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Grain size dependent distribution of contaminants in coarse-shredded commercial waste – results for As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, and Sb

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Abstract 150-250 words

When SRF is used to substitute primary fuels in the cement industry, certain legal and process-related quality criteria that are often expressed as limit values for several chemical elements have to be fulfilled. In order to produce high-quality SRF, the concentrations of these elements need to be monitored and, if necessary, altered. This requires prior knowledge about the fraction the elements are located in, and such fractions can be defined by materials, or by grain size as literature reporting increased concentration in the fine fractions of waste suggests. While more sophisticated techniques are required to remove certain materials, the fine fraction can be removed by screens. The work at hand aims at studying the grain size dependent distribution of several chemical elements more detailed and extensively.

For this purpose, 10 representative samples of a 40-ton pile of mixed commercial waste were taken, screened to generate nine different grain size fractions, and chemically analyzed in the laboratory with respect to 34 elements, 12 of which are discussed in this paper. For As, Ba, Co, Cr, Hg, Mn, Mo, and Ni higher concentrations were found in smaller grain size fractions. Removing the small grain size fractions would theoretically result in a concentration decrease of up to 44 % for single elements, and an increase in LHV and Sb and Cd concentrations. However, depending on the element, screening can represent an appropriate measure in order to decrease the concentrations of contaminants and increase SRF quality.

Keywords

Solid recovered fuel, heavy metals, contaminants, grain size, grain size dependent distribution, sieve analysis

1 Introduction

1.1 The use of SRF and the role of contaminants

In several European countries where the landfilling of untreated waste has been restricted, mixed municipal and commercial wastes are frequently processed to solid recovered fuels (SRF). This SRF can be used to substitute primary fuels in energy-intensive industries such as the cement industry, provided that quality criteria defined by the cement plant operators as well as legal criteria are met [1, 2]. In Austria, the Austrian waste incineration ordinance (WIO) [3] defines legal limit values for arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), and antimony (Sb). In addition, stricter or additional site-specific limit values might be defined by law decrees for single cement plants, or the cement plant operators demand additional limit values or quality characteristics from the SRF producers. Barium (Ba), copper (Cu), manganese (Mn), and molybdenum (Mo) represent some of the elements that can be subject to additional limit values.

It is obvious that previous knowledge about the main fractions containing the chemical elements of interest is required in order to produce high-quality SRF and to assure this quality. Such fractions can be defined by materials, but also by grain size, as suggested by sieving experiments of commercial waste: Adam *et al* [4] observed different distributions of Sb, Cd, Cr, and Ni among different grain sizes. This information is valuable for the production of SRF, as it implies that there might be a possibility for managing contaminant streams and maintaining or improving SRF quality through comparably simple means, such as sieving. For this reason, the work at hand aims at studying the grain size dependent distribution of several chemical elements more detailed and extensively.

1.2 Grain size dependent distribution and accumulation of heavy metals in the fine fraction

Some elements that accumulate in the fine fractions have already been observed in literature as results of sorting analyses. For example, in comparison with the other stated material fractions, high concentrations of Cl were reported in the fine fraction [5] and were linked to the presence of table salt or wood shavings from pressboards. Furthermore, elevated concentrations of Pb [6–9], Hg [8–10], Cr [9], Co [8, 9], and Ni [8, 9, 11, 12] were reported for fine fractions with different grain sizes. Some of these metals, especially Cr, Ni, and Co, but also Pb, are frequently used in metal alloys [13, 14], and high concentrations of these elements seem to occur in the fine fractions together [8, 9], sometimes also in combination with iron (Fe) [8]. This leads to the assumption, that small metal parts could be responsible for the elevated concentrations of these elements that were observed in some publications.

High concentrations of Pb were furthermore reported in ash [15], which could be another possible explanation for elevated Pb concentrations in the fine fraction. Elemental Hg, in contrast, is assumed to attach to materials with a high specific surface area [10], which is probably why elevated levels of Hg are also reported for vacuum cleaner bags [10]. Based on its industrial applications, high Hg concentrations in the fine fraction could also be a result of fluorescent tubes that still end up in mixed waste to some extent, mercury thermometers, or small coin cell batteries (depending on the sample preparation).

1.3 Aim

The aim of this work is to determine the grain size dependent distribution of several chemical elements in mixed commercial waste and to point out possible trends or tendencies. In the present approach variations in and the heterogeneity of the waste stream are accounted for by processing and analyzing a total of ten representative samples. This allows for a better interpretation of the data and considerably increases the confidence in the observed tendencies. Based on the observations, the overall aim is to draw conclusions regarding the removal of these elements in order to improve or maintain a high SRF quality. Although many more chemical elements have been analyzed, the present work focuses on the 12 chemical elements relevant to SRF that were introduced in chapter 1.1.

2 Materials and methods

Approximately 40 metric tons of mixed commercial waste from the area of Graz, Austria, were coarsely shredded using a mobile single-shaft coarse shredder (Terminator 5000 SD with F-type cutting unit) at 18.6 rpm and with a completely closed cutting gap. The shredder was fed using a wheel loader while slowly moving forward, forming a windrow of the material that was discharged via the conveyor belt included in the machine. In time intervals of 30 seconds, a total of 200 sample increments (each of them with a mass of ~12 kg) were taken from the falling waste stream at the end of the conveyor belt using sampling troughs (dimensions: 1.17x0.37x0.30 m). Representative samples were created by combining 20 of the sample increments taken in time intervals of 5 minutes. In total, 10 representative samples, each with a mass of ~ 240 kg, were generated.

