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

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# Abstract

The paper describes current applied research focused on heavy metal (HM) fixation in biochar after microwave pyrolysis (MP) of sewage sludge (SS).

The treatment of sewage sludge 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) and also in the Czech Republic (CR). Disposal of SS has received significant attention mainly due to new strict regulation of the SS landfilling and direct application in agriculture. Currently, the limiting criterion of its use in agriculture is the content of heavy metals (HM), in the near future the content of xenobiotics and microplastics will also be taken into account. Thermal treatment is often associated with incineration but there are also alternative methods such as gasification or pyrolysis that produces secondary feedstock: biochar, pyrolysis oil and pyrolysis gas (Syngas). MP as a promising of the thermal treatment has an assumption for reusing SS: circular economy principles, carbon footprint reduction, water retention and HM fixation in biochar for agriculture application.

Current research is performed in a laboratory and full-scale conditions at AdMaS Research Centre in the Czech Republic. MP units work at low temperature, less than 300 °C and a low pressure 800 hPa with 3 kW magnetron with 2.45 GHz. We present a new methodology for determination benchmarking balances of HM fixation before and after low MP process by extraction in *Aqua Regia* and water, determining the solubility and thereby potential impact of HM on the environment. The results of HM content in samples were compared, the significantly low level of biologically available HM after MP process was achieved in case with pelletization and with additive 2.0 % biochar of wood. We hypothesized that longer pyrolysis time process would lead to increasing immobilization of HM in biochar after MP. Therefore, this biochar of SS after MP seems to be applicable in agriculture use.

The MP as an eco-friendly treatment of SS with by-products, particularly biochar, may represent a solution in terms of circular economy. Biochar of MP will be used in agriculture application, most of HM would not be extracted and HM will not be available for plants. The aim of the applied research work presented in this paper is MP immobilization of SS into the product, biochar with HM fixation for application in the agriculture.

#### 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 criterion of its use in agriculture is the content of heavy metals (HM), in the near future the content of xenobiotics and microplastics 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 represents the most suitable solutions of SS disposal. In principal, it can be carried out either by using conventional heat transfer via conduction or microwave heating of pyrolyzed material. The microwave pyrolysis (MP) has already been tested for lignocellulosic materials, but its application for SS pyrolysis is reported only in few papers (Callegari et al., 2017; Capodaglio et al., 2016, 2017, Menéndez et al., 2002; Zhao et al., 2017).

From the chemical point of view, SS is a heterogeneous mixture of undigested organic matter (paper, plant residues, oils, etc.) 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 several hydrocarbons like proteins, peptides, lipids, polysaccharides, phenolic and aliphatic structures containing macromolecules, polycyclic aromatic hydrocarbons, etc. (Fonts et al., 2012). Dry SS contains also molecules containing nitrogen and phosphorus, which are nutrients for soils. The problematic substances for direct application in agriculture are considered xenobiotics, microplastics and HM.

MP represents an eco-friendly disposal of SS resulting in production of biochar, pyrolysis oil and pyrolysis gas (Syngas) (Callegari et al, 2018). Importantly, the nomenclature "biochar" refers solely to charcoal used as a soil amendment (Conte et al., 2015) and it is not commonly used for the product produced from 100 % SS, but we use this nomenclature in following text.

Biochar is an amorphous porous material which has received attention for its positive effect on soil stability and fertility (Conte, 2014). The transformation of SS into biochar represents one of the strategies to fix the HM into insoluble form and simultaneously to transform the harmful organic compounds into microbiologically inert amorphous carbon and/or carbonaceous compounds. Several authors (Zhao et al., 2017; Liu et al., 2017; Jin et al., 2016; Liu et al., 2018; Huang et al., 2016) have published detailed analysis of environmental risks caused by HM contamination in biochar obtained from 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 a positive effect of MP on HM bioavailability.

To sum it up MP seems to represent a solution in terms of circular economy, carbon footprint reduction, energy recovery, water retention and HM fixation in the field, where the EU legislation restricts the use of sludge for agricultural applications if the limit concentrations of HM are exceeded.

