BONUS PROMISE DELIVERABLE 2.3

Report on environmentally relevant heavy metals in P-fertilizer materials

Minna Sarvi, Kari Ylivainio, Eila Turtola
Phosphorus Recycling of Mixed Substances (BONUS PROMISE)

DELIVERABLE 2.3

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1. Summary
Food production in EU is largely dependent on imported non-renewable primary phosphorus (P) minerals. However, P reserves are depleting and their quality is declining in the future highlighting the importance of more effective recycling of organic materials containing P. Like inorganic P fertilizer, also the organic P sources contain heavy metals. In manures heavy metals originate mainly from feed and pharmaceuticals and concentrations vary both between and within the animal types. For municipal sewage sludges, industrial flows often increase their heavy metal contents. In this study we examined heavy metal concentrations in different P sources. We also studied the effectiveness of ASH DEC –process to reduce heavy metal contents in sewage sludge ash. Among the studied P sources zinc (Zn, 27 g kg\(^{-1}\) P), copper (Cu, 7 g kg\(^{-1}\) P), chromium (Cr, 0.8 g kg\(^{-1}\) P) and nickel (Ni, 0.4 g kg\(^{-1}\) P) were the most abundant heavy metals, whereas mercury (Hg, 5 mg kg\(^{-1}\) P) and cadmium (Cd, 17 mg kg\(^{-1}\) P) had the lowest concentrations. In manures, Zn and Cu concentrations were highest and their concentrations decreased in the order pig > poultry > cattle manure. In manures, heavy metal concentrations were generally higher than in superphosphate (where the apatite originates from Siilinjärvi mine), but lower than in solid sewage sludges. In solid sewage sludges the most abundant heavy metals were Zn, Cu, Cr, Ni, uranium (U) and lead (Pb) and concentrations were higher than in superphosphate. Sewage sludges sampled from Finland and Sweden had higher U concentrations (Sweden: 1072 mg kg\(^{-1}\) P, n=3; Finland: 593 mg kg\(^{-1}\) P, n=6) than those sampled in Germany (52 mg kg\(^{-1}\) P, n=1) probably due to the geology of these areas. Struvite, liquid fraction of sewage sludge and superphosphate had most often the lowest heavy metal concentrations. ASH DEC –process reduced Cd by 59% and Hg concentrations from 0.3 to <0.02 mg kg\(^{-1}\) DM compared to the sewage sludge used as feeding material, whereas Cr and Ni contents increased due to the corrosion of unprotected steel reactor walls of test equipment in contrast to refractory lined industrial equipment.

2. Introduction
Phosphorus (P) is an essential major plant nutrient that cannot be substituted by any other element and thus it is crucial for the food production. At present agriculture mainly uses P obtained from phosphate rock and is therefore dependent on non-renewable resources (Cordell et al. 2009, van Dijk et al. 2016). According to Cordell et al. (2009) easily exploitable rock phosphate reserves will be depleted in 50-100 years. Furthermore, the quality of the remaining rock phosphate reserves will decline in terms of heavy metals. The reserves are controlled by few countries, making P supply vulnerable to geopolitical issues. Cooper et al. (2011) highlighted that 77% of known P rock reserves are located in Morocco and its share is estimated to increase in the future. At present EU’s food production is already dependent on imported primary P (van Dijk et al. 2016). Both the declining quality and imbalanced regional distribution of P rocks will affect the accessibility and price of P fertilizers in the near future. Therefore more efficient utilization of the inorganic P as well as recycling of organic materials containing P has drawn more attention.

Despite of the growing awareness, P recycling rate and efficiency are relatively low at the EU level (van Dijk et al. 2016). While manures are almost fully recycled at the EU level (van Dijk et al. 2016), their use may be very inefficient. Manures are often spread near the production houses due to the high transportation costs because of low nutrient and high water content. This will result in high soil phosphorus level with increased P leaching risk near the animal production units (e.g. Ylivainio et al.
Sewage sludges are regionally even more concentrated. Because both manures and sewage sludges may contain inorganic (heavy metals) and organic contaminants (e.g. pharmaceuticals), there is a risk for their accumulation in soils as well and bioaccumulation in the food chain. For example, Sheppard and Sanipelli (2012) noticed Zn accumulation in soils with long-term manure application.

