



## Heavy metal fixation in biochar after microwave pyrolysis of sewage sludge

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### ABSTRACT

The sequestration of heavy metals (HMs) in sewage sludge (SS) caused by slow microwave pyrolysis (MP) treatment was studied. The MP was carried out using a full-scale unit working at 300°C and pressure 800 hPa with 3 kW magnetron at 2.45 GHz. To determine the efficiency of sequestration, a new methodology was used. The SS from three waste water treatment plants (WWTPs) differing in capacities, inflow and drying procedure were used to study the effect of pelletization and additives addition. The total HMs content in sludges and produced biochars was determined by extraction using *Aqua Regia*, while soluble fraction (bioavailable, potentially harmful fraction) was determined by extraction using deionized water. The analyses revealed significantly low concentration of biologically available HMs after MP process in biochars prepared by pelletization and with additives. Therefore, the slow MP showed its potential to immobilize most of HMs in biochar structure thereby preventing their fixation, solubilization, and bioavailability for plants and microorganisms and may enable its use in agriculture. We conclude that slow MP represents an eco-friendly way of SS disposal, which belongs among the important strategies of circular economy.

*Keywords:* Sewage sludge treatment; Microwave pyrolysis; Biochar; Heavy metal fixation

### 1. Introduction

Disposal of the sewage sludge (SS) is one of the most important issues in circular economy that is a part of the waste management strategy implemented by the European Union (EU). In the Czech Republic (CR) disposal of SS has received significant attention mainly due to new legislation, strictly regulating the SS landfilling and direct application in agriculture. Currently, the limiting hazardous substances of SS for agricultural use are the content of heavy metals (HMs) [1,2], and in the near future the content of organic pollutants [3] and microplastics [4] will also be taken into account. Implementation of circular economy strategy postulates a search for new ways of waste recycling, and its material and

energy exploitation. Thermal treatment of sewage sludge represents one of the suitable solutions of SS disposal.

#### 1.1. Pyrolysis of sewage sludge

Generally, thermal treatment, such as incineration, gasification, hydrothermal carbonation (HTC) and pyrolysis belong to the suitable solutions of SS disposal. The pyrolysis process can further be divided into two categories such as conventional and microwave pyrolysis (MP). In principle, it can be carried out either by using conventional heat transfer via conduction or microwave heating of pyrolyzed material. The MP has already been tested for lignocellulosic materials,

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but, to best of authors' knowledge, its application to SS was reported only in few papers [5–8].

There are two different strategies in SS pyrolysis, the first one is burning of SS for energy production and the second one is the transformation of SS into a new product for agricultural use as dry SS contains nitrogen and phosphorus, which are soil nutrients and their re-use is of a great interest. However, SS may also contain hazardous substances that restrict the direct application in agriculture including toxic HMs, organic pollutants and microplastics [9].

From the chemical point of view is SS a heterogeneous mixture of undigested organic matter (paper, plant residues, oils and so on) microorganisms, inorganic materials and water. The content of inorganic material in the SS is usually higher than 50%. The undigested organic matter of SS consists of proteins, peptides, lipids, polysaccharides, phenolic and aliphatic structures containing macromolecules, polycyclic aromatic hydrocarbons and others [10].

Thermochemical reductive pyrolysis treatment process of SS can be divided into four classes such as flash pyrolysis, fast pyrolysis, slow pyrolysis and mil pyrolysis. Some authors describe mild pyrolysis as the torrefaction [11,12], when biomass is heated in an inert atmosphere at temperature about 200°C–300°C for residence time between 30 min and 4 h without production of liquid products. In fact, the slow pyrolysis is the most common pyrolysis of SS. Table 1 presents the selected parameters of slow pyrolysis of SS at low temperature less than 300°C. The weight of the input dried materials was between 30 and 273 g. Residence times were in range from 10 min to 2 h. Table 1 represents the parameters such as pH, and contents of C, C<sub>org</sub>, H, N and O. Agrifioti et al. [15] used some SS samples with catalyst for impregnating biochar with K<sub>2</sub>CO<sub>3</sub> (0.5%, 1.0%) and H<sub>3</sub>PO<sub>4</sub> (0.5%, 1.0%). Antunes et al. [18] described MP as a promising technology to safely dispose SS, while producing value-added products, such as biochar. Antunes et al. [18] used granular activated carbon as additives to pyrolysis process.

Generally, in slow pyrolysis, with increasing treatment temperature, the pH, ash content and macronutrient and micronutrient content increased. On the contrary, a decrease was observed for the pyrolysis yield, percentages of H, N and O, molar ratios, polarity of biochar. The changes in the content of elemental C and in The Brunauer-Emmett-Teller (BET) surface area (S<sub>BET</sub>) were dependent on the type of SS.

As shown in Callegari et al. [5], MP represents an eco-friendly disposal of SS resulting in production of biochar, pyrolysis oil and pyrolysis gas (Syngas). Several authors [19,20] have defined the term biochar and described the use of this high carbon solid product. Feedstock for biochar production includes various biomass wastes including SS. The nomenclature "biochar" refers usually to charcoal used as a soil amendment [21] and it is not commonly used for the product produced from 100% SS, but we use this nomenclature in following text.

### 1.2. Heavy metals

The HMs represent the major inorganic soil contaminants. Generally, regarding the pH range of SS, HMs occur mainly in insoluble form. The availability and mobility of HMs from SS for plants and organisms is determined mainly by physical

and chemical properties of soil. Exceeding the limit of one HM can represent toxicity in the soil when used SS in agriculture.

The availability of HMs of SS decreases in the order (Cd + Zn) > (Ni + Cu) > (Pb + Cr), which is related to the differently strong bonding of these elements in soil [14]. Thus, Cd and Zn are most generally available HM for plants in the soil.

Some HMs, however, are biologically essential elements required at low concentrations as micronutrients (e.g., Co, Cu, Cr, Mn, Se and Zn). The non-essential HMs are phytotoxic, zootoxic, or both, and hence are known as toxic elements (e.g., As, Cd, Pb and Hg). Both groups of HMs are toxic to plants, animals and humans at exorbitant concentrations [22]. The Council Directive 86/278/EEC [23] of 1986 defines limit values for HMs such as Cd, Cu, Ni, Pb, Zn and Hg in SS for use in agriculture in EU and United States Environmental Protection Agency (USEPA) of 1999 [24] defines maximum permitted concentration in SS for following HMs: Cd, Cu, Ni, Pb, Zn, Hg and Cr for agricultural use in USA. According to International Biochar Initiative (IBI) [25] in Table 2 and European Biochar Certificate (EBC) [26] Guidelines for biochar certification summarized in Table 2, the selected parameters are eight HMs: As, Cd, Cr, Cu, Pb, Hg, Ni and Zn.

Table 3 presents the content of HMs in feedstock and in biochar after slow pyrolysis of SS under different temperature. As can be seen, the concentration of HMs in conventional slow pyrolysis was higher in most samples after pyrolysis in biochar.

### 1.3. Biochar

Biochar is an amorphous, microbiologically inert and porous material which has received attention for its positive effect on soil stability and fertility [27]. The transformation of SS into biochar represents one of the strategies to convert the HMs into insoluble forms.

Several authors [8,28–30] have published detailed analysis of environmental risks caused by HMs contamination in biochar obtained using MP of SS. The authors used an advanced BCR sequential extraction (Commission of the European Communities Bureau of Reference), which results in four fractions F1–F4 of different bioavailability. The results confirmed that MP decreases the HMs bioavailability.