Current research at Brno University of Technology, Faculty of Civil Engineering, AdMaS Research Centre (BUT AdMaS) focuses on low temperature slow MP of SS. This research is conducted in cooperation with engineering company Bionic E&M. The previous research (to be published in May 2018) showed, that HM could be fixed 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 HM would not be extracted and thus not available for plants.

The aim of this work is to present a new methodology for determination benchmarking balances of HM fixation using two kinds of extracts, extraction in *Aqua Regia* and extraction in water, minimizing the impact of HM on the environment. The HM content was measured before and after MP then weight SS and biochar was calculated. Compared with above literature review, our research was focused on two 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 conditions at WWTP. In this work, we focused on investigation of indicators of pyrolytic processes such as dry solids, MP process time, maximum temperature of the MP and the HM content. For this article, MP of SS was also investigated with the aim of obtaining data of HM fixation in the input drying sludge and the output biochar of the small full-scale MP unit.

## 2. Materials and methods

#### 2.1. Low temperature slow MP unit

At BUT AdMaS is installed one laboratory and two full-scale units of SS using low temperature slow MP (Raček et al., 2017). We used a small unit to simulate real conditions at WWTP. The scheme of the small full-scale MP unit is reported in Figure 1, with capacity around 10 kg/batch of dried SS, the device work discontinuously. It consists of one batch reactor equipped with one high 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 (max. 300 minutes), it increased maximally up to 250 °C. The glass condensator attached to the pyrolyzer was used for separation of the pyrolysis oil and gaseous products. For incoming and reflected waves is installed a tuner. The pyrolyzed materials were pellets of SS made by pelletizing press (pellets) or directly by belt dryer (noodle shape).



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

#### 2.2. Sewage sludge

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 HM originating largely from industrial wastewater (WW). The treatment processes at WWTP are unique and depend on design of WWTP especially the design of the biological treatment and sludge management. Thus, SS composition and characteristics were different for various WWTPs.

#### Raw dried samples of SS

The testing of MP at the BUT AdMaS was carried out with samples of anaerobically digested and thermally dried SS from two different municipal WWTPs.

The WWTP1 has a capacity of around 531 000 population equivalent (PE), 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, the sludge was dried using a belt dryer at temperature lower than 85 °C. Tested raw dried SS samples 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.

#### Additives and MP process

Our previous research was focused on pretreatment of dried SS prior to the MP, and it was focused on pelletization of SS and its mixing with additives (Raček et al., 2017). Based on the literature data (Lutcha et al., 2015; Vollmer et al., 2004), for pelletization of SS are important penetration depth of microwave radiation and batch height. Generally, the knowledge on 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 created a kind of "micro-reactor". This could be similar to the so-called "pop-corn" effect. Another considerable benefit of such pelletization is the simplicity 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.

These additives were used: a catalyst, an organic matter and other additive. 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 of wood with high surface area, was added to SS for HM fixation in the biochar after MP of SS.

The tests of HM fixation before and after MP of SS process can be classified into the three groups:

• Group 1: SS from WWTP1 with additive biochar of wood;

- Group 2: SS from WWTP1 without additive;
- Group 3: SS from WWTP2 without additive.

After pelletization, the anaerobically digested 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 was mixed and pelletized with additive biochar from a mixture of different wood with DS of 2.0 %. The test was performed in the reactor of small full-scale MP unit, the process time of the MP was 210 minutes. 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 test was performed in the reactor of small full-scale MP unit, the process time of the MP was 240 minutes. 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 noodles (not pelletized). The test was performed in the small fullscale MP unit with raw sample of SS without any additive, the shorter process time of the MP was operated for 50 minutes. The temperature was managed via magnetron power control, the maximum temperature 148 °C of the MP was measured. After the MP test of SS was completed.

## 2.3. Determination of heavy metals

HM were determined in both raw SS and biochar. In principle, the HM can occur in two forms such as water soluble (extractable, leachable) and insoluble (non-extractable, non-leachable). Together, they give the total content of HM in investigated materials. The soluble HM were determined by analysis of water extracts, the total HM content was determined after digestion of samples in *Aqua Regia*.

# 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  $1000\pm0.002$  mg.l<sup>-1</sup> in 5% HNO<sub>3</sub>, from Analytika Ltd., Czech Republic (Czech Metrological Institute). All other used chemicals were of analytical reagent grade.