In manures, heavy metals largely originate from feed since e.g. Cu, Zn and cobalt (Co) are used as feed additives to avoid deficiencies and promote animal health and growth (e.g. Poulsen 1998, Bolan et al. 2004, Sheppard and Sanipelli 2012). In general, heavy metal concentrations in manures reflect their concentrations in feedstuffs (Nicholson et al. 1999, Sheppard and Sanipelli 2012). Once ingested, heavy metals mainly pass through the animal and end up to manure (Sheppard et al. 2010, Sheppard and Sanipelli 2012). Other sources of heavy metals in livestock production are pharmaceuticals (e.g. Bolan et al. 2004, Sheppard and Sanipelli 2012). Heavy metal concentrations in manures vary between different animals and among the animal type. For example, Sheppard and Sanipelli (2012) noticed that layer manure had the highest heavy metal concentrations (except Cu) among poultry manure and among swine manures Cu and Zn concentrations were significantly higher in nursery barns than in other swine barns. In contrast the concentrations were much less variable in dairy manures. Nicholson et al. (1999) noticed that Zn and Cu were the most important heavy metals in manures and their concentrations decreased in the following order: pig manures > poultry manures > cattle manures.

In sewage sludges Cd, Cr, Cu, Hg, Ni, Pb, Zn and arsenic (As) are generally considered to be the most relevant heavy metals. They originate from discharge of households, run-off and industrial waste water (Sörme and Lagerkvist 2002). In addition, U, known to be chemotoxic, radiotoxic and carcinogenic element, can occur in sewage sludges (Bastian et al. 2005, Kratz et al. 2008, Jiménes et al. 2011). Naturally the heavy metal concentrations in sewage sludges vary depending on the activities in the catchment area and sources of the waste water entering the treatment plant. Industrial processes often elevate the heavy metal contents of sludges (Herzel et al. 2016). In a case study in Stockholm, Sörme and Lagerkvist (2002) calculated that households were the main source for Cu, Zn and Hg. The main source of Cu was from pipes and taps and roofs, Zn from food, pipes and taps but also from galvanized goods and car washes. Car washes dominated Cd, Pb and Cr emissions. The heavy metal concentrations in sewage sludges have decreased over the decades, however (e.g. Sörme and Lagerkvist 2002, European Commission 2010).

There are great variation in sewage sludge treatment methods and disposal practices between EU member states (Kelessidis and Stasinakis 2012, Hukari et al. 2016). Commonly used treatment methods in the EU are aerobic and anaerobic digestion, lime stabilization, composting, thermal drying and long-term storage (Kelessidis and Stasinakis 2012). According to Kelessidis and Stasinakis (2012) most of the sludge produced in the EU is used in agriculture (41%) followed by smaller shares of incinerating (19%), landfillsing (17%) and composting (12%). Incineration is most common in the Netherlands (68%), Belgium (53%) and Germany (51%). In case of sewage sludge ashes (SSAs) their low P availability together with elevated heavy metal contents often restricts their use as fertilizers unless further treated (Krüger and Adam 2015). By far many different technologies at various phase of development have been investigated to reduce heavy metal content in the end-product when recovering P from SSAs (Egle et al. 2015). One of these technologies is Outotec’s thermochemical ASH DEC –treatment, where sodium sulfate (Na₂SO₄) is mixed with SSA after which the mixture is
treated in a rotary kiln at high temperatures to produce more bioavailable P compounds with reduced heavy metal contents (Egle et al. 2015, Havukainen et al. 2016).