Current research at Brno University of Technology, Faculty of Civil Engineering, AdMaS Research Centre (AdMaS) focuses on low temperature slow MP of SS. The previous research [31] showed, that HMs could be sequestered in the biochar produced by low temperature slow MP of SS. Biochar of MP is planned to be used in agricultural applications, providing that most HMs would not be extracted and thus not available for plants.

The aim of this work is to present a new methodology for assessment of MP efficiency to fixation of HMs by extraction of HM in *Aqua Regia*, and in water. The HMs content was measured before and after MP and then the weight of SS and biochar were determined. The data was compared with the aforementioned literature. Our research focused on three different waste water treatment plants (WWTPs) with different capacities, inflow and drying procedure. The pelletization and without pelletization process was used, with and without additives. The MP tests were carried out by using full-scale MP unit, which corresponds to real

Table 1  
Selected parameters of slow pyrolysis of SS at temperature below 300°C [13–18]

Author	Sample (SS-sewage sludge, FS-feedstock, BC-temperature)	Description of the input SS sample	Additives	Process temperature (°C)	Weight input samples (g)	Residence time	Yield of biochar (%)
Lu et al. (3) [13]	SS BC300	SS dried at 25°C	–	– 300	100	– 2 h	– 10.0–15.0
Agrafioti et al. (1) [15]	SS BC300	Dewatered anaerobic SS and dried at 103°C in an oven for 24 h	Some SS samples were prepared with catalyst for impregnating biochar with K <sub>2</sub> CO <sub>3</sub> (0.5%, 1.0%) and H <sub>3</sub> PO <sub>4</sub> (0.5%, 1.0%)	– 300	30	– 30 min 60 min 90 min	– 47.7–62.9 47.2–65.7 32.9–64.2
Hossain et al. (1) [16]	SS BC300	Digested SS, dried at 36°C for 2 d	–	– 300	264–273	– 30 min	– 72.3
Roberts et al. (2) [17]	SS-1 BC300-1 SS-2 BC300-2	Air dried in a dewatering facility	–	– 300 – 300	200	60 min	– 67.5 – 70.1
Antunes et al. (1) <sup>a</sup> [18]	SS BC300	–	Granular activated carbon GAC (10%)	– 300	70	10 min	– 0.91
Author	Sample (SS-sewage sludge, FS-feedstock, BC-temperature)	pH	C (%)	C <sub>org</sub> (%)	H (%)	N (%)	O (%)
Lu et al. (3) [13]	SS BC300	– 7.2–7.5	23.8–33.2 21.7–31.5	6.0–8.4 7.7–11.2	4.4–4.9 2.8–3.3	4.0–5.6 3.4–5.4	– –
Agrafioti et al. (1) [15]	SS BC300	5.9 2.3–11.6	37.9 16.7–39.7	–	5.5 2.2–4.1	6.2 2.3–7.1	– –
Hossain et al. (1) [16]	SS BC300	4.42 5.32	32.3 25.6	–	4.47 2.55	3.27 3.32	18.36 8.33
Roberts et al. (2) [17]	SS-1 BC300-1 SS-2 BC300-2	–	23.3 24.5 28.0 32.8	–	4.5 2.9 5.1 3.6	4.3 4.0 4.8 5.4	–
Antunes et al. (1) <sup>a</sup> [18]	SS BC300	6.1 6.4	19.9 –	–	3.5 –	2.2 –	17.8 –

(1,2,3): numbers of different municipal WWTPs; – : is not defined; FS: feedstock; <sup>a</sup>: microwave pyrolysis (MP).

conditions at WWTP. In this article, MP of SS was investigated with the aim of obtaining data of HMs fixation in the input dried sludge and the output biochar produced by the small full-scale MP unit.

The aim of this pilot study is to present a full-scale reactor for MP of SS, outline the methods for HMs extraction and analysis and overview the available samples of SS from different WWTPs, in various forms of SS (pellets) and SS mixes with selected additives.

## 2. Materials and methods

### 2.1. Low temperature slow MP unit

At AdMaS research centre but are available 3 MP units [32], for this experiment was used a small full-scale MP unit which is representative for real conditions in industrial WWTP. The scheme of the small full-scale MP unit is reported in Fig. 1, the capacity is around 10 kg·batch<sup>-1</sup> of dried SS, i.e., it works discontinuously. It consists of one

Table 2  
Selected parameters of HMs for biochar certification according to guidelines IBI and EBC [25,26]

Selected parameter of HMs	Guidelines to biochar certification (mg·kg <sup>-1</sup> dry wt-mass)			
	International Biochar Initiative (IBI) [25]		European Biochar Certificate (EBC) [26]	
	Category A	Category B	Premium	Basic
As	13	100	13	13
Cd	1.4	20	1	1.5
Cr	93	100	80	90
Cu	143	6,000	100	100
Pb	121	300	120	150
Hg	1	10 <sup>a</sup>	1	1
Ni	47	400	30	50
Zn	416	7,400	400	400

<sup>a</sup>methyl mercury 10 mg·kg<sup>-1</sup>.

Table 3  
Content of HMs in feedstock and in biochar after conventional slow pyrolysis of SS [13,17]

Author	Sample (SS-sewage sludge, FS-feedstock, BC-temperature)	Heavy metals (mg·kg <sup>-1</sup> dry wt-mass)							
		As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Lu et al. (3) [13]	SS	–	2.28–5.26	–	401.0–611.3	136.5–224.5	–	–	629.1–1,237.9
	BC300	–	3.30–7.45	–	479.9–1,034.3	189.5–350.0	–	–	849.3–1,909.4
	BC400	–	3.76–9.82	–	548.6–1,197.7	194.2–438.3	–	–	911.6–2,103.6
	BC500	–	4.25–8.85	–	564.9–1,267.3	211.8–506.4	–	–	1,014.5–2,304.8
Roberts et al. (2) [17]	SS-1	9.7	2.2	19.3	493	47.7	1.73	22.7	970
	BC300-1	11.7	2.9	25.3	543	59.0	0.06	34.7	1,267
	BC450-1	12.3	3.5	30.7	490	65.0	<0.01	70.0	1,600
	BC600-1	10.3	3.6	29.0	487	68.7	<0.01	30.3	1,667
	BC750-1	9.0	0.24	26.3	563	55.7	<0.01	53.0	1,567
	SS-2	7.0	2.3	19.3	423	41.0	1.33	23.7	740
	BC300-2	7.5	3.1	27.0	533	54.3	0.10	50.3	970
	BC450-2	7.3	4.3	34.3	453	66.7	<0.01	60.3	1,267
BC600-2	6.1	6.3	30.3	527	67.0	<0.01	57.7	1,200	
BC750-2	5.2	0.27	25.3	543	59.0	<0.01	90.3	1,167	

(1,2,3): numbers of different municipal WWTPs.

batch reactor equipped with one highly efficient microwave generator of 3 kW output, at the frequency 2.45 GHz. Batches of dried SS were pyrolyzed at low pressure (800 hPa). The temperature was continuously monitored by an infrared thermometer, temperature never exceeded 300°C. The glass condensator attached to the pyrolyzer was used for separation of the pyrolysis oil and gaseous products. For incoming and reflected waves a tuner was installed. The pyrolyzed materials were pellets of SS made by pelletizing press (pellets) or directly by belt dryer (noodle shape) and by laboratory dryer lump shape.

## 2.2. Sewage sludge samples

The sludge composition depends on quality and quantity of the inflow and treatment processes at WWTP. The quality

and quantity of the inflow strongly influence the chemical composition and physicochemical properties of SS. The SS was contaminated by various HMs originating largely from industrial wastewater (WW). The treatment processes at WWTP are unique and depend on the design of WWTP, especially the design of the biological treatment and sludge management. Thus, SS composition and characteristics were different for each WWTP.