## Preparation of samples

Water extraction: 10 grams 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 hours. After 24 hours of extraction, the solution was filtered, diluted with distilled water in a ratio of 1:4 and subsequently analyzed.

Digestion in *Agua Regia*: 10 grams of the milled sample was transferred to a flask containing 60 ml of *Aqua Regia* (HCl:HNO<sub>3</sub> 3:1). The sample thus prepared was boiled under reflux for 2 hours. After cooling, the sample was filtered. For analysis, it was diluted with distilled water in a ratio of 1: 8.

## **Instrumentation**

Analyses of HM contents (As, Cd, Cr, Cu, Pb, Zn) were performed using atomic absorption spectrometer with electrothermal atomization ZEEnit 60 from Analytik Jena (Germany) with Zeeman background correction and selected hollow cathode lamp by Photron (Australia). Were used optimal measurement parameters and specific temperature program 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  $\mu$ l. All obtained results are the average of three separate independent determinations each were measured for atomic absorption spectrometer five times.

# 3. Results and discussions

### Content of HM

The total HM content and soluble HM 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 HM in the samples. Extracts in water represent HM biologically available for plants and other organisms. The resulting HM content of Group no. 1 is reported in Table 1 for samples of WWTP1 with pelletization and with additive biochar of wood in 2.0 % of DS weight concentration. Table 2 presents the content of HM in the samples of WWTP1 of Group no. 2 with pelletization, but without any additive. The element content of HM for

Group no. 3 can be observed in Table 3. The table describes HM such as Zn, Pb, As, Cr and Hg. The contents of Cd and Cu were not determined due to technical difficulties.

Description		Input /	Input / HM element content in the sample (mg/kg)								
Description		output	Zn	Cd	Pb	Cu	As	g) Cr 8.96 3.09 0.01 0.00	Hg		
Extraction in Aqua	CSSAR	SSIN	33.87	30.82	16.36	99.63	17.49	8.96	1.82		
Regia	CBCAR	BCOUT	32.45	5.79	3.81	23.74	11.35	kg) Cr 8.96 3.09 0.01 0.00	0.46		
E data di ancia	Cssw	SSIN	6.38	5.62	1.17	29.97	4.01	0.01	0.02		
Extraction in water	CBCW	BCOUT	9.25	5.79	0.00	4.54	0.00	0.00	0.00		

Table 1. HM content in the samples of WWTP1 with pelletization and with additive

Table 2. HM content in the samples of WWTP1 with pelletization, without additive.

Decomintion	Input /	HM element content in the sample (mg/kg)									
Description	output	Zn	Cd	Pb	Cu	As	Cr	Hg			
Extraction in Aqua	CSSAR	SSIN	33.87	30.82	16.36	99.63	17.49	8.96	1.82		
Regia	C <sub>BCAR</sub> BC <sub>O</sub>		107.83	13.71	19.80	24.73	19.26	8.20	0.73		
Extraction in water	Cssw	SSIN	6.38	5.62	1.17	29.97	4.01	0.01	0.02		
Extraction III water	CBCW	BCOUT	8.97	5.40	5.27	4.03	8.97	0.00	0.00		

Table 3, HM co	ontent in the samples of	of WWTP2	without 1	pelletization.	without additive.
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Description	Input /	HM element content in the sample (mg/kg)							
Description		output	Zn	Pb	As	As Cr H			
Extraction in Aqua Pagia	Cssar	SSIN	467.98	22.51	22.02	19.57	1.07		
Extraction in Aqua Regia	CBCAR	BCOUT	7.18	15.83	26.84	10.59	0.31		
Extraction in water	Cssw	SSIN	1.50	0.05	1.89	0.05	0.02		
Extraction in water	CBCW	BCOUT	2.09	5.20	5.19	2.57	0.00		

### Calculation of indicators

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

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

where BAHM<sub>SS</sub> represents biologically available HM in SS (mg),  $C_{SSW}$  is HM content in SS established by extraction in water (mg/kg) and SS<sub>IN</sub> is input weight of SS in (kg) to batch reactor of small full-scale MP unit.