The aim of this study was to examine the heavy metal contents in different kinds of organic P sources, derived from manures and sewage sludges as well as in struvite and ASH DEC –material (sewage sludge as a starting material). Different P sources were collected from Finland, Sweden and Germany and their suitability for agricultural use was evaluated. Here we focused on the total concentrations of heavy metals in relation to the present EU legislation, although solubility and bioavailability determines more accurately the risk for the environment and people (e.g. Bolan et al. 2004). In addition to the heavy metals (Cd, Cu, Hg, Ni, Pb, Zn) regulated by EU’s Sewage Sludge Directive, also Cr, As, Co and U were included in the study. Cr is regulated by national legislation in Finland, Germany and Sweden, whereas As is regulated only in Finnish legislation among these three countries (Ylivainio and Turtola 2016). At present there is no limit value for U concentrations in fertilizers, although its concentration in inorganic P fertilizers can be elevated (Kratz et al. 2016) and P fertilization can increase U concentrations in soils (Rogasik et al. 2008). In this report differences in concentrations between various materials are discussed together with the effectiveness of the ASH DEC –procedure to reduce the heavy metal contents in SSA.

3. Material and methods

3.1 Sampling
The sampled materials were various manures (dairy cattle, pig and poultry), digestates (derived from manure and sewage sludge), liquid P sources, struvite (from Germany) and ASH DEC –product. Struvite is a magnesium-ammonium-phosphate product from precipitation of dissolved P with magnesium compounds (Egle et al. 2015).

Total of 27 digestion plants from Finland (13 plants), Sweden (6) and Germany (8) were sampled. The distribution of plants according to manure types used as substrate is described by Bloem and Lehmann (2016). From each biogas plant samples were taken before anaerobic digestion, from the reactor or right after the reactor and from the end-products that were ready to be spread to the fields. However, heavy metal contents were analyzed only from the samples allowed to be spread to agricultural fields as P sources. Thus e.g. undigested sewage sludge samples and samples taken from reactor were excluded from heavy metal analyses. Manure derived digestates also often had different kinds of plant materials and industrial waste streams as feeding materials. The total amount of samples was 70 including mineral P fertilizer (superphosphate) as a reference P source. Raw material (apatite) used for producing superphosphate originated from Siilinjärvi mine (Finland).

In order to evaluate the effect of ASH DEC –process in reducing heavy metal concentrations in SSAs, samples were taken from different process steps. First step was the gasification of the sewage sludge to get sewage sludge ash (SSA) for the ASH DEC –treatment, in which SSA with specific additives was treated in a rotary kiln at high temperatures. Before the treatment in the rotary kiln SSA was sieved >630 µm to separate the bed material from the SSA. The process is described in detail by Hermann and Schaaf (2016). First sample was taken from the sludge used in the ASH DEC –process, second from dried sewage sludge (same as previous, but dried), third from the SSA, fourth from sieved (>630 µm) SSA and fifth from the ASH DEC –product.
3.2 Determination of heavy metals
Heavy metal analyses were done from dried (at 37 °C in temperature controlled cabinet) and ground (with a ball mill) samples to ensure homogeneity of the samples. Samples were digested with aqua regia and heavy metal (As, Cd, Cr, Cu, Ni, Pb, Zn, Co) concentrations in the extracts were analyzed with ICP-OES (Thermo Jarrel Ash Iris Advantage) and U by analyzing $^{238}$U isotope with high resolution sector field ICP-MS (Element XR, Thermo). Part of the Hg measurements were done from aqua regia extracts with Varian Cetac M-6000 A Mercury Analyzer, but due to the equipment failure, rest of the Hg determinations were done directly from the air-dried samples by Teledyne Hydra IIc according to the EPA 7473 method. The comparability of Hg determinations with two different methods was checked by analyzing four samples with both methods. According to this comparison EPA 7473 method gave higher (53% at the highest) concentrations. However, all Hg concentrations were very low being well below limit values set by EU and thus differences between two different methods can be considered to be negligible. Duplicates were done frequently to ensure reliability of the results. Dry matter contents (105 °C) were determined in three replicates.