### 2.2.1. Sewage sludge (SS) samples

Anaerobically digested and thermally dried SS from three different municipal WWTPs were pyrolyzed.

The WWTP1 has a capacity of around 531,000 population equivalent (PE). WW is predominantly municipal WW originating from households. Only 12%–15% are industrial

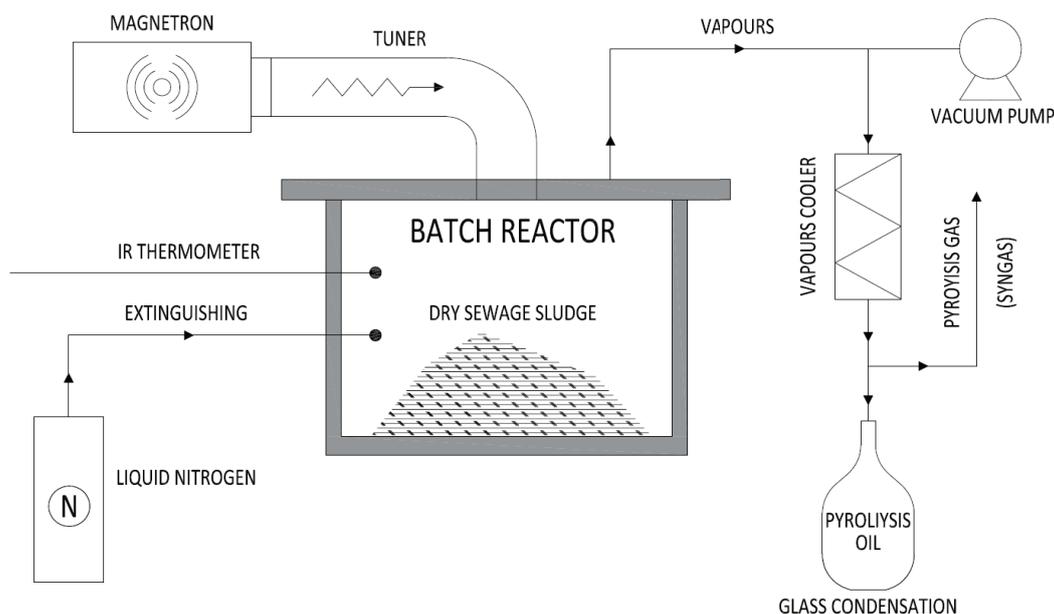


Fig. 1. Scheme of the small full-scale unit at AdMaS.

influent, but generally this WW mostly has the character of municipal WW. The sludge was dried using a paddle dryer at temperature lower than 100°C. Tested raw dried samples of SS from WWPT1 had dry solids (DS) around 91.5%–91.9% and output fraction from dryer was a powder like material with particle fraction 1–8 mm.

The WWTP2 has a capacity of around 90,000 PE. WW is a typical municipal WW from households, part of WW came from hotels and restaurants. Several percent are industrial WW originating from the production of mineral water which contains relatively higher concentrations of As. The sludge was dried using a belt dryer at temperature lower than 85°C. Tested raw dried SS sample from WWTP2 had DS around 90% and output fraction from dryer was a noodle of around 25 mm in length and around 5 mm in diameter.

The WWTP3 has a capacity less than 10,000 PE. WW is a typical municipal WW from households, industrial WW is only about 3% and originates from the automotive industry. The sludge was dried using a laboratory dryer at temperature lower than 100°C. Tested raw dried SS sample from WWTP3 had DS around 95% and output fraction from dryer was a different lump shape around 30–50 mm. Random tests revealed that the hygroscopic water content was below 2%.

### 2.2.2. Additives and MP process

Our previous research was focused on pretreatment of dried SS prior to the MP, namely on pelletization of SS and its mixing with additives [32]. Based on the literature data [33], the parameters of pellets should comply with the depth of microwave radiation and batch height. Generally, the knowledge of penetration depth is important for homogeneously irradiated MP processed output. Thus, SS was mixed with additives and consequently pelletized for

MP process. The pellets with 6 mm diameter were pressed and passed through a hot die of the pelletizing press, the surface became smooth and partially “baked”. Such an encapsulated pellet thus formed a kind of “micro-reactor” and processes during pyrolysis were similar to the so-called “pop-corn” effect responsible for pores formation [31]. Another considerable benefit of such pelletization is the ease of handling the produced biochar, which otherwise leads to problems with dust. On the contrary, the disadvantage of pelletizing of SS is energy demanding treatment process at the WWTP.

Based on our previous article [31] several additives were tested, and the additives were dosed at different concentrations. The catalyst (additive with theoretically catalytic effect), various types of zeolites, was added and mixed with SS to absorb microwave radiation after evaporation of moisture and to support catalytic cracking of specific hydrocarbons. The organic matter, such as wood sawdust, lignin and hay, was mixed with SS in order to adjust physical properties of pellets, to increase the ratio of organic matter and surface area in the biochar. An additive, such as zeolite and biochar produced from wood with high surface area, was added to SS for HMs fixation in the biochar.

In this paper, as an additive was also used biochar prepared from wood. This biochar with 90% DS was produced by the same MP unit. As a feedstock, 6 mm diameter wood pellets made from spruce sawdust with 0.5% zeolite were used. Zeolite was supposed to transport the HMs from surface into the structure of inert amorphous carbon and/or carbonaceous compounds.  $S_{\text{BET}}$  of this biochar of wood was in hundreds of  $\text{m}^2 \text{g}^{-1}$ .

The tests of HMs fixation before and after MP of SS process can be classified into the four groups, and the feedstocks before MP process are shown in Fig. 2:

- Group 1: SS from WWTP1 with pelletization and with additive wood biochar;
- Group 2: SS from WWTP1 with pelletization and without additive;
- Group 3: SS from WWTP2 without pelletization and without additive;
- Group 4: SS from WWTP3 without pelletization and without additive.

After pelletization, the anaerobically digested/aerobically stabilized and thermally dried samples of SS were named SS input ( $SS_{IN}$ ) and after MP the samples, biochar product, were named biochar output ( $BC_{OUT}$ ).

In Group 1, the raw SS as a feedstock for MP process was mixed and pelletized with additive biochar from the mixture of different woods with DS of 2.0%. The process time of the MP was 210 min. The temperature was managed via magnetron power control, the maximum temperature 211°C of the MP was measured. After the MP test of SS was completed, the vacuum pump was stopped.

In Group 2, the raw sample of SS was pelletized without any additive. The process time of the MP was 240 min. The temperature was managed via magnetron power control, the maximum temperature 190°C of the MP was measured. After the MP test of SS was completed, the vacuum pump was stopped.

In Group 3, the raw sample of SS was noodle shape (not pelletized). The test was performed without any additive, the process time was only 50 min. The temperature was managed

via magnetron power control, the maximum temperature 148°C of the MP was measured.

In Group 4, the raw sample of SS was lump shape (not pelletized). The test was performed with a raw sample of SS without any additive, the process time was only 60 min. The temperature was managed via magnetron power control, the maximum temperature 144°C of the MP was measured.

### 2.3. Determination of Heavy metals

HMs were determined in both raw SS and biochar. Two basic forms of HMs -water soluble (extractable, leachable) and water insoluble (non-extractable, non-leachable), which gave the total content of HMs in investigated materials were tested. The soluble HMs were determined by analysis of water extracts, the total HMs content was determined after digestion of samples in *Aqua Regia*.

