Metals and rare Earth's elements in landfills: case studies

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Abstract

Landfills are considered as places where the life cycle of products ends and materials have been "disposed forever". The landfill mining (LFM) approach can deal with former dumpsites and this material may become important for circular economy perspectives within the concept "Beyond the zero waste". Potential material recovery should include perspectives of recycling of critical industrial metals where rare Earth elements (REEs) are playing more and more important role. Real-time applied LFM projects in the Baltic Region have shown the potential of fine-grained fractions (including clay and colloidal matter) of excavated waste as storage of considerably large amounts of valuable metals and REEs. Analytical screening studies have extended a bit further the understanding of fine fraction contents of excavated, separated and screened waste in a circular economy perspective. The Swedish Institute and Latvian Research Program "Res Prod" supported the research.

1. Introduction

Thousands of landfills as potential polluting objects are located close to the Baltic, Black and other seas and thus can become primary objects for both remediation and landfill mining (LFM) in the future. Metals including rare Earth elements (REEs) are fundamental to economy and growth [1] as well as often are essential for maintaining and improving technological processes especially concerning so-called "green technologies". Securing reliable, sustainable and undistorted access of certain raw materials is of growing concern within the EU and across the globe. In the case of critical raw materials, supply from the EU sources is even more limited [2].

On the other hand, landfills and dumpsites that are significant sources of landscape pollution due to the presence of hazardous waste including heavy metals, nevertheless being potential storages of valuables and scarce resources buried in past. Landfill mining (LFM) can be described as ''a process for extracting minerals or other solid natural resources from waste materials that have been previously disposed of by burying into the ground'' [3]. The process involves the excavation, screening, and separation of material from older landfills [4,5]. The comparison of pilot results from LFM and industrial sites in Latvia, Estonia and Sweden is given, screening type of analysis give a bit of the step further to shed the light on REEs and other elemental contents in dumps. Analysis of excavated waste is an initial step for scientists and entrepreneurs to re-inject lost material of growing concern within the EU and across the globe back into the economic cycle [3,4,5].

The circular economy (CE) has got an important attention through the work of Ellen MacArthur's concept [6]. The key idea of linear economy is unsustainable from both the material and environmental point of view. Linear thinking regards resources in a "take, make, dump". It is non-justifiable in a world where resources become increasingly scarce with considerable environmental impacts from extracting [7].

CE closes the loop in cyclical manner: an idea firstly stated in the area of industrial ecology [8]. The first loop is the material loop where materials are reused and not enter natural environment again. The second - biological loop takes nutrients etc. once again to the biosphere. However, it should ideally keep the natural ecosystem in a scope of saving resources in different stages of these circular loops.

Fine fraction material (including clay and colloidal matter) contains considerably large amounts of valuable metals including REEs. The aim of this study was to determine the rare metals content in fine fraction from excavated waste during landfill mining (LFM) projects. This was done in order to provide science-based information for recovery potential of rare metals. Analytical research by using wet acid digestion for homogenised samples were followed by atomic absorption spectrometry (AAS) and inductively coupled plasma mass-spectrometry (ICP-MS) measurements to provide results on potentially recoverable scarce metals in landfill waste from case studies of municipal and industrial dumps in Baltic adjacent countries.

Determination (screening) of toxic and potentially toxic elements is also important step to recognize potential hazard risks due to significant role in the organisation of further standing re-cultivation management of landfills and dump sites [9-11]. Remains of number of heavy metals transformed into water-soluble compounds may induce threats to the environment due to their toxic properties even in micro- and nano- gram level. This problem arises from different migration forms of chemical elements [12]. According to H.J.M. Bowen [13], the most known pollutants found in high concentration in soils are such metals as Hg, Pb, Cr, Cu, Zn intensively used by industry and agriculture.

Quantitative and qualitative analysis of trace and major metals in landfill mass is crucial [11,12,14]. Range of rapid analytical tools for site exploration during the excavation process is needed and this study provided the insight in relatively "screening mode" [15-23]. Conventional analytical methods were chosen best for fast track analyses available spectrometric techniques such as field portable X-Ray fluorescence in the field environment, atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) at stationary laboratories [15-23]. Results from last two methods are presented in the paper.