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

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

where THM<sub>SS</sub> in (mg) stands for total HM in SS input and  $C_{SSAR}$  represents HM content in SS established by extraction in *Aqua Regia* (mg/kg). These HM amount were taken as 100 % if HM input weight entering the MP system (Figure 2).

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

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

where  $BAHM_{BC}$  in (mg) represents biologically available HM in biochar after MP,  $C_{BCW}$  is HM content in biochar established by extraction in water (mg/kg) and  $BC_{OUT}$  is output weight of biochar in (kg) from batch reactor of small full-scale MP unit.

The total HM in biochar (BAHM $_{BC})$  after MP used small full-scale MP unit was determined based on the equation:

Eq. 2

Eq. 1

Eq. 3

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

where  $THM_{BC}$  in (mg) stands for total HM in biochar output after MP and  $C_{BCAR}$  represents HM content in biochar after MP established by extraction in *Aqua Regia* (mg/kg).

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

$$HM_{FIXSS} = THM_{SS} - BAHM_{SS}(mg)$$
 Eq. 5

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

$$HM_{FIXBC} = THM_{BC} - BAHM_{BC}(mg)$$
 Eq. 6

The  $HM_{ND}$  represents non-detected HM in biochar and  $HM_{ND}$  was calculated by equation:

$$HM_{ND} = THM_{SS} - THM_{BC}(mg)$$
 Eq. 7



Figure 2. Transformation HM before (SS) and after MP process (biochar).

Transformation of HM by MP is illustrated in Figure 1 with columns in %, the left for HM in SS before MP and right for HM in biochar after MP process. The graph interprets biologically available HM by extraction in water (BAHM), HM fixation by extraction in Aqua Regia ( $HM_{FIX}$ ) and non-detected HM in biochar HM<sub>ND</sub>. The total HM in biochar THM<sub>BC</sub> was calculated by Eq. 4.

#### HM fixation

The content of HM (Zn, Cd, Pb, Cu, As, Cr and Hg) in the samples from WWTP1 and HM (Zn, Pb, As, Cr and Hg) in the samples from WWTP2 are reported in Table 1, 2 and 3.

As aforementioned, extraction in *Aqua Regia*  $C_{SSAR}$  (mg/kg) represents the total amount of HM in SS while  $C_{BCAR}$  (mg/kg) represents the total amount of HM in biochar and this amount includes also BAHM. The results of samples from WWTP1 with pelletization and additive indicate the HM fixation are reflected in indicators  $C_{SSAR}$ ,  $C_{BCAR}$  which were reduced after MP process, for example: Zn content 33.87 mg/kg was reduced to 32.45 mg/kg. For samples of WWTP1 with pelletization and without additive is HM fixation described by indicators  $C_{SSAR}$ ,  $C_{BCAR}$  for Cd, Cu, Cr and Hg, which were reduced and for Zn, Pb and As was HM fixation higher than before MP process, for example Pb content 16.36 mg/kg has increased to 19.80 mg/kg. Similar results were achieved with samples from WWTP2 without pelletization and without additive for As.

The results of extracts in water are reflected by indicator  $C_{SSW}$  (mg/kg), which represents biologically available HM in SS and  $C_{BCW}$  (mg/kg) representing biologically available HM in biochar. The results of samples from WWTP1 with pelletization and additive are characterized by biologically available HM for Pb, Cu, As, Cr and Hg  $C_{SSAR}$ ,  $C_{BCAR}$  were reduced after MP process, for example: Cu content 29.97 mg/kg was reduced to 4.03 mg/kg whereas for Zn and Cd were biologically available HM higher than before MP process, for example extractable Zn content 6.38 mg/kg increased to 8.97 mg/kg. Similar situation was observed with samples from WWTP1 with pelletization and without additive where biologically available Cd, Cu, Cr and Hg were reduced after MP process and HM of Zn, Pb and As was higher after MP process. Similar situation occurred with samples from WWTP2 without pelletization and additive, biologically available Hg was reduced after MP process and HM of Zn, Pb, As and Cr were higher after MP process.

The contents of HM 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. Weight of HM in the SS and biochar samples were calculated and results are reported in Table 4, 5 and 6 for Group no. 1-3.