#### 2.3.1. Chemicals

For comparison, primary and secondary samples were measured by two optimization methods. For the optimization of the AMA and AAS methods for determination of selected metals were used certified reference materials of calibration standard solutions ASTASOL® with concentration of measured metal  $1,000 \pm 0.002 \text{ mg}\cdot\text{l}^{-1}$  in 5%  $\text{HNO}_3$ , from Analytika Ltd., Czech Republic (Czech Metrological Institute). All other used chemicals were of analytical reagent grade.

#### 2.3.2. Preparation of samples

Water extraction was performed as follows: 10 g of the milled sample was transferred to an Erlenmeyer flask containing 100 mL of distilled water. After closing, the flask was shaken on a shaker (LT2, Czech Republic) for 24 h. After 24 h of extraction, the solution was filtered, diluted with distilled water in a ratio of 1:4 and subsequently analyzed.

Digestion in *Aqua Regia* was performed as follows: 10 g of the milled sample was transferred to a flask containing 60 mL of *Aqua Regia* ( $\text{HCl}:\text{HNO}_3$  3:1). The sample thus prepared was boiled under reflux for 2 h. After cooling, the sample was filtered. For analysis, it was diluted with distilled water in a ratio of 1:8.

Table 4  
Thermal programs for the determination of selected HMs: As, Cd, Cr, Cu, Pb and Zn

Metal	Wavelength (nm)	Drying 1/2/3 (°C)	Pyrolysis (°C)	Atomization (°C)	Cleaning (°C)
As	193.70	90/100/110	1000	2200	2400
Cd	228.80	90/105/110	500	1500	2300
Cr	357.90	90/110/120	1000	2100	2400
Cu	324.80	90/110/130	1000	1800	2300
Pb	283.30	90/100/110	1100	2000	2300
Zn	213.90	90/105/120	600	1800	2300



Fig. 2. Feedstocks of dried SS prior to the MP process (a) pelletized SS with additive; (b) noodle shape without additive; (c) lump shape without additive.

2.3.3. Instrumentation

Analyses of HMs contents were performed using atomic absorption spectrometer with electrothermal atomization ZEE nit 60 from Analytik Jena (Germany) with Zeeman background correction and selected hollow cathode lamp by Photron (Australia). Optimal measurement parameters and specific temperature program were used for each metal. Other conditions were graphite cuvette with platform, slit width 0.2–0.8 nm, used current was 3–8 mA and injection volume 20 µL. According thermal programs for the determination of selected HMs reported in Table 4, all obtained results are the average of three separate independent determinations, each was measured for atomic absorption spectrometer five times. Hg was analysed on atomic spectrometer Advanced Mercury Analyzer AMA 254 (Altec, s. r. o., Czech Republic) at wavelength 253.65 nm under conditions reported in Table 5.

2.4. Calculations

The input weight of SS for small full-scale MP unit was measured and biologically available HMs (BAHM<sub>SS</sub>) in SS were calculated by using the following equation:

$$BAHM_{SS} = C_{SSW} \cdot SS_{IN} \text{ (mg)} \tag{1}$$

where BAHM<sub>SS</sub> represents biologically available HMs in SS (mg), C<sub>SSW</sub> is the HMs content in SS established by extraction in water (mg·kg<sup>-1</sup>) and SS<sub>IN</sub> is the input weight of SS in (kg) to batch reactor of small full-scale MP unit.

The content of total HMs in SS (THM<sub>SS</sub>) before MP was determined based on the following relationship:

$$THM_{SS} = C_{SSAR} \cdot SS_{IN} \text{ (mg)} \tag{2}$$

where THM<sub>SS</sub> (mg) stands for total HMs in SS input and C<sub>SSAR</sub> represents HMs content in SS established by extraction in *Aqua Regia* (mg·kg<sup>-1</sup>). This HMs amount was taken as 100% of HM input weight entering the MP system (Fig. 3).

The biologically available HM in biochar (BAHM<sub>BC</sub>) after MP of SS can be expressed as follows:

$$BAHM_{BC} = C_{BCW} \cdot BC_{OUT} \text{ (mg)} \tag{3}$$

where BAHM<sub>BC</sub> (mg) represents biologically available HMs in biochar after MP, C<sub>BCW</sub> is the HMs content in biochar determined by extraction in water (mg·kg<sup>-1</sup>) and BC<sub>OUT</sub> is the output weight of biochar (kg) from batch reactor of small full-scale MP unit.

Table 5  
Temperature mode of the AMA 254, for the determination of Hg

Process	Drying (°C)	Decomposition (°C)	Waiting (s)
Cleaning	60	120	45
Blank	60	60	45
Calibration	60	120	45
Determination	10	200	50

The total HMs in biochar (THM<sub>BC</sub>) after MP used small full-scale MP unit was determined based on the equation:

$$THM_{BC} = C_{BCAR} \cdot BC_{OUT} \text{ (mg)} \tag{4}$$

where THM<sub>BC</sub> (mg) stands for total HMs in biochar output after MP and C<sub>BCAR</sub> represents HMs content in biochar after MP established by extraction in *Aqua Regia* (mg·kg<sup>-1</sup>).

The HM<sub>FIXSS</sub> represents the fixed HMs in SS and HM<sub>FIXSS</sub> was calculated by using the equation:

$$HM_{FIXSS} = THM_{SS} - BAHM_{SS} \text{ (mg)} \tag{5}$$

The HM<sub>FIXBC</sub> represents the fixed HMs in biochar and HM<sub>FIXBC</sub> was calculated by using the equation:

$$HM_{FIXBC} = THM_{BC} - BAHM_{BC} \text{ (mg)} \tag{6}$$

The HM<sub>ND</sub> represents non-detected HMs in biochar and HM<sub>ND</sub> was calculated by equation:

$$HM_{ND} = THM_{SS} - THM_{BC} \text{ (mg)} \tag{7}$$

Transformation of HMs by MP is illustrated in Fig. 3 with columns in %, the left for HMs in SS before MP and right for HMs in biochar after MP process. The graph interprets biologically available HMs by extraction in water (BAHM), HMs fixation by extraction in *Aqua Regia* (HM<sub>FIX</sub>) and non-detected HMs in biochar HM<sub>ND</sub>. The total HMs in biochar THM<sub>BC</sub> was calculated by Eq. (4).

3. Results and discussions

3.1. Content of HMs

The total HMs content and soluble HMs were determined by digestion of the samples in *Aqua Regia* and in water, respectively, in samples before and after MP. Extracts in *Aqua Regia* represent the total amount fixed HMs in the samples. Extracts in water represent HMs biologically available for plants and other organisms. The resulting HMs content of Group 1 is reported in Table 6 for sample of WWTP1 with pelletization and with

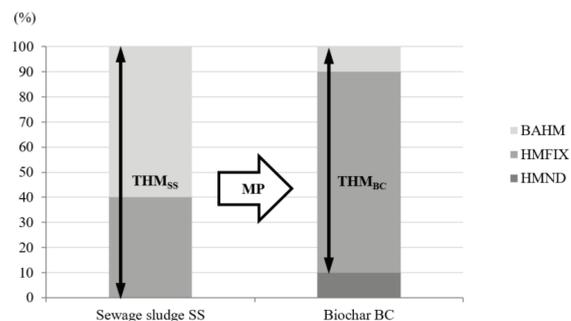


Fig. 3. Transformation HMs before (SS) and after MP process (biochar).

additive biochar of wood in 2.0% of DS weight concentration. Table 7 presents the content of HMs in the sample of WWTP1 of Group 2 with pelletization, but without any additive. The element content of HMs for Group 3 without pelletization and without additives can be observed in Table 8. The table describes HMs such as Zn, Pb, As, Cr and Hg. The contents of Cd and Cu were not determined due to technical difficulties. Table 9 presents the content of HMs in the sample of WWTP3 of Group 4 without pelletization and without any additive.