The performed work in field as well as laboratory conditions provide fast useful information for decision-makers selecting screening analytical methods for remediation programs, potential material recovery and evaluation of LFM in a scientific and industry modes.

2. Materials and Methods

Four different landfills were studied: "*BLB Baltijas Termināls*" (further – BLB) as industrial landfill soil in Latvia; Vika as industrial landfill in Sweden, Kudjape and Torma as municipal landfills in Estonia (Fig.1).

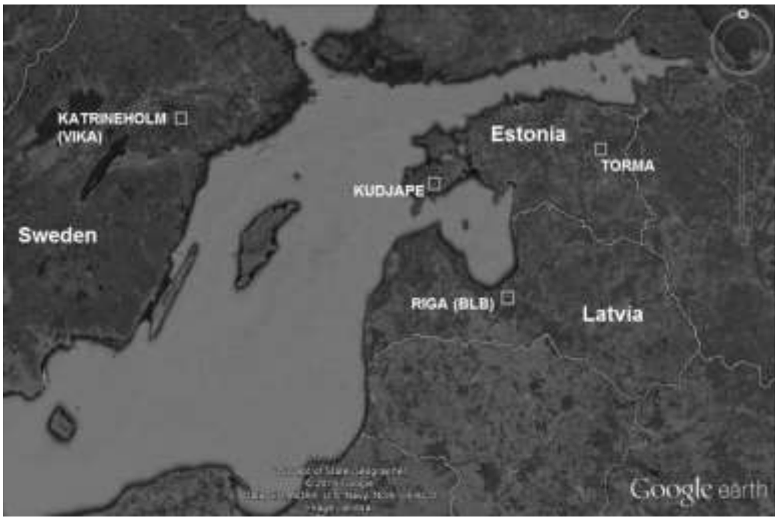

Figure 1: Case study sites in Latvia, Estonia and Sweden (courtesy map from Google Earth).

Various number of test-pits at sites in Kudjape, Torma and Vika were excavated, excavation was done from the vertical waste walls (Kudjape and Torma) or heaps (Vika); drilling works were performed on acid tailings type of soil in Latvia (technogenic sediments in BLB). From the end of 19^{th} century, BLB area was used for several industrial purposes including the manufacturing of superphosphates with tailings organized just nearby. Mentioned factory operated there until the 1960s; later on, an oil product terminal was established in this area. The main soil pollution source was superphosphate production waste (slag) with large contents of Pb, Cu, Zn and As. The equipment used for excavations from test-pits was tread excavator or tractor with a bucket size of around 1 m^3. A layer of weathered waste was removed to create so-called 'fresh cut' and topsoil 0.3 to 0.5 m was removed. The waste after shredding, separating and homogenization was studied by analytical research. At the BLB drilling works were performed by auger technique with the total depth of up to 5 m at 10 borings (BLB samples were homogenized without shredding). Samples gained from all sites were treated by acid digestion and analyses followed by ICP-MS and AAS measurements. The relatively (for landfills) fine fraction (e.g., at Kudjape landfill) 0–40 mm was identified with such proportions 80 % <10 mm, and 20 % 10-40 mm particle size. Metals that were possible to identify visually in the fraction of 0-40 mm were calculated at ~0.6 % (mostly Fe, Al, Cu). The fraction of fines <10mm was prepared in order to analyse contents of metals and toxic elements if those could be used as recovery material in distant future.