4. Results

4.1 Heavy metal concentrations in P sources
Studied P sources were grouped as described in Table 1. One digestate contained pig slurry, sewage sludge and biowastes. This digestate was included in solid digestates, not in sludges. Heavy metal concentrations were calculated per P kilogram (Fig 1) and mineral P fertilizer, superphosphate, was used as a reference P source. In addition, heavy metal loads per hectare were calculated using P fertilizing rate of 10 kg ha$^{-1}$ (Table 3). Heavy metal concentrations in dry matter (DM) are presented in Appendices I and II.

Table 1. Grouping of studied P sources.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cattle</td>
<td>Cattle manures and slurries</td>
</tr>
<tr>
<td>Pig</td>
<td>Pig manures and slurries</td>
</tr>
<tr>
<td>Poultry</td>
<td>Poultry manures</td>
</tr>
<tr>
<td>Cattle and pig</td>
<td>Mixture of cattle and pig manure</td>
</tr>
<tr>
<td>Digestates (s)</td>
<td>Solid fraction of biogas digestates derived from manure</td>
</tr>
<tr>
<td>Digestates (l)</td>
<td>Liquid fraction of biogas digestates derived from manure</td>
</tr>
<tr>
<td>Sludge (s)</td>
<td>Solid sewage sludge including both digested and composted sludges</td>
</tr>
<tr>
<td>Sludge (l)*</td>
<td>Liquid fraction after centrifugation and struvite precipitation of digested sludge</td>
</tr>
<tr>
<td>Struvite</td>
<td>Magnesium-ammonium-phosphate</td>
</tr>
<tr>
<td>ASH DEC –product</td>
<td>Product from Outotec’s thermochemical ASH DEC –treatment</td>
</tr>
</tbody>
</table>

*Due to the low dry matter content of the liquid, the sample amount wasn’t enough for dry matter analysis after heavy metal determinations and thus the results are calculated on air-dried basis unlike in the other samples where results are on a dry matter basis.
Variation of heavy metal concentrations within the same group of studied P sources were quite large reflecting the heterogeneity of the materials (Fig. 1, Appendices I-II). Due to this large variation, differences between countries with few exceptions were not observed (Appendices I-II). Because of the variation and limited number of samples in some specific sample groups, results per P kilogram from the same sample group were pooled (Fig. 1). However, some trends can be thought seen in the results.

Generally within the studied P sources (excluding ASH DEC-product), Zn, Cu, Cr and Ni were the most abundant heavy metals, with the mean concentrations of 27, 7, 0.8 and 0.4 g kg\(^{-1}\) P, respectively (Table 2). The rarest heavy metals were Hg and Cd with the mean concentrations of 5 and 17 mg kg\(^{-1}\) P, respectively (Table 2). In comparison, the most abundant heavy metals in superphosphate used as a reference material were Cu, Zn, Cr and Pb, with the mean concentrations of 1.4, 1.1, 0.08, 0.06 g kg\(^{-1}\) P, respectively (Table 2). Among the European mineral P fertilizers, studied superphosphate had much lower Zn, Cr, Cd, Ni and As concentrations per P kilogram, whereas Pb concentration was at the same level (Nziguheba and Smolders, 2008). The rarest heavy metal in superphosphate was Hg (Table 2). Struvite together with superphosphate and sludge (l) had most often the lowest heavy metal concentrations (Fig. 1). Among all the studied P sources, sludge (l) had though one of the highest As (126 mg kg\(^{-1}\) P) and Ni (498 mg kg\(^{-1}\) P) concentrations. Related to struvite, only Pb and Hg concentrations were slightly higher than in superphosphate (Fig. 1). However, it must be noticed that in this study only one struvite, sludge (l) and superphosphate sample was studied.