The 10 representative samples were subsequently screened with a batch drum screen and – if appropriate – reduced in size to generate 9 grain size fractions: < 5 mm, 5 - 10 mm, 10 - 20 mm, 20 - 40 mm, 40 - 60 mm, 60 - 80 mm, 80 - 100 mm, 100 - 200 mm, 200 - 400 mm. The sampling procedure, sample processing, and calculations are described in detail elsewhere [16]. Every grain size fraction > 20 mm was manually sorted to determine the material composition, and was reunited for chemical analyses.

All 9 grain size fractions of each qualified sample (a total of 90 samples) were chemically analyzed in order to determine the grain size dependent distribution of 34 chemical elements. The samples were dried to constant mass at 105°C, comminuted to a size < 0.5 mm, reduced in mass, and homogenized. Hard impurities (e.g. metals parts) were removed during sample preparation, weighed, and their weight was accounted for when the results were calculated. For this reason, metal parts (unless very small, e.g. abrasions) and other hard impurities were not part of the analysis, which is usually the state of the art in laboratory analyses.

Microwave-assisted acid-digestion (ÖNORM EN 13656) followed by ICP-MS analysis (based on ÖNORM EN 15411 and ÖNORM EN 17294-2) was used to determine the concentrations of lithium (Li), beryllium (Be), sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), strontium (Sr), molybdenum (Mo), palladium (Pd), silver (Ag), cadmium (Cd), tin (Sn), antimony (Sb), tellurium (Te), barium (Ba), tungsten (W), mercury (Hg), thallium (Tl), and lead (Pb). The chlorine (Cl) content was determined by ion chromatography (DIN EN ISO 10304-1) after calorimetric digestion (ÖNORM EN 14582).

3 Results and discussion

3.1 Grain size dependent distribution

To assess the grain size dependent distribution and to identify possible tendencies or trends, the concentrations of the analytes in the nine grain size fractions are plotted as boxplots. For every gain size, the single data points are presented left to the corresponding boxplot. The whiskers of the boxplots represent the range that lies within 1.5 times the interquartile range (IQR) of each boxplot, which is why all data points that are located above the upper or below the lower whisker are considered as outliers.

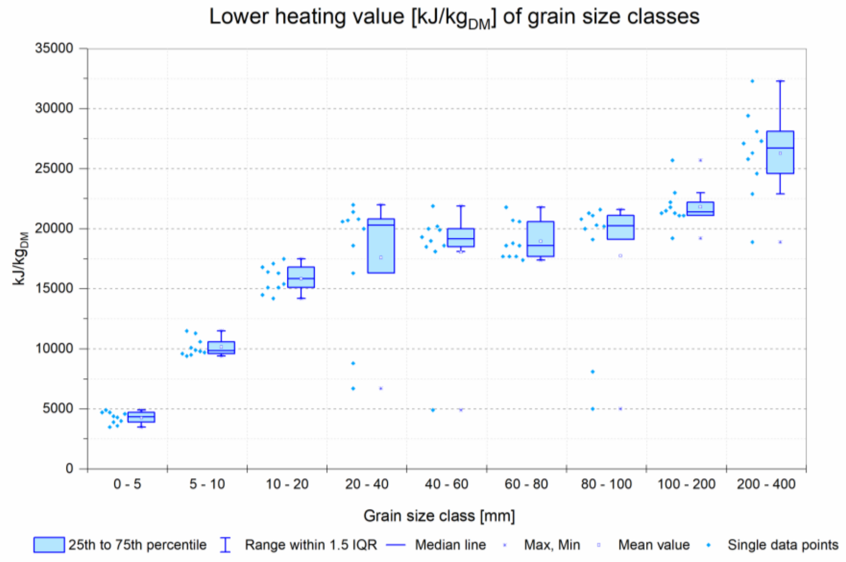

Fig. 1 Lower heating value (LHV) of the generated grain size classes of mixed commercial waste in kJ/kg dry mass

The concentrations of the elements are plotted as mg/kg. Emphasis has to be put on the fact, that limit values for several elements are given in mg/MJ (compare chapter 1.1). Plotting the data in mg/MJ however alters the picture and leads to (even stronger) trends of higher concentrations in smaller grain size fractions, because small grain size fractions feature significantly lower LHVs (Fig. 1). The obtained data show a clear trend for the LHV: it increases with increasing grain sizes and stays rather constant at grain sizes between 20 and 100 mm. However, the focus of the following chapters is to present and discuss analyte concentrations on a mg/kg basis, and specific characteristics of the data when plotted in mg/MJ will only be mentioned briefly.

Three different behaviors were identified for the grain size dependent distribution of analyte concentrations, which is why the results are presented in three groups:

1. analytes for which (sometimes slight) tendencies towards higher concentrations in smaller grain size fractions can be suggested (As, Ba, Co, Cr, Hg, Mn, Mo, and Ni),
2. analytes that are distributed among larger and smaller grain size classes (Cu, Pb),
3. analytes that show a tendency towards increasing concentrations with larger grain sizes (Sb, Cd).

3.1.1 Elements showing higher concentrations in smaller grain size fractions: arsenic (As), barium (Ba), cobalt (Co), chromium (Cr), mercury (Hg), manganese (Mn), molybdenum (Mo), and nickel (Ni)

The highest concentrations for As, Ba, Co, Cr, Hg, Mn, Mo, and Ni were found in the grain size fractions of 0 – 5 mm, often followed by the grain size fraction 5 – 10 mm. Slight and sometimes stronger tendencies of increasing concentrations with decreasing grain sizes are visible (Fig. 2 to 9).