Sample preparation for analysis by advanced analytical techniques such as AAS and ICP-MS requires the release of elements of interest from the sample matrix and transfer of solid samples to liquid analytical solutions. Wet digestion was selected as appropriate screening waste sample preparation method [22-24]. One gram of each sample was weighed on analytical scales in a glass beaker, 50 ml of concentrated nitric acid (65% w/v, Merck) and 5 ml of concentrated hydrogen peroxide (30% w/v, Merck) were added (analytically pure reagents were used); after hold for 24 hours solutions were heated until half of volume evaporated. Adding of HNO_3 and heating was repeated until complete sample mineralisation. Solutions were filtered through 0.45 µm filters (Simplepure). Each sample was prepared in triplicates. Content of major and trace elements (core and refractory) Ca, Al, Fe, Ba, Cu, Cr, Fe, K, Na, Mg, Mn, Pb, Zn, Co, Ni in digested analytical solutions were analysed using AAS (Perkin Elmer AAnalyst200). ICP-MS device (Perkin Elmer ELAN DRC-e) was used for analysis of Ba, Sr, Rb, As, Cs, Th as well as REEs: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu.
Results were calculated and statistics performed using Microsoft Office Excel 2007.

3. Results and Discussions

The landfill mining (LFM) approach provides a unique opportunity to close landfills and remediate (recover) polluted territories; and at the same time use of their own material for recovery is possible. The research in the field of Kudjape, Vika and Torma LFM projects provided possibilities to analyse the potential of the landfill material.
Some of the major and trace elements are particularly important for life on Earth, e.g., major elements that make up, e.g., plant tissues are oxygen, carbon, sulphur, phosphorous, hydrogen, nitrogen, calcium, magnesium, potassium, sodium, also aluminium, iron, strontium, barium can be counted hereby. Other elements are necessary for plant physiology, if consider geochemical studies these are called minor elements - mainly if to talk about copper, manganese, zinc, boron and molybdenum and others. Figures 2 and 3 show the content of major elements. Amount of Ca and Fe in the waste is of dominion proportion and is measurable in g per kg. Slightly smaller is the amount of Al. If to rely on the age of the landfill - Torma is the youngest one and possibly the amount of dry matter contains less metallic as well as major / trace elements included as it can be seen in Fig. 2-5.

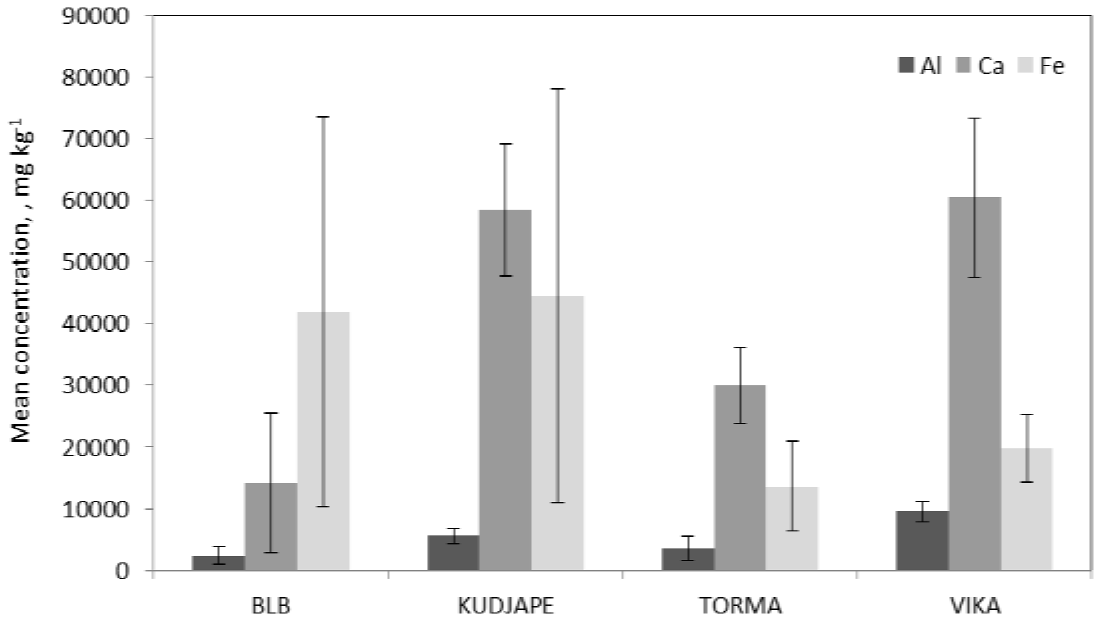

Figure 2. Content of major elements in waste and standard deviation: aluminium, calcium and iron.