In manures, the most abundant heavy metals were Zn and Cu, whereas Pb, As and Hg concentrations were often under the detection limits (Fig. 1, Appendix I). In general, manures contained more heavy metals per kilogram of P than superphosphate, with the exceptions of Cd and U, which were at the same level (Table 2). Compared to solid sludges, manures contained, in average, less heavy metals per P kilogram with the exception of Zn (Table 2). Heavy metal concentrations varied largely among different animal types reflecting different feeding systems. Concentrations of Zn and Cu between different manures followed the same pattern as found by Nicholson et al. (1999) in England and Wales: The concentrations decreased in the following order: pig > poultry > cattle manures (Fig. 1, Appendix I). In Swedish pig and poultry manure Zn concentration was higher than in the other countries (Appendix I). Also Swedish cattle and pig manure mixture contained more Zn, Cu and Cd than German one, whereas German mixture contained more Pb and Cr (Appendix I). However, only one cattle and pig manure mixture sample was studied from both countries. In general, heavy metal (Zn, Cu, Cd, Pb, Cr, Ni, As, Hg) concentrations (mg kg\(^{-1}\) DM) in different manures were lower or at the same level as reported by Nicholson et al. (1999) and Amlinger et al. (2004). When calculated per P kilogram, only Hg concentration in cattle manures was above the values reported by McBride and Spiers (2001). In pig manures mean Zn, Cu, Cd, Pb and Ni concentrations in relation to the P content were lower and Cr concentration higher than reported by Kumaragamage et al. (2016). Compared to the studies by Moore et al. (1998) and Ihnat and Fernandes (1996), only P related Cr concentration in poultry manure were higher, whereas Zn, Cu, Cd, Pb, Ni and As concentrations were either under the values reported or at the same level. Mean U concentration in manures (cattle 0.27, pig 0.55, poultry 0.82 mg kg\(^{-1}\) DM) were at the same level with the study by Kratz et al. (2008), where U concentration in cattle manure ranged from 0.03 to 2.8, in pig manure from 0.05 to 11.1 and in poultry manure from 0.19 to 11.6 mg kg\(^{-1}\) DM. When manures are used as a P fertilizer at fertilization rate of 10 kg P ha\(^{-1}\), highest heavy metal loads come from Zn, Cu, Cr, Ni and Pb (Table 3).
Solid sludges contained more heavy metals per kilogram of P than superphosphate (Fig. 1, Table 2). The most abundant heavy metals in solid sludges were Zn, Cu, Cr, Ni, U and Pb (Table 2, Fig. 1). German solid sludges contained more Zn, Pb and Cr (mg kg⁻¹ DM) than Finnish and Swedish sludges (Appendix II). The large variation in Cr concentration of German solid sludges results from one sample with exceptionally high Cr concentration (664 mg kg⁻¹ DM). Concentrations of Zn, Cu, Cd, Pb, Cr, Ni and Hg in dry matter basis were at the range reported in EU countries (Amlinger et al. 2004). Concentration of U varied largely between countries, concentration being highest in Sweden (mean 1072 mg kg⁻¹ P, variation 358-2335 mg kg⁻¹ P) and Finland (mean 593 mg kg⁻¹ P, variation 72.9-1565 mg kg⁻¹ P)(Fig. 1, Appendix II). Most probably this is due to high U concentrations in bedrock, soils and groundwater in specific areas in Sweden and Finland. Weathering of bedrock releases natural radionuclides to soil and thus the highest aqua regia –soluble U concentrations in European agricultural soils are found in Sweden, Portugal and Finland (Reimann et al. 2014).

Table 2. Mean heavy metal concentrations in manures, solid sludges, average for all studied P sources, ASH DEC-product and Siilinjärvi superphosphate (g kg⁻¹ or mg kg⁻¹ of P in the material). Standard deviation is presented in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>g kg⁻¹ P</th>
<th>mg kg⁻¹ P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn/P</td>
<td>Cu/P</td>
</tr>
<tr>
<td>Manures</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n=26)</td>
<td>32.3</td>
<td>(17.8)</td>
</tr>
<tr>
<td>Sludge (s)</td>
<td>18.4</td>
<td>(4.6)</td>
</tr>
<tr>
<td>(n=12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>All studied P</td>
<td>26.5</td>
<td>(14.6)</td>
</tr>
<tr>
<td>sources</td>
<td>(n=68)</td>
<td></td>
</tr>
<tr>
<td>ASH DEC-product</td>
<td>27.2</td>
<td>14.3</td>
</tr>
<tr>
<td>Siilinjärvi</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>superphosphate</td>
<td>(n=1)</td>
<td></td>
</tr>
</tbody>
</table>