The biologically available HM in SS BAHM<sub>SS</sub> (mg) before MP presented in Table 4, 5 and 6 were calculated by equation Eq. 1 using data of Table 1, 2 and 3. The total HM in SS THM<sub>SS</sub> (mg) before MP were calculated by using Eq. 2. The biologically available HM in biochar BAHM<sub>BC</sub> (mg) after MP were calculated by using Eq. 3. The total HM in biochar THM<sub>BC</sub> (mg) after MP is shown in Table 1, 2 and 3, these data were calculated by Eq. 4. The difference between the total HM in SS before MP THM<sub>SS</sub> and biologically available HM in SS before MP by Eq. 5 represents fixed HM in SS HM<sub>FIXSS</sub> (mg) which are biologically available for plants. Similarly, the difference between the total HM in biochar after MP THM<sub>BC</sub> and biologically available HM in biochar BAHM<sub>BC</sub> by Eq. 6 represents fixed HM in biochar HMFIX<sub>BC</sub> (mg), which are biologically unavailable.

Non-detected HM in biochar  $HM_{ND}$  (mg) after MP is calculated by using equation Eq. 7 for the difference between total HM in SS before MP and total HM in biochar after MP. The  $HM_{ND}$  can be identified by the HM, which probably volatized out of batch reactor of MP via the vapors to pyrolysis gas and pyrolysis oil. We cannot also reject a hypothesis that a part of non-detected HM could be fixed to structure of biochar and it is not extractable even by *Aqua Regia*.

						W	eight of I	HM (mg)						
Description	Z	'n	С	d	Р	'b	С	u	A	s	C	Cr	H	Ig
	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT
HM <sub>FIXSS</sub>	291.44	-	267.04	-	161.01	-	738.38	-	142.92	-	94.80	-	19.09	-
HM <sub>FIXBC</sub>	-	144.88	-	0.00	-	23.79	-	119.89	-	70.88	-	19.28	-	2.87
BAHM <sub>SS</sub>	67.60	-	59.61	-	12.39	-	317.73	-	42.46		0.15	-	0.16	-
BAHM <sub>BC</sub>	-	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	9.04	326	5.65	173	3.40	105	6.11	185	5.38	94	.95	19	.26

Table 4. Weight (mg) of HM in the samples of WWTP1 with pelletization and with additive.

Table 5. Weight (mg) of HM in the samples of WWTP1 with pelletization, without additive.

		Weight of HM (mg)													
Description	Z	'n	С	d	Р	'b		Cu	A	ls	C	r	I	łg	
	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCout	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT	
HM <sub>FIXSS</sub>	329.69	-	302.08	-	182.14	-	835.28	-	161.67	-	107.24	-	21.60	-	
HM <sub>FIXBC</sub>	-	722.83	-	60.80	-	106.21	-	151.39	-	75.20	-	59.93	-	5.33	
BAHM <sub>SS</sub>	76.47	-	67.43	-	14.02	-	359.42	-	48.04	-	0.17	-	0.18	-	
BAHM <sub>BC</sub>	-	65.62	-	39.45	-	38.56	-	29.43	-	65.62	-	0.01	-	0.01	
HM <sub>ND</sub>	-	0.00	-	269.26	-	51.38	-	1013.87	-	68.88	-	47.47	-	16.45	
THM	406	5.15	369	9.51	196	5.16	119	94.70	209	9.71	107	7.41	21	.78	

The data reported in Table 4 and Table 5 come from the same WWTP1 and represent the same raw pelletized input SS. The difference is that the data in Table 4 represents result of pelletized samples with additive, biochar of wood with concentration 2.0 %. The process time was operated for 210 and 240 minutes, the maximum temperature 211 and 190 °C, these were similar conditions. Weight of biologically available HM in biochar after MP BAHM<sub>BC</sub>, is shown in Table 4, is lower for all measured HM than BAHM<sub>SS</sub> before MP process. This similar result applies for Zn, Cd, Cu, Cr and Hg for sample of WWTP1 with pelletization and

without additive. 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).