The content of iron and arsenic in the technogenic soil of the industrial object BLB (Latvia) is high as superphosphate factory in former times has used the pyrite as the raw material for the production industry (Fig. 2,5). Magnesium, however, is largely coupled with the calcium (Fig. 2,3) and is coming from calcareous particles of the soil found in waste (debris of the construction waste and similar). Therefore, iron with accessory elements found in this mineral can be found in dumped soil after the enlarging of the port area by using the industrial tailings as the geotechnical stabilized soil. Area is close to the river in Riga situated in the northeastern part of the Freeport. The total amount of toxic heavy metals throughout the whole research area was estimated at 1264 t or 15 kg m^{-2} of slag or: 755 t of copper, lead 85 t, zinc 358 t, 66 t of arsenic [25]. The further studies led to possible remediation technology comparison [26], and the results provided in this screening study approve that former tailings can potentially raise the interest for recycling (landfill mining) of distinct elements such as As, Pb, Cu, Zn, also the REEs content is close to Vika dump site parameters (Fig. 6). Some of unofficial sources report that German forces did have interest for mining these tailings for recovery purposes already during the occupation of Riga in 1940-ties nevertheless circumstances of the war did not allow to force these actions to reality.

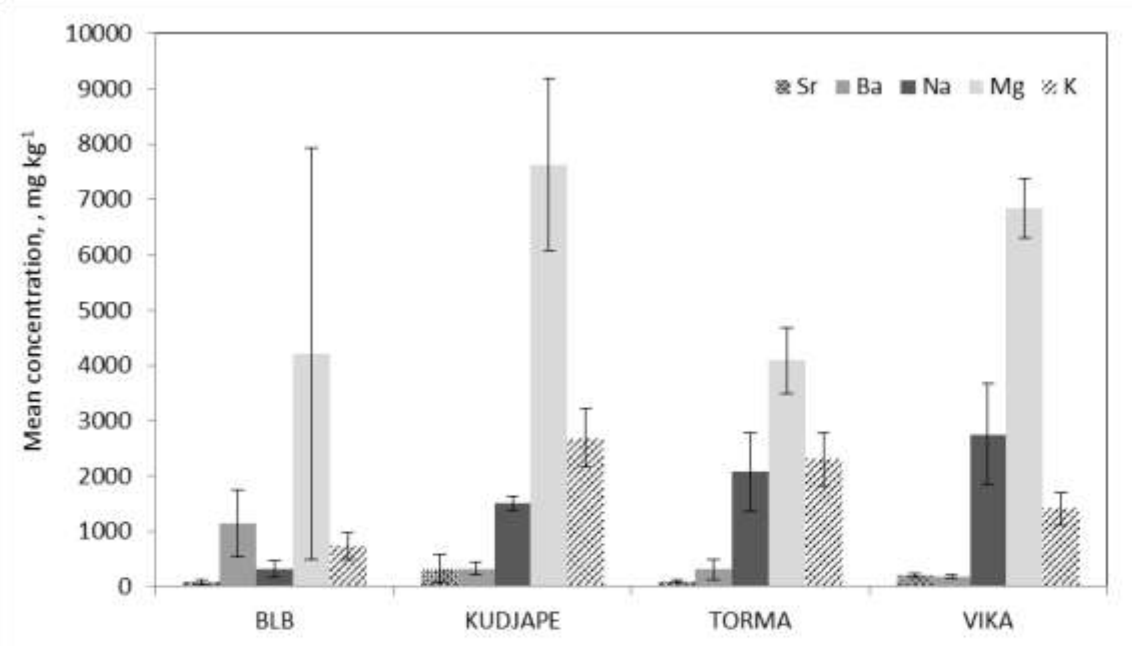

Figure 3. Content of major elements in waste and standard deviation: magnesium, potassium, sodium, barium and strontium.

Major elements like Na, K, Sr and Ba also can create concerns for potential leaching from contaminated areas therefore analyses performed show real amount of total salts as these elements are often associated with more toxic ones (Fig. 3).