*n is number of samples

**excluding superphosphate and ASH DEC-product

Table 3. Heavy metal loads (g ha⁻¹) with P fertilization rate of 10 kg ha⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cu</th>
<th>Cr</th>
<th>Cd</th>
<th>Pb</th>
<th>Co</th>
<th>Ni</th>
<th>As</th>
<th>Hg</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cattle</td>
<td>225</td>
<td>52</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Poultry</td>
<td>304</td>
<td>54</td>
<td>4</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Pig</td>
<td>453</td>
<td>148</td>
<td>4</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cattle and pig</td>
<td>527</td>
<td>106</td>
<td>5</td>
<td>0</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sludge (s)</td>
<td>184</td>
<td>100</td>
<td>25</td>
<td>0</td>
<td>5</td>
<td>2</td>
<td>7</td>
<td>1</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>Digestes (s)</td>
<td>267</td>
<td>61</td>
<td>5</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Digestes (l)</td>
<td>236</td>
<td>44</td>
<td>4</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sludge (l)</td>
<td>39</td>
<td>12</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Struvite</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Superphosphate</td>
<td>11</td>
<td>14</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ASH DEC</td>
<td>272</td>
<td>143</td>
<td>599</td>
<td>0</td>
<td>9</td>
<td>2</td>
<td>314</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
According to Reimann et al. (2014) European agricultural soils contain 0.77 mg U kg\(^{-1}\) DM (median, range <0.04-24 mg kg\(^{-1}\) DM, \(n=2108\)) and permanent grasslands 0.74 mg kg\(^{-1}\) (median, range 0.047-73 mg kg\(^{-1}\) DM, \(n=2024\)). In contrast to northern Europe, U concentration in agricultural soils of central Europe are low (Reimann et al. 2014), which may explain much lower U concentration in studied German solid sludge sample (52 mg kg\(^{-1}\) P) compared to those taken from Finland and Sweden. However, in this study U was analyzed only from one German solid sludge sample. From soil and bedrock, U dissolves to water for household consumption, which finally ends up to sewage water treatment plants. According to Lahermo et al. (2002), mean U concentration in Finnish manmade shallow wells (\(n=739\)) is 0.846 µg l\(^{-1}\), maximum being 36.6 µg l\(^{-1}\), whereas in drilled bedrock wells (\(n=263\)) mean concentration is 13.7 µg l\(^{-1}\) maximum being 643 µg l\(^{-1}\). Locally concentrations can be much higher and U concentration as high as 15 mg l\(^{-1}\) is found in wells drilled in bedrock in Helsinki region (Åström et al. 2009). This spatial variation may explain the large variation in U concentrations in Finnish solid sludges. The maximum concentrations in Finnish (52 mg kg\(^{-1}\) DM) and Swedish solid sludges (75 mg kg\(^{-1}\) DM) are higher than maximum value in German sewage sludges (18 mg kg\(^{-1}\) DM) reported by Kratz et al. (2008).

When solid sludges are used as a P-fertilizer with fertilizing rate of 10 kg P ha\(^{-1}\), highest heavy metal loads come from Zn, Cu, Cr (Table 3). Average U load is 7 g ha\(^{-1}\), which is more than evaluated by Kratz et al. (2008) for sewage sludges (mean 3.2 g ha\(^{-1}\), range 0.001-19 g ha\(^{-1}\), P rate 22 kg ha\(^{-1}\)) but is within the range of mineral P fertilizers. Also the maximum loads (16 g ha\(^{-1}\) in Finland and 23 g ha\(^{-1}\) in Sweden) are within the range of U loads from mineral P fertilizers (Kratz et al. 2008).

Among the solid and liquid digestates, Zn, Cu, Cr and Ni had the highest concentrations and only U concentrations were lower than in superphosphate (Fig. 1). German liquid digestates contained more Zn, Cu, Cd, Cr and As than the Finnish ones (Appendix II).