Possible reasons for the high concentrations of some of these elements were briefly discussed in chapter 1.2. In the examined waste stream, high concentrations of Co, Cr, and Ni all occur in the same grain sizes, and the data suggests slight correlations in the grain sizes < 20 mm between Co and Ni ($R^2 = 0.71$), Co and Cr ($R^2 = 0.83$), Cr and Ni ($R^2 = 0.91$), and between Fe and Co, Fe and Ni, and Fe and Cr ($R^2 > 0.7$). Therefore, it is well possible that the increased concentrations are caused by small metal parts, e.g. abrasions from stainless steel, etc. These metal parts were not part of the analysis in larger grain size fractions, as they were removed during sample preparation.

When the data for As, Co, Cr, Hg, and Ni, for which limit values exist in the Austrian WIO, is plot as mg/MJ, it turns out that these limit values are often, and for some elements always exceeded in the analyzed fractions < 5 mm. For this reason, screening can be a possible measure to remove fractions with high concentrations of these elements. However, the masses of these fractions need to be taken into account as well, which is done in chapter 3.3.

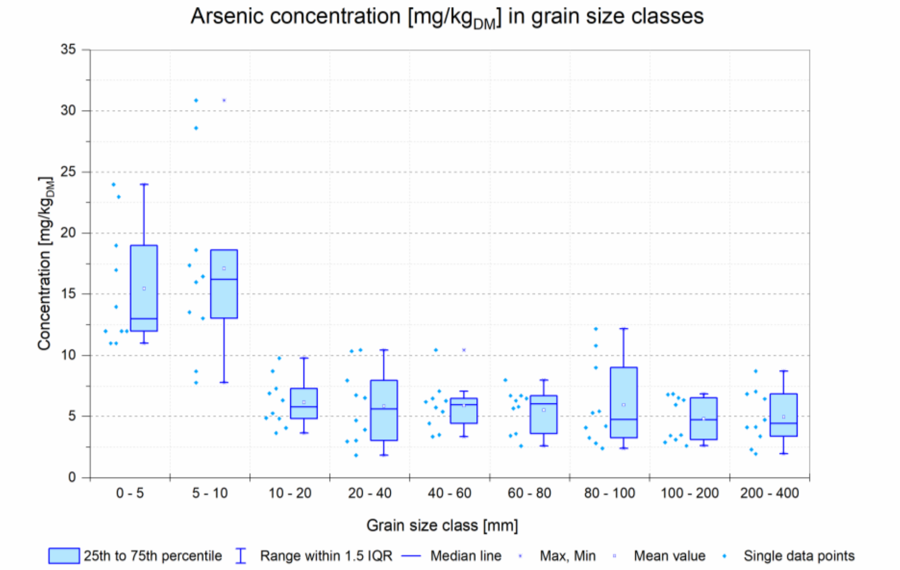

Fig. 2 Arsenic concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

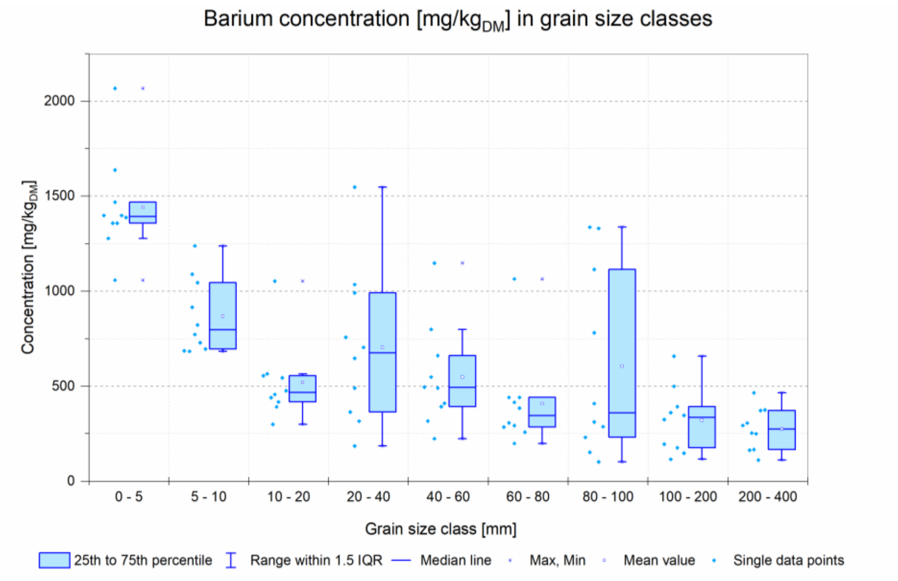

Fig. 3 Barium concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

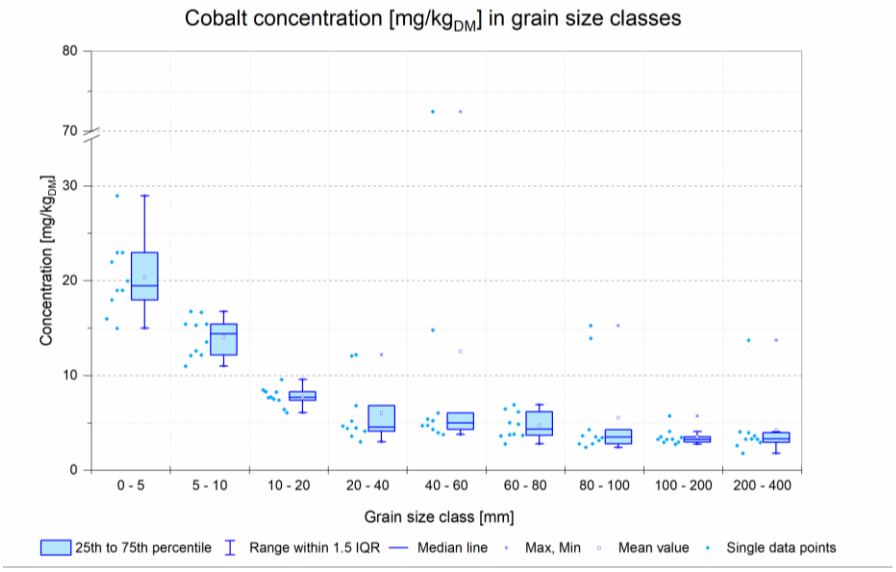

Fig. 4 Cobalt concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

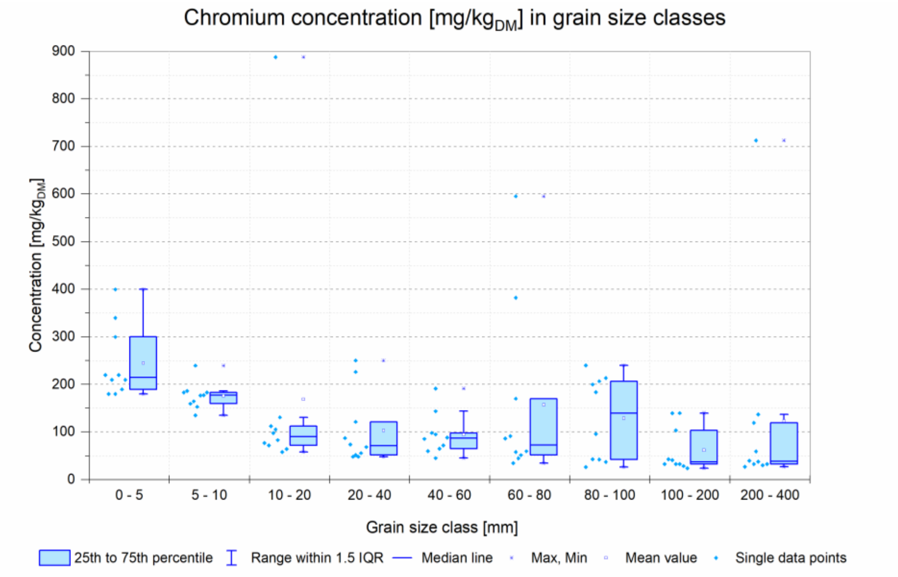

Fig. 5 Chromium concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

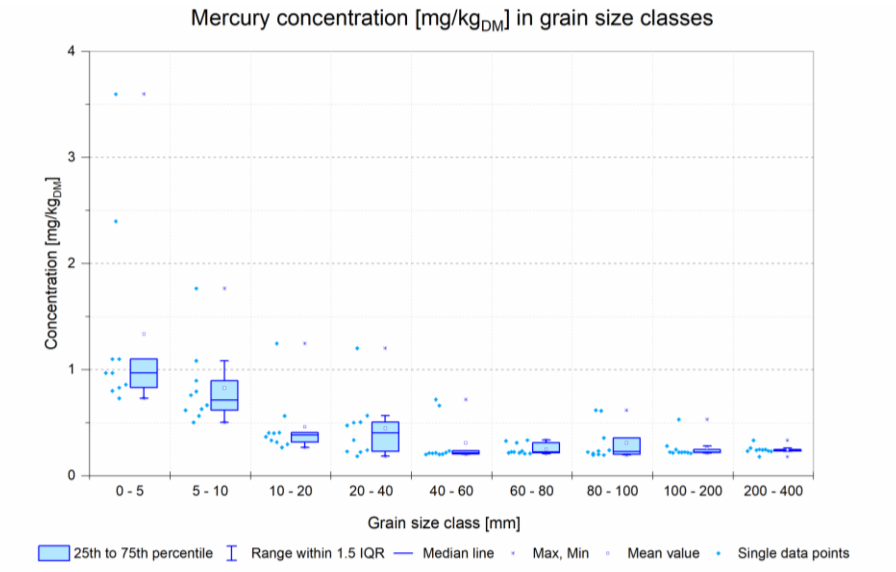

Fig. 6 Mercury concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

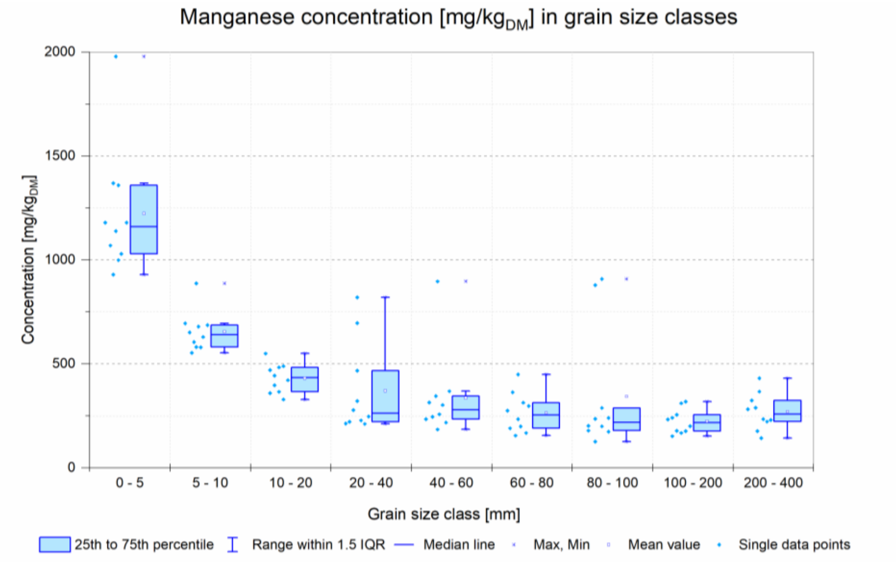

Fig. 7 Manganese concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

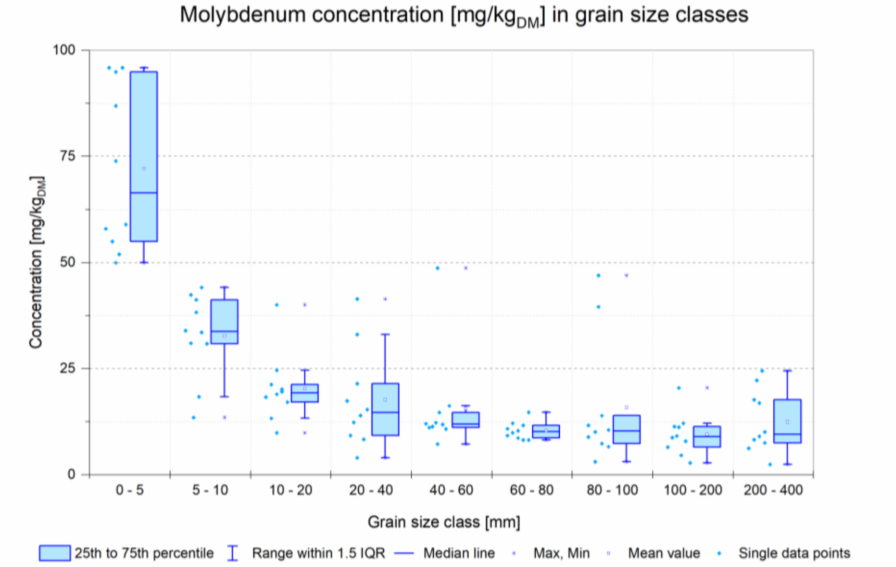

Fig. 8 Molybdenum concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

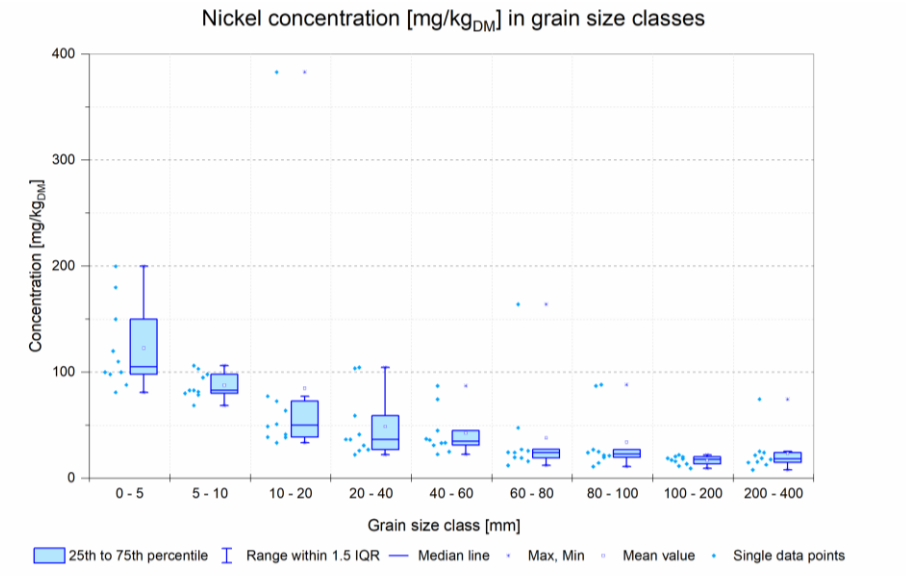

Fig. 9 Nickel concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

