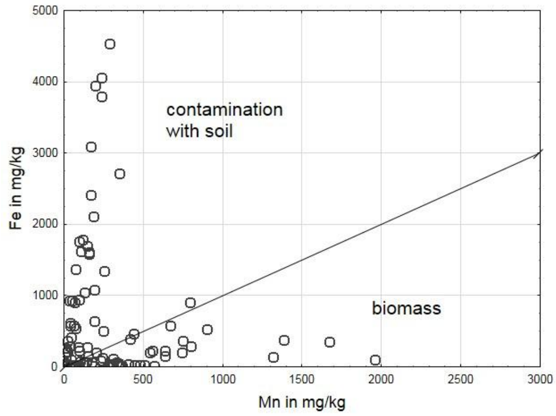

Figure 2: Fe concentration in relation to Mn concentration in wood chip samples. The dataset indicates two groups. Classification of samples as “biomass” and “contamination with soil” is given by the balance line.

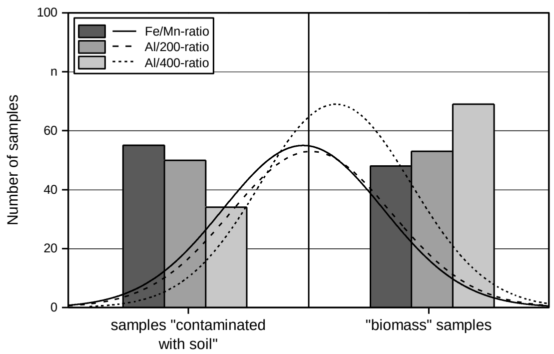

Figure 3: Number of samples classified as “contaminated with soil” and “biomass” and distribution of data according to the developed indices.

3.2 Plausibility checks

Using data from previous research projects (*n* = 5296) in Bavaria, plausibility checks of the developed fuel indexes were performed. (Figure 4).

The biomass fuel indexes for the contamination with soil (BFICS) divide tree biomass and soil material into two significantly different groups (Figure 4). Only 2.7 % of the tree samples exceed the threshold value of 1 for the Fe/Mn-index and only 3.3 % exceed 1 for Al/200.

Biomass samples exceeding the limit of the Fe/Mn-index originated mostly from projects in which samples were collected by cutting trees down[7]. This way, contamination of samples with soil material might occur, explaining most of the Fe/Mn-indexes > 1. However, the newly developed biomass fuel indexes for contamination with soil (BFICS) can be generally used to distinguish between biomass and soil material for most tree species. Only for samples from *Pinus sylvestris*, fuel indexes might not be suitable as pine needles already display high Al-concentrations, resulting in Al/200 indices > 1.

In total, 63 % of these samples exceeding the threshold value of 1 (Al/200), while only 3.2 % exceed the Fe/Mn-index threshold (Figure 5).

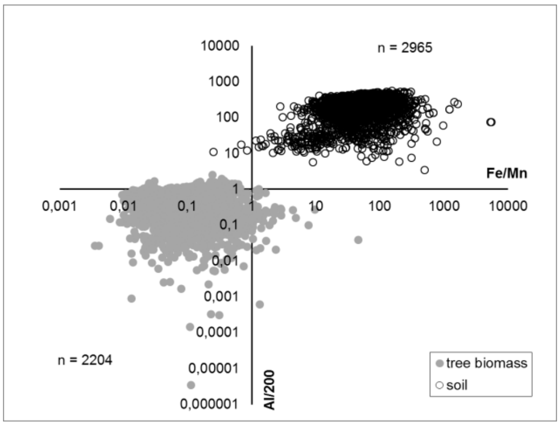

Figure 4: Fe/Mn-ratio and Al/200-ratio of tree biomass samples (*n* = 2204) excluding *Pinus sylvestris*) [6],[7] and soil material (*n* = 2965) incl. humus layers (*n* = 34) [6],[7].