The content of HMs (Zn, Cd, Pb, Cu, As, Cr and Hg) in the sample from WWTP1 and HMs (Zn, Pb, As, Cr and Hg) in the sample from WWTP2 is reported in Tables 6–9.

As aforementioned, extraction in *Aqua Regia*  $C_{SSAR}$  ( $\text{mg}\cdot\text{kg}^{-1}$ ) represents the total amount of HMs in SS while  $C_{BCAR}$  ( $\text{mg}\cdot\text{kg}^{-1}$ ) represents the total amount of HMs in biochar and this amount includes also BAHM.

The results of sample from WWTP1 with pelletization and additive indicate the HMs fixation which is reflected in

indicators  $C_{SSAR}$ ,  $C_{BCAR}$  which show reduction of HMs after MP process. Zn content  $33.87 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $32.45 \text{ mg}\cdot\text{kg}^{-1}$ , Cd content  $30.82 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $5.79 \text{ mg}\cdot\text{kg}^{-1}$ , Pb content  $16.36 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $3.81 \text{ mg}\cdot\text{kg}^{-1}$ , Cu content  $99.63 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $23.74 \text{ mg}\cdot\text{kg}^{-1}$ , As content  $17.49 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $11.35 \text{ mg}\cdot\text{kg}^{-1}$ , Cr content  $8.96 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $3.09 \text{ mg}\cdot\text{kg}^{-1}$ , Hg content  $1.82 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $0.46 \text{ mg}\cdot\text{kg}^{-1}$ .

Sample of WWTP1 in Table 7 with pelletization and without additive is HMs fixation described by indicators  $C_{SSAR}$ ,  $C_{BCAR}$  for Cd, Cu, Cr and Hg, which were reduced, Cd content  $30.82 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $13.71 \text{ mg}\cdot\text{kg}^{-1}$ , Cu content  $99.63 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $24.73 \text{ mg}\cdot\text{kg}^{-1}$ , Cr content  $8.96 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $8.20 \text{ mg}\cdot\text{kg}^{-1}$ , Hg content  $1.82 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $0.73 \text{ mg}\cdot\text{kg}^{-1}$ . While for Zn, Pb and As HMs fixation was higher in raw SS than after MP process. Zn content  $33.87 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $107.83 \text{ mg}\cdot\text{kg}^{-1}$ , Pb

Table 6  
HMs content in the Group 1 sample of WWTP1 with pelletization and with additive

Description	Input/ output	HMs element content in the sample ( $\text{mg}\cdot\text{kg}^{-1}$ dry matter (DM))							
		Zn	Cd	Pb	Cu	As	Cr	Hg	
Extraction in <i>Aqua Regia</i> <sup>a</sup>	$C_{SSAR}$	SS <sub>IN</sub>	33.87	30.82	16.36	99.63	17.49	8.96	1.82
	$C_{BCAR}$	BC <sub>OUT</sub>	32.45	5.79	3.81	23.74	11.35	3.09	0.46
Extraction in water <sup>a</sup>	$C_{SSW}$	SS <sub>IN</sub>	6.38	5.62	1.17	29.97	4.01	0.01	0.02
	$C_{BCW}$	BC <sub>OUT</sub>	9.25	5.79	0.00	4.54	0.00	0.00	0.00

pH SS<sub>IN</sub>: 7.134; BC<sub>OUT</sub>: 6.954; electrical conductivity (EC) SS<sub>IN</sub>:  $1,052 \mu\text{S}\cdot\text{cm}^{-1}$ ; BC<sub>OUT</sub>:  $577 \mu\text{S}\cdot\text{cm}^{-1}$   
<sup>a</sup>standard deviation of  $\pm 5\%$  was not exceeded.

Table 7  
HMs content in the Group 2 sample of WWTP1 with pelletization, without additive

Description	Input/ output	HMs element content in the sample ( $\text{mg}\cdot\text{kg}^{-1}$ DM)							
		Zn	Cd	Pb	Cu	As	Cr	Hg	
Extraction in <i>Aqua Regia</i> <sup>a</sup>	$C_{SSAR}$	SS <sub>IN</sub>	33.87	30.82	16.36	99.63	17.49	8.96	1.82
	$C_{BCAR}$	BC <sub>OUT</sub>	107.83	13.71	19.80	24.73	19.26	8.20	0.73
Extraction in water <sup>a</sup>	$C_{SSW}$	SS <sub>IN</sub>	6.38	5.62	1.17	29.97	4.01	0.01	0.02
	$C_{BCW}$	BC <sub>OUT</sub>	8.97	5.40	5.27	4.03	8.97	0.00	0.00

pH SS<sub>IN</sub>: 7.134; BC<sub>OUT</sub>: 6.567; EC SS<sub>IN</sub>:  $1,052 \mu\text{S}\cdot\text{cm}^{-1}$ ; BC<sub>OUT</sub>:  $790 \mu\text{S}\cdot\text{cm}^{-1}$   
<sup>a</sup>standard deviation of  $\pm 5\%$  was not exceeded.

Table 8  
HMs content in the Group 3 sample of WWTP2 without pelletization, without additive

Description	Input/ output	HMs element content in the sample ( $\text{mg}\cdot\text{kg}^{-1}$ DM)					
		Zn	Pb	As	Cr	Hg	
Extraction in <i>Aqua Regia</i> <sup>a</sup>	$C_{SSAR}$	SS <sub>IN</sub>	467.98	22.51	22.02	19.57	1.07
	$C_{BCAR}$	BC <sub>OUT</sub>	7.18	15.83	26.84	10.59	0.31
Extraction in water <sup>a</sup>	$C_{SSW}$	SS <sub>IN</sub>	1.50	0.05	1.89	0.05	0.02
	$C_{BCW}$	BC <sub>OUT</sub>	2.09	5.20	5.19	2.57	0.00

pH SS<sub>IN</sub>: 6.167; BC<sub>OUT</sub>: 7.127; EC SS<sub>IN</sub>:  $1,972 \mu\text{S}\cdot\text{cm}^{-1}$ ; BC<sub>OUT</sub>:  $973 \mu\text{S}\cdot\text{cm}^{-1}$   
<sup>a</sup>standard deviation of  $\pm 5\%$  was not exceeded.

content  $16.36 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $19.80 \text{ mg}\cdot\text{kg}^{-1}$ , As content  $17.49 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $19.26 \text{ mg}\cdot\text{kg}^{-1}$ .

Similar results were achieved with sample from WWTP2 without pelletization and without additive for As (see Table 8). As content  $22.02 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $26.84 \text{ mg}\cdot\text{kg}^{-1}$ . Pb content  $22.51 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $15.83 \text{ mg}\cdot\text{kg}^{-1}$ , Cr content  $19.57 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $10.59 \text{ mg}\cdot\text{kg}^{-1}$ , Hg content  $1.07 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $0.31 \text{ mg}\cdot\text{kg}^{-1}$ . We have no explanation for an increase in Zn content in Table 8 ( $\text{SS}_{\text{IN}}$ ,  $\text{BC}_{\text{OUT}}$ ).

Sample of WWTP3 in Table 9 without pelletization and without additive is HMs fixation described by indicators  $C_{\text{SSAR}}$ ,  $C_{\text{BCAR}}$  for As and Hg, which were reduced, As content  $8.77 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $7.62 \text{ mg}\cdot\text{kg}^{-1}$ , Hg content  $50.94 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $18.63 \text{ mg}\cdot\text{kg}^{-1}$ . While for Zn, Cd, Pb, Cu and Cr HMs fixation was higher in raw SS than after MP process. Zn content  $433.43 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $661.13 \text{ mg}\cdot\text{kg}^{-1}$ , Cd content  $0.01 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $2.53 \text{ mg}\cdot\text{kg}^{-1}$ , Pb content  $28.11 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $35.25 \text{ mg}\cdot\text{kg}^{-1}$ , Cu content  $209.85 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $291.13 \text{ mg}\cdot\text{kg}^{-1}$ , Cr content  $102.17 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $291.13 \text{ mg}\cdot\text{kg}^{-1}$ .