3.1.2 Elements distributed throughout different grain size fractions: copper (Cu) and lead (Pb)

For some elements, no grain size dependent distributions can be observed for the examined waste stream. From the elements discussed in this paper, this seems to be the case for Pb (Fig. 10) and Cu (Fig. 11). The highest Pb concentrations are found in the small fractions < 10 mm, but the concentrations are quite variable, and high concentrations were also observed for larger grain size fractions.

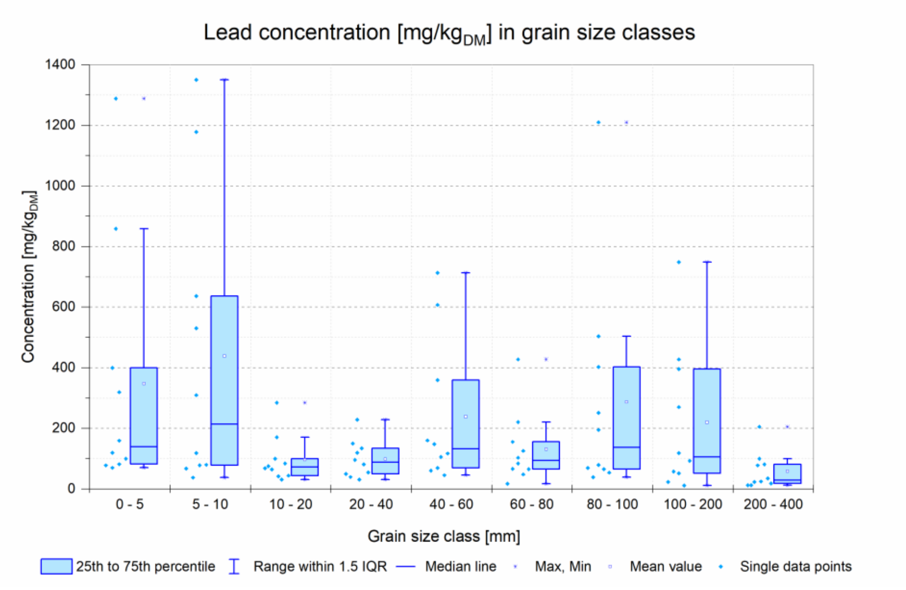

Fig. 10 Lead concentration (in mg/MJ) of different grain size classes of mixed commercial waste

The data for Cu show quite a lot of variation and some outliers with very high concentrations in several grain size fractions. These variations and the comparably large amount of outliers could have been caused by the presence of fine copper wires or filaments from cables, which were not large or hard enough to be removed during sample preparation, or might have been missed.