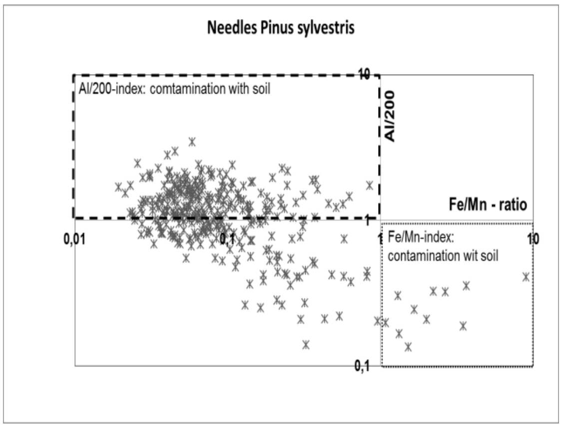

Figure 5: Fe/Mn-ratio and Al/200-ratio for needles of *Pinus sylvestris*. Many samples are located in the areas typical for soil material (see rectangles).

3.3 Theoretical limits of the indices

Wood chips with soil material of 10 w-% can be classified as “contaminated” (Fe/Mn-index > 1) if the Fe/Mn-ratio of the soil material is ≥ 2 and of the pure tree biomass < 0.9. Wood chips with soil material of 2 w-% require soil material with an Fe/Mn-ratio of ≥ 7 and for pure tree biomass of < 0.9, thus soil material can be detected. Overall, 96 % of the soil samples (n = 3087) have Fe/Mn–ratios above this level. The Al/200-index is even more useful for the investigated samples. If wood chips contain 2 w-% soil material, this contamination can easily be detected using the Al/200 index as 99,7 % of the soil samples have Al/200-ratios > 7. Wood chips with 10 w-% soil material could always be detected by the index as all soil samples have Al/200 ratios > 2.

3.4 Scopes of application for contamination indices

The presented study [4] showed that in some cases up to 10 w-% dry weight of individual wood chip samples derives from contamination with mineral soil material. This may lead to problems during combustion. Moreover, contamination with mineral soil can increase transport costs. In Bavaria, container trucks with a payload of around 20 t (approx. 10 t dry weight) are common in wood chip transportation. In the worst case, 10 w-% of mineral soil stand for 2 t of the payload.Biomass fuel indexes for contamination with soil (BFICS) can be used to detect high shares of non-combustible material and to prove the effectivity of pre-treatments like screening. Correlations show that “biomass” has only ash contents up to 3.1 w-%, whereas samples classified as “contaminated” with soil reach values up to 19.6 w-% (Figure 6). In addition the correlation of ash to Si (see Poster 2.BV.1.4), shows that high ash contents are presumably caused by mineral soil material. Hence pre-treatments such as screening to separate soil material from samples might help to reduce ash formation. Moreover, the newly developed fuel indexes might help to determine the source of critical elements for combustion such as critical elements for aerosol formation (K, Na and heavy metals like Pb and Zn). The correlation between aerosol forming elements and ash content in wood chips classified as “biomass” is much stronger than in samples classified as “contaminated” (Figure 6). Moreover, ash content in “biomass” shows a significant correlation (r^2=0.90) to the sum of Mg und Ca whereas “contaminated” samples strongly correlate to Si (r^2 = 0.96).

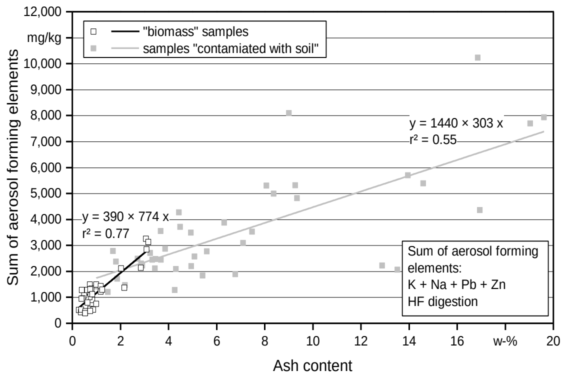

Figure 6: Aerosol forming elements (sum of K, Na, Pb, Zn) in wood chip samples related to ash content (in w-%) and correlation coefficients for “biomass” and “contaminated” samples.

4 CONCLUSION

Biomass fuel indexes for the contamination with soil (BFICS), i. e. Fe/Mn- and Al/200-indexes, were considered suitable for the evaluation of whether or not a biofuel sample is contaminated with mineral soil. For *Pinus sylvestris* an adapted Al-index should be used.

So far, indexes where tested for biofuels from wood. Applicability for non-woody biofuels has to be tested.

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7 LOGO SPACE

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