The results of extracts in water are reflected by indicator  $C_{\text{SSW}}$  ( $\text{mg}\cdot\text{kg}^{-1}$ ), which represents biologically available HMs in SS and  $C_{\text{BCW}}$  ( $\text{mg}\cdot\text{kg}^{-1}$ ) representing biologically available HMs in biochar.

The results of sample from WWTP1 with pelletization and additive are characterized by biologically available Pb, Cu, As, Cr and Hg while  $C_{\text{SSAR}}$ ,  $C_{\text{BCAR}}$  were reduced after MP process. Pb content  $1.17 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $0.00 \text{ mg}\cdot\text{kg}^{-1}$ , Cu content  $29.97 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $4.03 \text{ mg}\cdot\text{kg}^{-1}$ , Cu content  $29.97 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $4.54 \text{ mg}\cdot\text{kg}^{-1}$ , As content  $4.01 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $0.00 \text{ mg}\cdot\text{kg}^{-1}$ , Cr content  $0.01 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $0.00 \text{ mg}\cdot\text{kg}^{-1}$ , Hg content  $0.02 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $0.00 \text{ mg}\cdot\text{kg}^{-1}$ . Whereas for Zn and Cd the content of biologically available HMs was higher than before conducting the MP process, i.e., extractable Zn content  $6.38 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $9.25 \text{ mg}\cdot\text{kg}^{-1}$ , Cd content  $5.62 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $5.79 \text{ mg}\cdot\text{kg}^{-1}$ .

Similar situation was observed with sample from WWTP1 with pelletization and without additive where biologically available Cd, Cu, Cr and Hg were reduced after MP process, Cd content  $5.62 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $5.40 \text{ mg}\cdot\text{kg}^{-1}$ , Cu content  $29.97 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $4.03 \text{ mg}\cdot\text{kg}^{-1}$ , Cr content  $0.01 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $0.00 \text{ mg}\cdot\text{kg}^{-1}$ , Hg content  $0.02 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $0.00 \text{ mg}\cdot\text{kg}^{-1}$ . The content of Zn, Pb and As was higher after MP process, Zn content

$6.38 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $8.97 \text{ mg}\cdot\text{kg}^{-1}$ , Pb content  $1.17 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $5.27 \text{ mg}\cdot\text{kg}^{-1}$ , As content  $4.01 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $8.97 \text{ mg}\cdot\text{kg}^{-1}$ .

Similar situation occurred with samples from WWTP2 without pelletization and additive, where biologically available Hg was reduced after MP process while Zn, Pb, As and Cr were higher after MP process, Zn content  $1.50 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $2.09 \text{ mg}\cdot\text{kg}^{-1}$ , Pb content  $0.05 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $5.20 \text{ mg}\cdot\text{kg}^{-1}$ , As content  $1.89 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $5.19 \text{ mg}\cdot\text{kg}^{-1}$ , Cr content  $0.05 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $2.57 \text{ mg}\cdot\text{kg}^{-1}$ .

Sample of WWTP3 in Table 9 without pelletization and without additive where biologically available Cu, As and Cr were reduced after MP process, Cu content  $0.80 \text{ mg}\cdot\text{kg}^{-1}$  in raw SS was reduced to  $0.00 \text{ mg}\cdot\text{kg}^{-1}$ , As content  $0.17 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $0.03 \text{ mg}\cdot\text{kg}^{-1}$ , Cr content  $0.05 \text{ mg}\cdot\text{kg}^{-1}$  was reduced to  $0.00 \text{ mg}\cdot\text{kg}^{-1}$ . Cd and Pb content was the same before and after MP. The content of Zn and Hg was higher after MP process, Zn content  $0.55 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $0.94 \text{ mg}\cdot\text{kg}^{-1}$ , Hg content  $0.03 \text{ mg}\cdot\text{kg}^{-1}$  increased to  $0.10 \text{ mg}\cdot\text{kg}^{-1}$ .

### 3.2. HMs fixation

The contents of HMs in the samples before and after MP were calculated. The MP process results in reduction of the weight of samples via production of pyrolysis gas and pyrolysis oil. Content (weight) of HMs in the SS and biochar samples were calculated, and results are reported in Tables 10–13 for Groups 1–4.

The biologically available HMs in SS  $\text{BAHM}_{\text{SS}}$  (mg) before MP presented in Tables 10–13 were calculated by Eq. (1) using data of Tables 6–9. The total HMs in SS  $\text{THM}_{\text{SS}}$  (mg) before MP were calculated by using Eq. (2). The biologically available HMs in biochar  $\text{BAHM}_{\text{BC}}$  (mg) after MP were calculated by using Eq. (3). The total HMs in biochar  $\text{THM}_{\text{BC}}$  (mg) after MP is shown in Tables 6–9, these data were calculated by Eq. (4). The difference between the total HMs in SS before MP  $\text{THM}_{\text{SS}}$  and biologically available HM in SS before MP by Eq. (5) represents fixed HMs in SS  $\text{HM}_{\text{FIXSS}}$  (mg) which are biologically unavailable for plants. Similarly, the difference between the total HMs in biochar after MP  $\text{THM}_{\text{BC}}$  and biologically available HMs in biochar  $\text{BAHM}_{\text{BC}}$  by Eq. (6) represents fixed HMs in biochar  $\text{HM}_{\text{FIXBC}}$  (mg), which are biologically unavailable.

Non-detected HMs in biochar  $\text{HM}_{\text{ND}}$  (mg) after MP was calculated by using Eq. (7) for the difference between total HMs in SS before MP and total HMs in biochar after MP.

Table 9  
HMs content in the Group 4 sample of WWTP3 without pelletization, without additive

Description	Input/output	HMs element content in the sample ( $\text{mg}\cdot\text{kg}^{-1}$ DM)							
		Zn	Cd	Pb	Cu	As	Cr	Hg	
Extraction in <i>Aqua Regia</i> <sup>a</sup>	$C_{\text{SSAR}}$	$\text{SS}_{\text{IN}}$	433.43	0.01	28.11	209.85	8.77	102.17	50.94
	$C_{\text{BCAR}}$	$\text{BC}_{\text{OUT}}$	661.13	2.53	35.25	291.13	7.62	291.13	18.63
Extraction in water <sup>d</sup>	$C_{\text{SSW}}$	$\text{SS}_{\text{IN}}$	0.55	0.00	0.01	0.80	0.17	0.05	0.03
	$C_{\text{BCW}}$	$\text{BC}_{\text{OUT}}$	0.94	0.00	0.01	0.00	0.03	0.00	0.10

pH  $\text{SS}_{\text{IN}}$ : 7.388;  $\text{BC}_{\text{OUT}}$ : 6.842; EC  $\text{SS}_{\text{IN}}$ :  $3,950 \mu\text{S}\cdot\text{cm}^{-1}$ ;  $\text{BC}_{\text{OUT}}$ :  $1,105 \mu\text{S}\cdot\text{cm}^{-1}$   
<sup>a</sup>standard deviation of  $\pm 5\%$  was not exceeded.