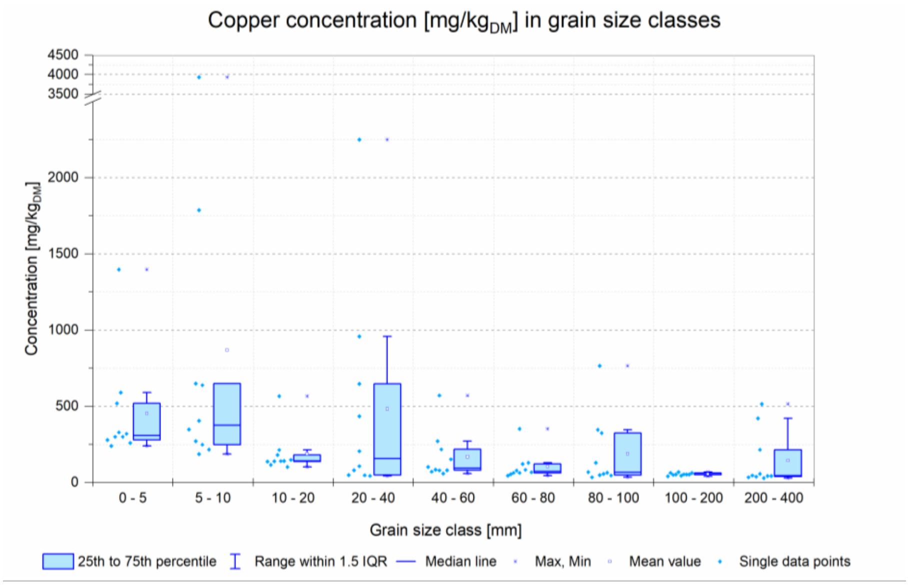

Fig. 11 Copper concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

3.1.3 Elements related to larger grain size fractions: antimony (Sb) and cadmium (Cd)

The third group consists of analytes that are rather related to larger grain sizes. For the elements evaluated in this paper, this is indicated for Sb (Fig. 12) and Cd (Fig. 13), and it can probably be liked to the elements' industrial uses and the flexibility of the materials containing Sb and Cd.

Major uses of Sb comprise the application as a synergist in flame retardants, which are used in plastics, textiles, etc., and the use as a catalyst for the production of polyethylene terephthalate (PET) [17], which is why PET bottles, but also polyester based textiles often contain Sb at concentrations of around 200 - 300 mg/kg [18, 19]. It is likely that major part of these rather flexible materials is not comminuted to very small sizes with just one shredding step and therefore ends up in larger grain size fractions.

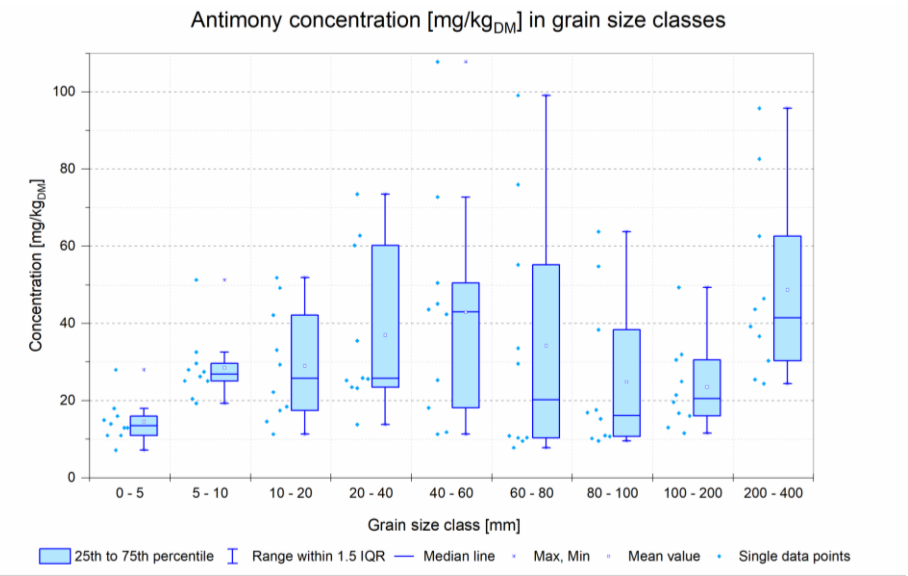

Fig. 12 Antimony concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

Cd is as well often related to plastics, due to its (former) use as a stabilizer or pigment for several polymers [20]. Furthermore, batteries and electronic materials are important cadmium carriers [15], but although it cannot be excluded, it is rather unlikely that these materials affected the analyses as the sample preparation process included the removal of hard impurities before comminuting the samples on a laboratory scale.