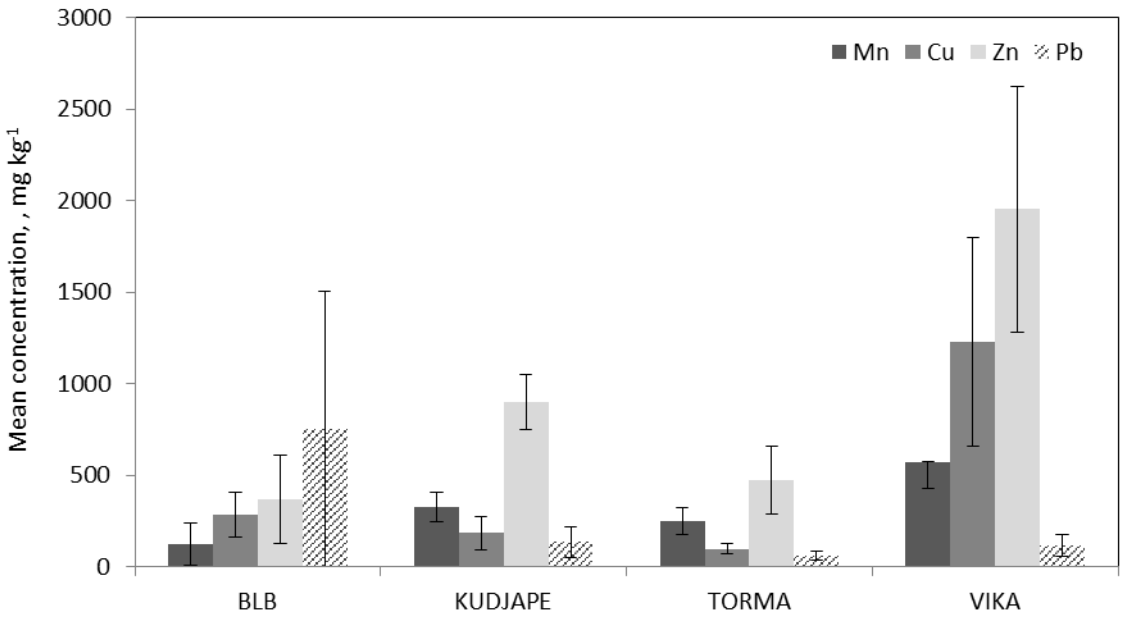

Figure 4. Content of minor elements of potential toxicity in waste and standard deviation: manganese, copper, zinc, lead.

The results of the fine fraction research have shown that minor elements with higher potential toxicity, if linked to the legislation standards for soil quality (e.g., in Latvia), such as Cu, Zn and in some cases Pb had the threshold concentration exceeded as well as especially for Cr, Ni and As (BLB in Latvia) (Fig. 4, 5). Therefore, additional research of metal speciation in the fine fraction of waste as well as the leaching behaviour under various pH should be studied by accurate sequential extraction tests followed by analytical ICP-MS measurements