The  $HM_{ND}$  represents the HMs, which probably volatilized out of batch reactor of MP via the vapours to pyrolysis gas and pyrolysis oil. We cannot also reject a hypothesis that a part of non-detected HMs could be fixed to structure of biochar and it is not extractable even by *Aqua Regia*.

The data reported in Tables 10 and 11 refer to the same WWTP1 and represent the same raw input SS before pelletization process. The difference is that the data in Table 10 represents result of pelletized samples with additive, wood biochar with concentration 2.0%. The process time was operated for 210 and 240 min, the maximum temperature 211°C and 190°C, thus the conditions were similar. Content of biologically available HMs in biochar after MP  $BAHM_{BC}$ , shown in Table 10, is lower for all measured HMs than  $BAHM_{SS}$  before MP process. Similar result applies for Zn, Cd, Cu, Cr and Hg for sample Group 2 of WWTP1 with pelletization and without additive. But the biological availability was increased for Pb (14.02 mg in SS and 38.56 mg in biochar) and As (48.04 mg in SS and 65.62 mg in biochar).

The Content of HMs in the samples Group 3 of WWTP2 without pelletization and additive were characterized by Eqs. (1)–(7) and results are reported in Table 12. The process time was operated for 50 min the maximum temperature was 148°C. These reported values of Zn, Pb, As, Cr and

Hg contained significant different content compared to Tables 6 and 7.

The content of HMs in the samples Group 4 of WWTP3 without pelletization and additive were characterized by Eqs. (1)–(7) and results are reported in Table 13. The process time was operated for 60 min, the maximum temperature was 144°C. These reported values of Zn, Cr, Pb, Cu, As, Cr and Hg contained significant different content compared to Tables 10 and 11.

### 3.3. Comparison of results

The graphical representation in Figs. 4–7 is performed to evaluate the four Groups 1–4 of content results in %. For each individual HMs, the left column represents HMs before MP (SS) and after MP (BC).

Fig. 4 represents content in % for sample Group 1 of WWTP1 with pelletization and with additive 2.0% biochar of wood. The columns illustrate reduction of biologically available  $BAHM$  such as Pb, As, Cr and Hg. For these four HMs, the  $HM_{ND}$  volatilized out of MP batch reactor via the vapours to pyrolysis gas and oil, and part can be sequestered in biochar. Similar situation occurred for Cd and Cu were a reduction in biologically available HM was observed. A low

Table 10  
Content (mg) of HMs in the sample Group 1 of WWTP1 with pelletization and with additive

Description	Content of HMs (mg)													
	Zn		Cd		Pb		Cu		As		Cr		Hg	
	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$
$HM_{FIXSS}$	291.44	–	267.04	–	161.01	–	738.38	–	142.92	–	94.80	–	19.09	–
$HM_{FIXBC}$	–	144.88	–	0.00	–	23.79	–	119.89	–	70.88	–	19.28	–	2.87
$BAHM_{SS}$	67.60	–	59.61	–	12.39	–	317.73	–	42.46	–	0.15	–	0.16	–
$BAHM_{BC}$	–	57.77	–	36.17	–	0.00	–	28.36	–	0.00	–	0.00	–	0.00
HMND	–	156.39	–	290.49	–	149.61	–	907.85	–	114.50	–	75.67	–	16.38
THM	359.04		326.65		173.40		1,056.11		185.38		94.95		19.26	

Table 11  
Content (mg) of HMs in the sample Group 2 of WWTP1 with pelletization, without additive

Description	Content of HMs (mg)													
	Zn		Cd		Pb		Cu		As		Cr		Hg	
	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$	$SS_{IN}$	$BC_{OUT}$
$HM_{FIXSS}$	329.69	–	302.08	–	182.14	–	835.28	–	161.67	–	107.24	–	21.60	–
$HM_{FIXBC}$	–	722.83	–	60.80	–	106.21	–	151.39	–	75.20	–	59.93	–	5.33
$BAHM_{SS}$	76.47	–	67.43	–	14.02	–	359.42	–	48.04	–	0.17	–	0.18	–
$BAHM_{BC}$	–	65.62	–	39.45	–	38.56	–	29.43	–	65.62	–	0.01	–	0.01
HMND	–	0.00	–	269.26	–	51.38	–	1013.87	–	68.88	–	47.47	–	16.45
THM	406.15		369.51		196.16		1,194.70		209.71		107.41		21.78	

Table 12  
Content (mg) of HMs in the sample Group 3 of WWTP2 without pelletization, without additive

Description	Content of HMs (mg)									
	Zn		Pb		As		Cr		Hg	
	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>
HM <sub>FIXSS</sub>	1,715.25	–	82.60	–	74.01	–	71.74	–	3.85	–
HM <sub>FIXBC</sub>	–	15.06	–	31.44	–	64.03	–	23.73	–	0.92
BAHM <sub>SS</sub>	5.52	–	0.18	–	6.97	–	0.20	–	0.08	–
BAHM <sub>BC</sub>	–	6.18	–	15.39	–	15.36	–	7.60	–	0.00
HMND	–	1,699.53	–	35.96	–	1.58	–	40.62	–	3.00
THM	1,720.76		82.78		80.97		71.94		3.93	

Table 13  
Content (mg) of HMs in the sample Group 4 of WWTP3 without pelletization, without additive

Description	Content of HMs (mg)													
	Zn		Cd		Pb		Cu		As		Cr		Hg	
	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>	SS <sub>IN</sub>	BC <sub>OUT</sub>
HM <sub>FIXSS</sub>	226.83	–	0.01	–	14.72	–	109.54	–	4.51	–	53.51	–	26.68	–
HM <sub>FIXBC</sub>	–	242.29	–	0.93	–	12.93	–	106.84	–	2.79	–	106.84	–	6.80
BAHM <sub>SS</sub>	0.29	–	0.00	–	0.01	–	0.42	–	0.09	–	0.03	–	0.01	–
BAHM <sub>BC</sub>	–	0.34	–	0.00	–	0.00	–	0.00	–	0.01	–	0.00	–	0.04
HMND	–	0.00	–	269.26	–	1.80	–	3.11	–	1.80	–	47.47	–	19.86
THM	227.12		0.01		14.73		109.96		4.60		53.53		26.69	

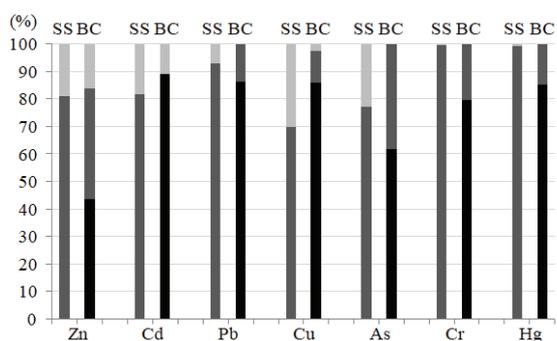


Fig. 4. Content (%) of HMs in the sample of WWTP1 with pelletization and with additive.

reduction in the BAHM was achieved with Zn. The highest HM<sub>FIX</sub> after MP was achieved in Zn and As, these HMs are biologically unavailable.

Fig. 5 presents the results of sample from WWTP1 with pelletization and without additive. The columns illustrate reduction of BAHM in Zn, Cd and Cu. After MP process, the biologically available BAHM in biochar is higher in Pb and As. The high levels of non-detected HMs were achieved in Cd, Cu and Hg, these HMs were probably transported

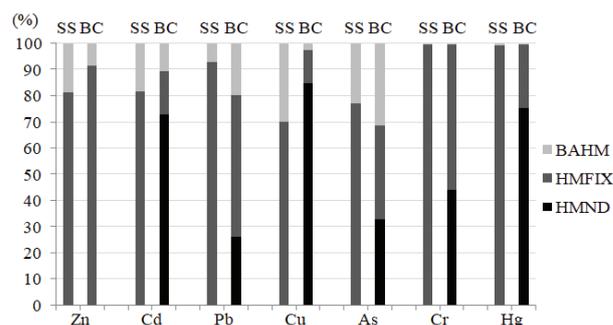


Fig. 5. Content (%) of HMs in the sample Group 2 of WWTP1 with pelletization and without additive.

by vapours to pyrolysis gas and oil, and/or were fixed in structure of biochar.