		Weight of HM (mg)													
Description	Z	Zn	Pb		A	s		Cr	Hg						
	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT	SSIN	BCOUT					
HM <sub>FIXSS</sub>	1715.25	-	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	-	1699.53	-	35.96	-	1.58	-	40.62	-	3.00					
THM	172	0.76	82	.78	80	.97	71	.94	3.	93					

Table 6. Weight (mg) of HM in the samples of WWTP2 without pelletization, without additive.

The weight of HM in the samples of WWTP2 without pelletization and additive were characterized by equations Eq. 1 - Eq. 7 and results are reported in Table 6. The process time was operated for 50 minutes, the maximum temperature was 148 °C. These reported values of Zn, Pb, As, Cr and Hg contained significant different weight compared to Table 4 and 5.

The graphical representation in Figures 3-5 is performed to evaluate the three Groups no. 1-3 of weight results in %. For each individual HM, the left column represents HM before MP (SS) and after MP (BC).



Figure 3. Weight (%) of HM in the samples of WWTP1 with pelletization and with additive.

Graph in Figure 3 represents weight in % for samples from WWTP1 with pelletization and with additive 2.0 % biochar of wood. The columns illustrate reduction of these biologically available BAHM: Pb, As, Cr and Hg. For these four HM, the HM<sub>ND</sub> volatized out of MP batch reactor via the vapors to pyrolysis gas and oil, and part can be fixed to micropores of biochar. A similar situation occurred for Cd and Cu there has been a reduction in biologically available HM. A low reduction in the BAHM has been achieved with Zn. The highest HM<sub>FIX</sub> after MP has been achieved in Zn and As, these HM are biologically unavailable.



Figure 4. Weight (%) of HM in the samples of WWTP1 with pelletization and without additive.

Figure 4 represents the results of samples 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 HM were achieved in Cd, Cu and Hg, these HM were probably transported by vapors to pyrolysis gas and oil, and were fixed in structure of biochar.



Figure 5. Weight (%) of HM in the samples of WWTP2 without pelletization and without additive.

Figure 5 shows the weight in % of HM in the samples of WWTP2 without pelletization and without additive. The samples represent noodle shape of SS before and after MP process. A low reduction in biologically available HM (BAHM) was observed only in case of Hg. The high level of biologically available HM after MP process was achieved in Zn, Pb, As and Cr. The high levels of non-detected HM were achieved in Zn and Hg, these HM have been probably also transported by vapors to pyrolysis gas and oil, and were fixed in structure of biochar.

## Summarizing discussion

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

HM measurements revealed a significant structural heterogeneity of the SS. The  $HM_{ND}$  volatized out of batch reactor of MP via the vapors to pyrolysis gas and pyrolysis oil. The reported value of HM in Figure 3-5 shows thus significant reduction of Hg. It can be assumed that, under MP conditions, Hg was desorbed/vaporized and transported to pyrolysis gas and/or oil. In general, the significant level  $HM_{ND}$  was achieved in samples of Group no. 1, WWTP1 with pelletization and additive. Potential Hg evaporation was

partially expected due to reasons mentioned by Kistler (Kistler et al., 1987) and due to non-clear level of influence of vacuum

The biochar of wood was tested as an additive in samples of the Group no. 1. Generally, mixing of this additive with SS has received significant attention for low temperature slow MP of SS, additive is assumed to increase the surface area and the HM fixation in biochar.

The results of content HM in samples were compared in graphs in Figure 3-5, the significantly low level of biologically available HM after MP process was achieved in case of WWTP1 with pelletization and with additive 2.0 % biochar of wood. The process time in the Group no. 1 was operated for 210 minutes, longer than for samples of Group no. 3 which were operated for 50 minutes. We hypothesized that longer pyrolysis time process would lead to increasing immobilization of HM in biochar after MP. Therefore, this biochar of SS after MP seems to be applicable in agriculture use.

## 4. Conclusions

At the present first part, the applied research team of AdMaS Research Centre focused on new methodology for determination benchmarking balances of HM fixation low temperature slow full-scale MP of SS using two kind of extractions, extraction in Aqua Regia and extraction in water, accompanied by an impact on the environment. This method is suitable for the determination of HM content before and after pyrolysis in SS. The following research will be focused on BCR sequential extraction method and biomass additive evaluations. The significant required low level of biologically available HM after MP process, accompanied by an impact on the environment, was achieved with additive 2.0 % biochar of wood and longer MP process time.