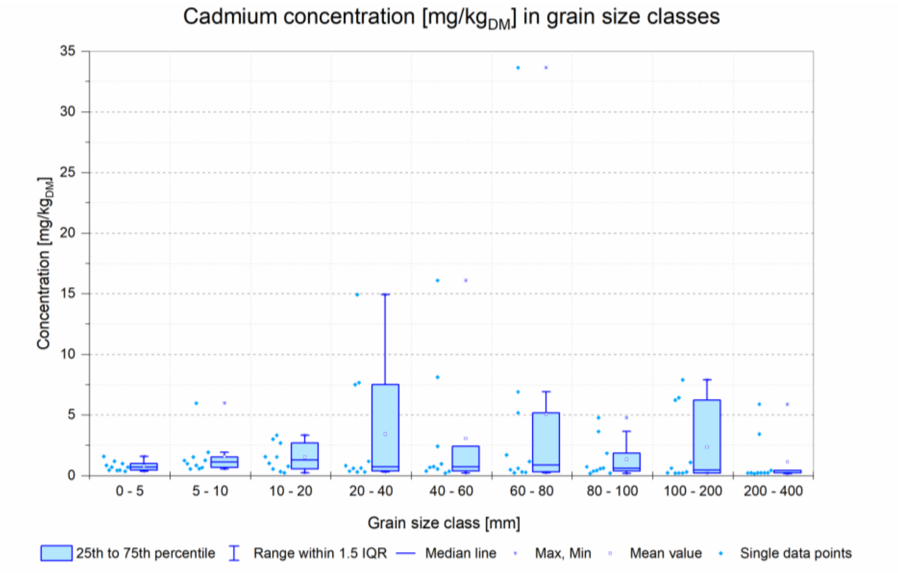

Fig. 13 Cadmium concentration (in mg/kg dry mass) of different grain size classes of mixed commercial waste

3.2 Percentage distribution of the total loads of analytes

Taking the total masses of every grain size fraction into account, the grain size fraction that contributes the highest amount of the analyte can be identified. Fig. 14 depicts the average percentage distribution of the total load of the 12 analytes. Results show that the fine fraction < 5 mm makes the biggest contribution to the total amount of Mo, Mn, Hg, Co, Ni, Ba, As, Cu, and Cr. In the case of Mo, even 48 % of the element is located in the fraction < 5 mm. More than 50% of the total amount of Mo, Mn, Hg, and Co is found in the material < 10 mm.

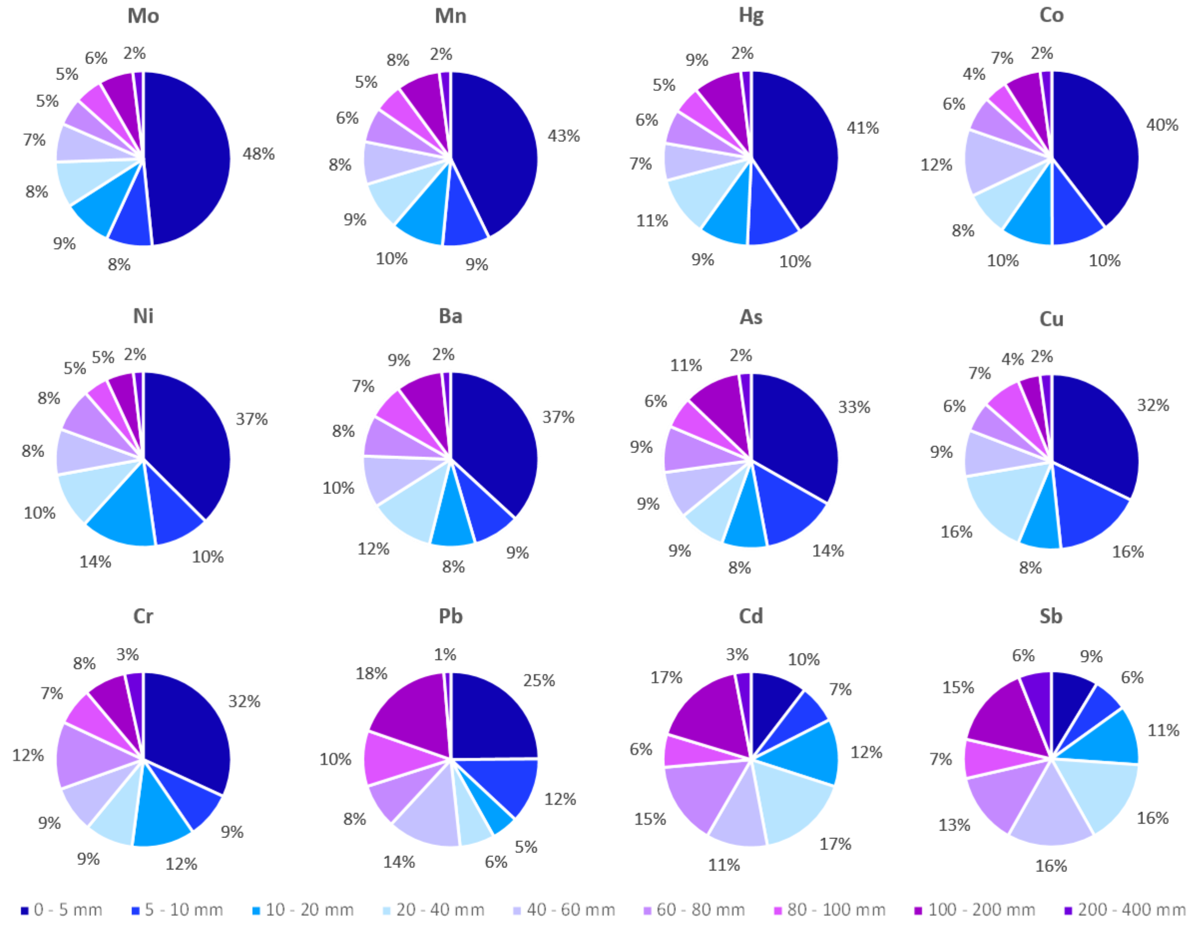

Fig. 14 Average contributions [%] of the different grain size fractions to the total content of Mo, Mn, Hg, Co, Ni, Ba, As, Cu, Cr, Pb, Cd, and Sb

Although the fraction < 5mm also carries the highest load of Pb, this analyte is rather spread among the different grain size fractions, and large amounts are also located in the fraction 100 – 200 mm. The larger grain size fractions also contain significant amounts of Cd and Sb. These observations allow for the conclusion that by screening and removing the screen underflow, the quality of the waste stream can be improved for certain elements.