Fig. 6 shows the content in % of HMs in the sample from WWTP2 without pelletization and without additive. The samples represent noodle shape of SS before and after MP process. Small reduction in biologically available HM (BAHM) was observed only in case of Hg. The high level of biologically available HMs after MP process was achieved in Zn, Pb, As and Cr. The high levels of non-detected HMs

were achieved in Zn and Hg, these HMs were probably also transported by vapours to pyrolysis gas and oil, and/or were fixed in structure of biochar.

Fig. 7 represents the results of sample from WWTP3 without pelletization and without additive. The columns illustrate reduction of BAHM in Cd and As. The high levels of non-detected HMs were achieved in Pb, As and Hg, these HMs were probably transported by vapours to pyrolysis gas and oil, and were fixed in structure of biochar.

Fig. 8 represents the BAHM results of sample from WWTP1 with pelletization and with additive 2.0% wood biochar.

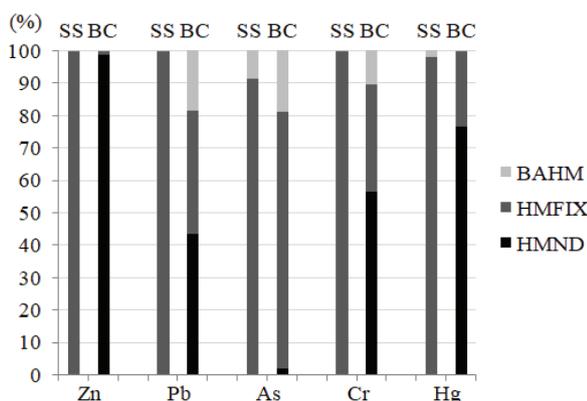


Fig. 6. Content (%) of HMs in the sample Group 3 of WWTP2 without pelletization and without additive.

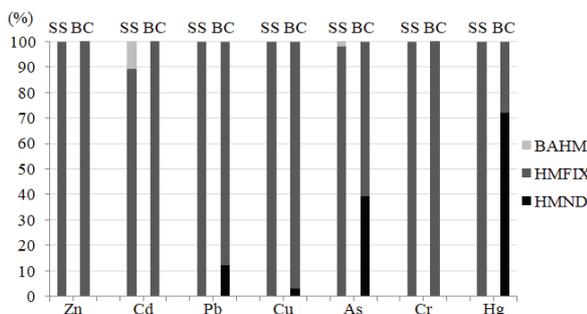


Fig. 7. Content (%) of HMs in the sample Group 4 of WWTP3 without pelletization, without additive.

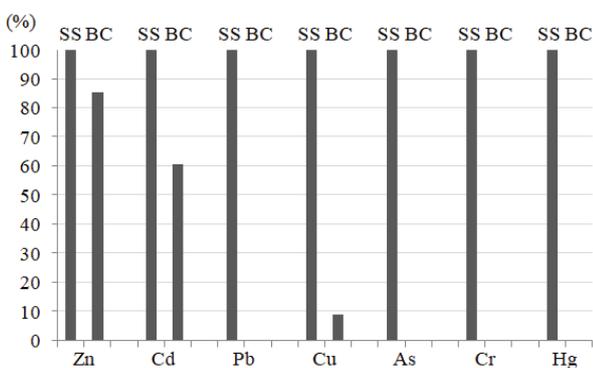


Fig. 8. Content (%) of BAHM in the sample Group 1 of WWTP1 with pelletization and with additive.

The results show low concentration of biologically available Zn, Cd and Cu, and significant reduction of Pb, As, Cr and Hg, which is desirable for SS biochar application.

### 3.4. Summarizing discussion

In this research, we present our new methodology for determination benchmarking balances of HMs fixation before and after low temperature slow MP of SS. The experiments were performed by using two kinds of extractions such as extraction in *Aqua Regia* and water, reflecting the solubility and thereby potential impact of HMs on the environment.

HMs measurements revealed a significant structural heterogeneity of the SS. The  $HM_{ND}$  volatilized out of batch reactor of MP via the vapours to pyrolysis gas and pyrolysis oil. The reported values of HMs in Figs 4–7 show significant reduction of Hg. Namely mix in sample group 1 of WWTP1 showed good potential for HMs fixation for Pb, Cu, As, Cr and Hg. Thus, we can say that 2.0% biochar additive mix and pelletization process are a promising method to reduce HMs leaching into soil.

Number of HMs tests has shown difference between initial and resulting content of particular metal, namely Hg. It can be assumed that, under MP conditions, Hg was desorbed/vaporized and transported to pyrolysis gas and/or pyrolysis oil. Potential Hg evaporation was partially expected due to reasons mentioned by Kistler et al. [34] and due to non-well-understood influence of vacuum.

The biochar of wood was tested as an additive in samples of the Group 1. The experiments have shown that mixing SS with additive(s) has shown a great potential for low temperature slow MP of SS, as the additive is assumed to increase the surface area of SS and thus the capacity to fix HMs in biochar.

The results of HMs content in samples were compared in Figs. 4–7 and in Fig. 8, the significant content of biologically available HMs after MP process was achieved in case of WWTP1 with pelletization and with additive of 2.0% biochar of wood. The process time in the Group 1 was operated for 210 min, longer than for samples of Group 3 which were operated only for 50 min. We hypothesized that longer pyrolysis time process would lead to increasing immobilization of HMs in biochar after MP. Therefore, this biochar of SS after MP seems to be theoretically applicable in agriculture use.

## 4. Conclusions

In this work, we presented a new complex methodology for determination benchmarking balances of HMs fixation via low temperature slow full-scale MP of SS using two kinds of extractions such as extraction in *Aqua Regia* and water, which gave a rough estimation of bioavailability of HMs in SS before and after pyrolysis. A new knowledge of this work was the implementation of the water leachate and its comparison in the acid leachate. The comparison of SS and the shape of the input samples affected the MP process. Additives have been added to improve the MP process and then to increase organic matter. The additives were mixed with dried SS and then pelletized. The pelletizing process closed the SS with the additive into the pellets that were suitable for the MP process.

The low content of biologically available HMs after MP process was achieved with additive of 2.0% wood biochar and longer MP process time. The article describes a wide range based on four different samples of SS, various shape and additive under different process time. This wide range has shown the need to mix dried SS and accompanied by the pelletizing process that appears to be acceptable for biochar use in agriculture.

The next research will be focused on BCR sequential extraction method, which can prove more detail information on the form of HMs in biochar. Furthermore, the attention will be given to addition of other types of biomass to investigate the influence of organic matter on the HMs fixation.

The circular economy strategy of sludge management in EU postulates a search for new ways of reusing SS by thermal treatment, it takes into account either burning of SS for energy production or the transformation of SS into new product, especially for agricultural use. The biochar of SS represents a challenge for further research for agricultural use. This research suggests that MP of SS can be considered as a suitable available technology for eco-friendly disposal of SS or different waste materials as well as with respect to the use of this technology to produce resources for agriculture use. Currently applied research of MP treatment of SS is a solution in terms of circular economy, carbon footprint reduction, HMs fixation, energy recover and water retention.

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