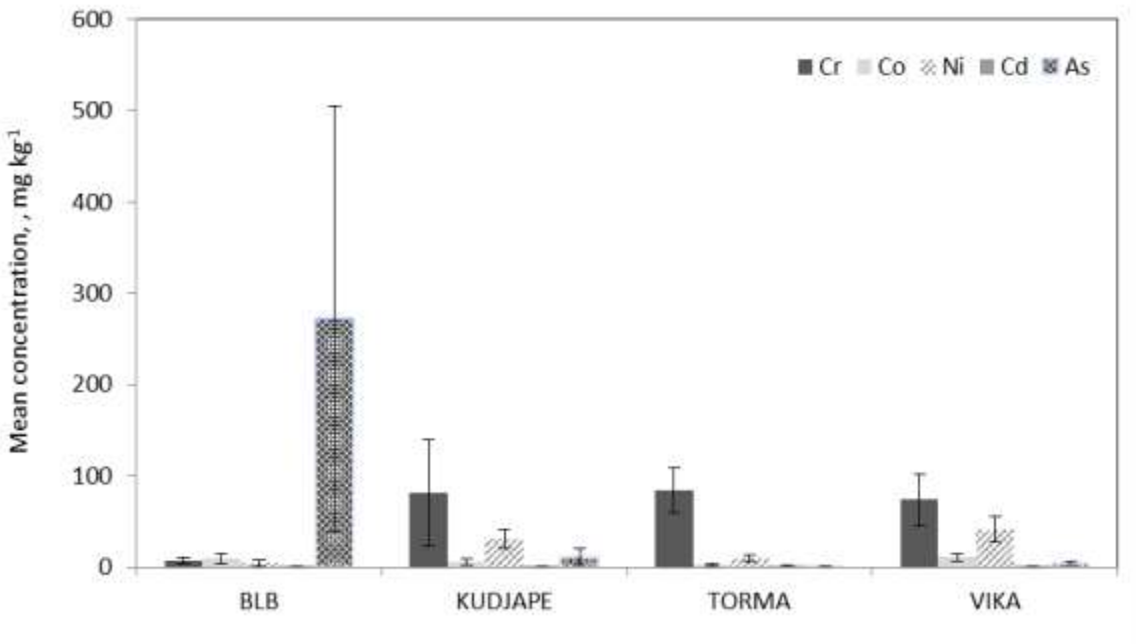

Figure 5. Content of minor trace elements in waste with higher toxicity risk and standard deviation.

Other reason for preferring the LFM can also be the high interest for recovery of such interesting metals as are REEs. Fig. 6 provides information on summary amount of REEs found in fine fraction from four landfills studied. Screening has shown that contents of REEs in fine fraction of waste is not as high as found in conventional ores, nevertheless, this information allows to explain the interest for these elements if the LFM approach is planned to be used. Fig. 2-5 gave information about core and refractory metals potentially feasible for extraction in a meaningful future; therefore REEs also should be taken in account for the future research.

From Fig. 6 it can be seen that industrial landfills have higher content of REEs comparing to municipal ones. However, profound analysis is to be done and more data should be collected from as many landfill as possible for statistical comparison. Certain hypothesis however can be pushed forward that these REEs are found because of close geochemical associations with core and refractory metals.

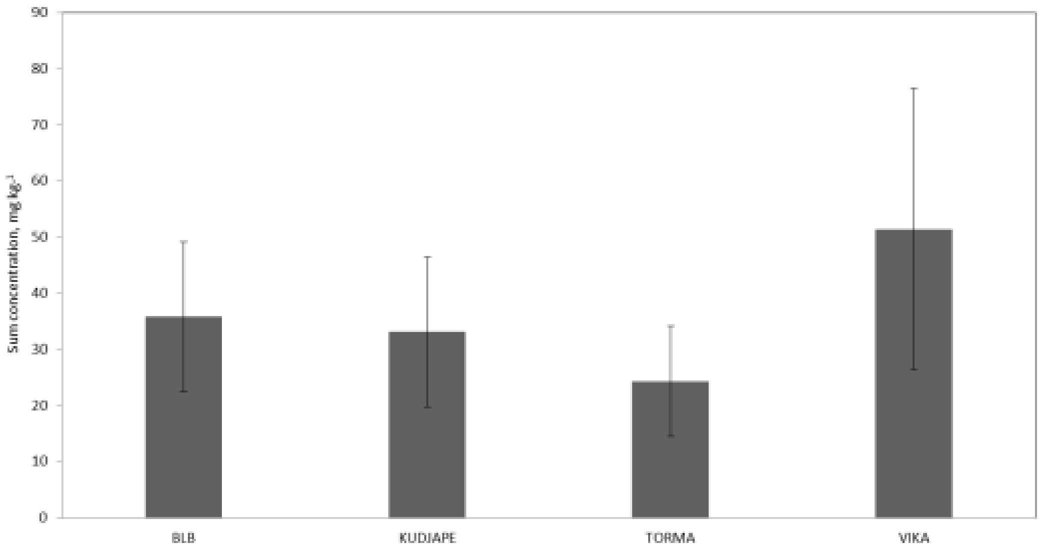

Figure 6: **.**The comparison of REE summary content in fine fraction of various landfills and standard deviation.