For the ASH DEC-product, only Cd and Hg concentrations were lower than in superphosphate (Fig. 1, Table 2) and the main heavy metals were Cr, Ni, Zn and Cu (Fig. 1, Table 3). However, exceptionally high Cr and Ni concentrations result from the technical problem encountered in the process as discussed in the following chapter.
Fig. 1. Heavy metal concentrations (±SD) in studied P sources and in Siilinjärvi superphosphate calculated per kilogram of P. Number of samples is presented in parenthesis. Abbreviations: s = solid fraction, l = liquid fraction, x = result of one deviating sewage sludge sample.
4.2 ASH DEC-process

As described in chapter 4.1 the main heavy metals in ASH DEC-product were Cr (3.5 g kg\(^{-1}\) DM), Ni (1.9 g kg\(^{-1}\) DM), Zn (1.6 g kg\(^{-1}\) DM) and Cu (0.8 g kg\(^{-1}\) DM). Along the process heavy metal concentrations decreased (except Ni) during gasification and increased after sieving the most bed material away (except Ni) meaning that the bed material diluted the concentrations during the gasification (Fig. 2). ASH DEC-process reduced Cd (59%) and Hg (from 0.3 to <0.02 mg kg\(^{-1}\) DM) concentrations compared to sewage sludge used as feeding material. On the contrary, Cr and Ni concentrations were elevated due to the corrosive attack of sewage sludge on unprotected steel walls of the reactors in the reducing conditions (Hermann and Schaaf 2016). When produced in industrial scale, however, corrosion is easily overcome by protecting the reactor walls by refractory material (Hermann and Schaaf 2016).
Fig. 2. Heavy metal concentrations (mg kg\(^{-1}\) DM) along the ASH DEC-process. SSA is sewage sludge ash.
5. Conclusions

Variation in heavy metal concentrations was large within the same manure type and other group of P sources. Despite of this large variation, some trends could be seen in the results. Among all studied P sources, Zn, Cu, Cr and Ni were the most abundant heavy metals, whereas Hg and Cd were the rarest. For manures, Zn and Cu concentrations were highest in pig manures and lowest in cattle manures. In Swedish pig and poultry manure Zn concentration was higher than in the other countries. Compared to the superphosphate, manures contained more heavy metals per kilogram of P with the exceptions of Cd and U. However, manures contained mostly less heavy metals than the solid sludges. Compared to the literature, P related heavy metal concentrations were mostly at the same level, only Hg content in cattle manures and Cr content in pig and poultry manures were higher.

Heavy metal concentrations in solid sludges were higher than in superphosphate and the most abundant heavy metals were Zn, Cu, Cr, Ni, U and Pb. Concentrations were at the range reported in the EU. Uranium concentrations were higher in Swedish and Finnish sludges possibly due to the geology of these areas. At present, studies about uranium in sewage sludges and other organic P sources are scarce and the issue should be studied further.

In both solid and liquid fractions of manure derived digestates the main heavy metals were Zn, Cu, Cr and Ni and only U concentrations were lower than in superphosphate. Struvite, liquid fraction of sludge and superphosphate had most often the lowest heavy metal concentrations.

ASH DEC – process reduced Cd and Hg concentrations compared to the sewage sludge used as a feeding material, whereas Cr and Ni contents increased due to the corrosion of unprotected steel reactor walls of test equipment in contrast to refractory lined reactor walls of industrial equipment.
6. References


Appendix I. Heavy metal concentrations (mg kg$^{-1}$ in dry matter) in manures and solid sludges (sludge (s)) sampled from different countries (±SD). Dotted line shows respective concentration in mineral P fertilizer (superphosphate) originating from Siilinjärvi, Finland.
Appendix II. Heavy metal concentrations (mg kg\(^{-1}\) in dry matter) in sludges, digestates and struvite sampled from different countries (±SD). Dotted line shows respective concentration in mineral P fertilizer (superphosphate) originating from Siilinjärvi, Finland. Abbreviations: s = solid, l = liquid.