This research suggests that MP of SS can be considered as suitable available technologies for ecofriendly 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, HM fixation, energy recover and water retention.

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#### **References**:

Callegari A. Hlavinek P. and Capodaglio A.G. (2017) Production of energy (biodiesel) and recovery of materials (biochar) from pyrolysis of waste urban sludge. Revista Ambiente e Agua ISSN 1980-993X, Revista Ambiente & Água, Brazil, 2018.

Capodaglio AG, Callegari A, Dondi D. Microwave-Induced Pyrolysis for Production of Sustainable Biodiesel from Waste Sludges. Waste and Biomass Valorization. 2016;7(4):703-709. doi:10.1007/s12649-016-9496-2.

Capodaglio AG, Callegari A. Feedstock and process influence on biodiesel produced from waste sewage sludge. J Environ Manage. April 2017. doi:10.1016/J.JENVMAN.2017.03.089.

Conte, P., Biochar, soil fertility, and environment. Biology and Fertility of Soils, 2014. 50(8): p. 1175-1175.

Conte, P., H.-P. Schmidt, and G. Cimò, Research and Application of Biochar in Europe, in Agricultural and Environmental Applications of Biochar: Advances and Barriers, M. Guo, Z. He, and M. Uchimiya, Editors. 2015, SSSA: 5585 Guilford Rd., Madison, WI 53711, USA.

Fonts I., Gea G., Azuara M., Abrego J., Arauzo J., Sewage sludge pyrolysis for liquid production: A review, Renewable and Sustainable Energy Reviews 16 (2012) 2781–2805.

Huang H., Yuan X., The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge, Bioresource Technology 200 (2016) 991–998.

Jin J., Li Y., Zhang J., Wu S., Cao Y., Liang P., Zhang J., Wong M.H., Wang M., Shan S., Christie P., Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge, Journal of Hazardous Materials, Volume 320, 2016, Pages 417-426, ISSN 0304-3894.

Kistler R.C., Widmer F., Brunner P.H.: Behavior of Chromium, Nickel, Copper, Zinc, Cadmium, Mercury and Lead during pyrolysis of sewage sludge, Environ. Sci. Technol. 21, 704-708 (1987)

Liu T., Liu Z., Zhengc O., Lang Q., Xia Y., Peng N., Gai Ch., Effect of hydrothermal carbonization on migration and environmental risk of heavy metals in sewage sludge during pyrolysis, Bioresource Technology 247 (2018) 282–290.

Liu X., Wang Y., Gui C., Li P., Zhang j., Zhong H, Wei Y., Chemical forms and risk assessment of heavy metals in sludge-biochar produced by microwave-inducted pyrolysis, RSC Adv. 6, 101960-101967, 2016. Lutcha J., Biomass microwave pyrolysis, Personal communication, lutchovi@volny.cz, (2015).

Menéndez JA, Inguanzo M, Pis JJ. Microwave-induced pyrolysis of sewage sludge. Water Res. 2002;36(13):3261-3264. doi:10.1016/S0043-1354(02)00017-9.

Raček J., Capodaglio A., Ševčík J., Chorazy T., Hlavínek P. Microwave pyrolysis treatment of sewage sludge: Performed at laboratory and full-scale conditions. In 17 th International multidisciplinary scientific geoconference SGEM 2017. International multidisciplinary geoconference SGEM. Bulgaria: SGEM, 2017. s. 107-114. ISBN: 978-619-7408-28-7. ISSN: 1314-2704.

Vollmer M., Physics of the microwave oven, Physics education 39, 74 - 81, (2004), doi: 10.1088/0031-9120/39/1/006.

Zhao B., Xu X., Xu S., Chen X., Li H., & Zeng F. (2017). Surface characteristics and potential ecological risk evaluation of heavy metals in the bio-char produced by co-pyrolysis from municipal sewage sludge and hazelnut shell with zinc chloride. Bioresource technology, 243, 375-383.