3.3 Estimating the effect of removing fine fractions

Based on the analytical data, the average effect of screening at 5 mm or 10 mm and removing the underflow material on the element concentrations in mg/kg and mg/MJ can be calculated. The results are presented in Fig. 15, and show the following effects:

- Removing the sieve underflow with a grain size < 5 mm or < 10 mm leads to an increase in LHV [MJ/kg] by 15 – 20 % because the fine fraction with a low LHV is removed.
- The share of mass that is removed by screening is 17.1 % (< 5 mm) or 23.5 % (< 10 mm), respectively.
- The concentrations of Mo, Mn, Hg, Co, Ni, Ba, As, Cu, Cr, and Pb are decreased by 9 to 38 % (removal of grain size fraction < 5 mm), or 18 to 44 % (removal of grain size fractions < 10 mm), respectively.
- At the same time, the concentrations of Cd and Sb increase, because grain size fractions that only contain little amounts of these elements are removed, while the mass of the waste stream is reduced. With respect to the WIO limit values, it has to be mentioned that when the concentrations are calculated as mg/MJ the increase in concentration [mg/kg] is compensated by the increasing heating values.

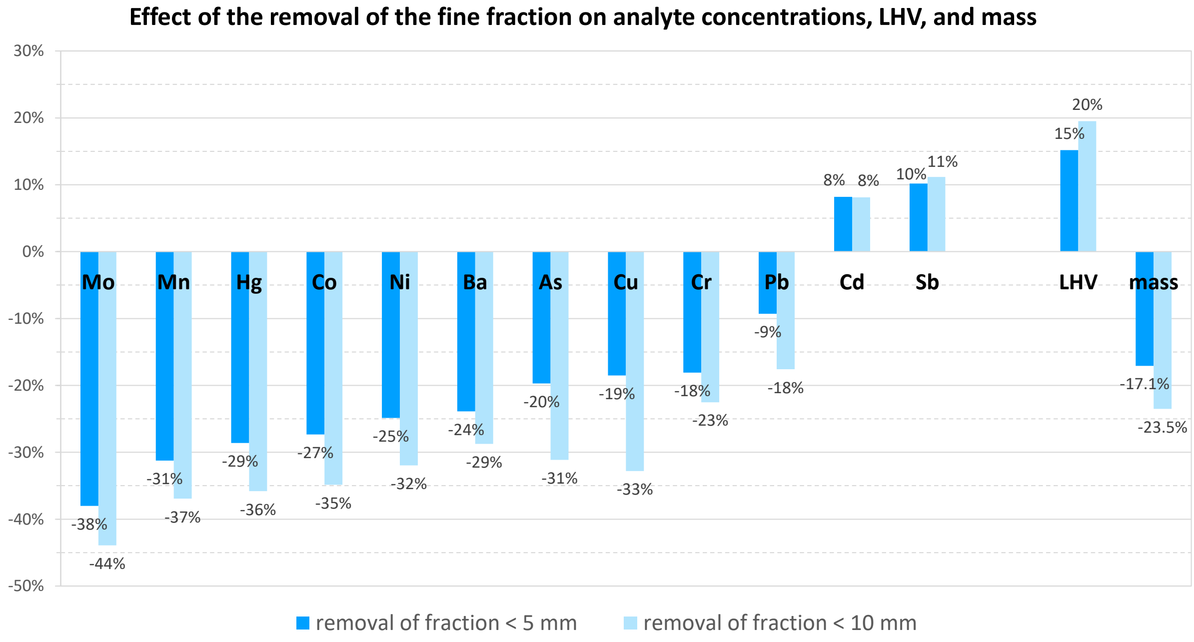

Fig. 15 Average effect of removing the screen underflow < 5 mm and < 10 mm on analyte concentrations, LHV, and total mass of the waste stream. The effect is depicted as the percentage change in mass (referring to kg), LHV (referring to MJ/kg), or analyte concentrations (referring to mg/kg)

It is important to note that while the quality of the screen overflow is improved with respect to heating value and several relevant contaminants, the screen underflow represents a waste fraction with a very low LHV and high contaminant concentrations. The underflow also exceeds many of the limit values defined by the Austrian WIO for the use in cement plants. For this reason, treatment pathways for this fractions have to be discussed if such a fraction is removed from the waste stream (note: waste incineration is legally and technically a possible option). As a consequence, screening at larger sizes could also be beneficial, as this might offer the possibility to produce two fractions with different qualities that can both be used for co-incineration.

4 Outlook

The results show that if an SRF producer aims at decreasing the concentrations of Mo, Mn, Hg, Co, Ni, Ba, As, Cu, Cr, and Pb, it is likely that this can be achieved by removing the small grain size fraction below 5 or below 10 mm. Losing about 20% of the mass, the contaminant concentrations can be significantly decreased, and the heating value can be slightly increased. However, a treatment for the removed fraction that is rich in contaminants has to be found.

Future work will include the analysis of the grain size dependent distribution of more than 20 elements that were analyzed as well. The data will be combined with the material composition that was determined by sorting analyses of the grain size fractions, and correlations between different elements, as well as elements and material classes will be examined. Furthermore, the effect of removing small grain size fractions will be tested and evaluated in future experiments with different streams of commercial and residual waste in order to validate the obtained results.

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