The REEs have many important uses, prices are volatile and recycling rates of those are extremely low. Fig. 7 is given for the evaluation of statistical distribution of distinct elements in the summary content of REEs in fine fraction of landfills studied.

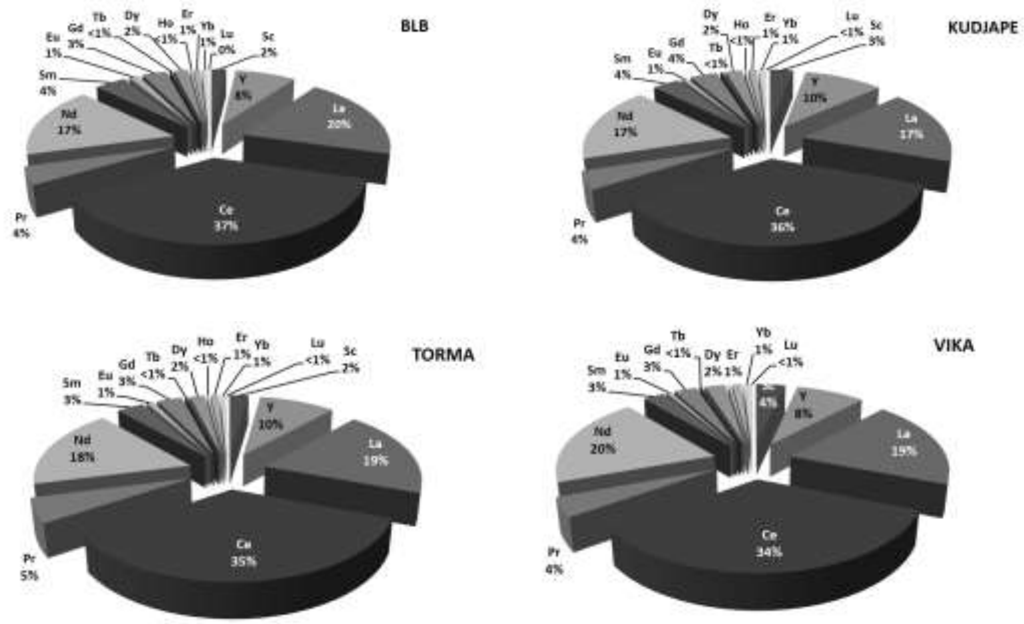

Figure 7. Proportions of REE content in fine fraction of various landfills.

As seen in Fig. 7, the proportion of distinct REEs in all landfills tested in these screening studies is almost the same, which is largely consistent with the hypotheses about geochemical association principles regarding general distribution of REEs in the Earth core, soil and in associations. Geologically REEs are found mainly in specific alkaline igneous and secondary deposited rocks; however, here we have purely anthropogenic loads so the fine fraction is coming from the alloys, electronic wastes, nanomaterials and many other sources.

Proportionally higher amount of Cs, La, Nd and Y in the fine fraction of waste can also mirror the proportional intensities of the use of REEs in the industry - the beginning of the circular technological loop.

Conclusions

Research provided results on fine fraction elemental content for landfill waste containing potentially recoverable scarce metal and REE resources. Amount of rare Earth elements can be feasible if the landfill mining approach for remediation of landfills and degraded industrial soils would be applied. Although the concentration of REEs is significantly lower than in mining areas, the concentration of elements such as Fe, Al, Cu, Pb, Ni and other is interesting for extraction in nearest future. Studies on speciation and potential hydrometallurgical approaches for extraction of metals, metalloids and REEs are to be continued. Only small proportion of REE deposits including anthropogenically loaded can be exploited using existing technologies and therefore these can be referred as “reserves”. For environmental purposes, it is beneficial to handle potential hazardous materials including toxic metals and REEs that exist in landfills and make sure these do not reenter the natural environment and are recycled. The environmental value in itself might not be enough to cover the economic cost however other aspects such as ecosystem services restoration and real estate regain can add feasibility to the landfill mining projects in a circular economy perspectives.

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