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Research Article

INFLUENCE OF CHARCOAL CALCINATION IN FIELD CONDITIONS ON HEAVY METAL CONTENT IN PLANTS AND IN THE IMMEDIATE VICINITY OF THE RETORTS

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ABSTRACT
One of the ways of charcoal producing is its calcination in charcoal kilns called retorts in field conditions. In the charcoal production wood of deciduous trees is being subjected to the process of dry distillation. The process affects the surrounding environment. During the process a lot of pollutants are emitted to natural environment. One of them is ash, which contains heavy metals. The paper aimed at determining the effect of charcoal calcination on heavy metal content in the soil and plant material in the immediate vicinity. Charcoal calcination causes the alkalinization of the soil to 10 metres. In the closest vicinity, the calcination process increases Mn, Cd, Ni and Cu concentrations in the soil material. The influence of charcoal production on the concentrations Fe, Zn, Pb, Cr in soil material cannot be determined unanimously. The effect of the process on heavy metal content in plant material cannot be determined unanimously.

Keywords: charcoal, dry distillation, heavy metals, effect.

INTRODUCTION

Charcoal is one of the basic products produced during the wood “dry distillation” process. It is a light, black substance of low density, whose main factor (80%) is carbon [Encyklopedia... 2008]. It is used in everyday life, in metallurgical industry and for manufacturing carbonaceous electrodes, it was once used for producing activated carbon for water purification [Dębowski 1987]. Developing industry brought a necessity for developing a fast and easy way of its manufacturing, therefore, the Department of Forest Utilization and Forest Engineering, SGGW developed a technology of charcoal calcination in field conditions [Laurow 1996, 1997].

The best raw material for charcoal production is wood of deciduous trees. During a process of dry distillation occurring in special charcoal kilns called retorts organic matter is exposed to thermal energy at simultaneously limited access of atmospheric air [Rzedkowski 1999]. Finally, the percentage of final products is as follows: charcoal (35%), water (26.6%), gases (15.8%), mainly carbon dioxide, carbon oxide, ethylene, methane and tar sediment (8.11%), soluble tar (5.9%), acetic acid (6%), methanol (2.1%) and acetone (0.2%) [Rzedkowski 1999].

Initially, calcination was regarded as safe for the environment, because it generates pollution, the same as wood used for heating houses. The first investigations revealed that the only hazard was emission of temperature, CO and CO_2 into the air. Subsequent research pointed to the content of suspended and falling particulate matter and CO, SO_2, CH_2O and $C_2H_4O_2$ [Laurow 1996].

It was established that the harmful effect of the process is perceptible only in the close proximity of calcination site, not exceeding 50 m [Rzedkowski 1999].

The authors of charcoal calcination technology did not take into consideration possible emission of heavy metals to the environment, which might accumulate in the immediate vicinity. Therefore, a question arose whether charcoal production in field conditions influences heavy metal content in the soil and plants in direct vicinity of the installation.

METHODS

The soil material for analyses was collected in the area of active charcoal calcination area in the podkarpackie province, Komańcza Forest Inspectorate. The area around the calcination place was fresh mountain forest site, on three sides surrounded by closed forest, whereas to the south by grasses with some bushes. A small watercourse was flowing nearby. The installation for charcoal calcination in field conditions was constructed of 12 active retorts and auxiliary infrastructure, situated in a valley on three sides (to the north, east and west) surrounded by hills. Wood of deciduous trees (mainly alder and beech) was burned in the retorts. The set of retorts selected for the research was active during the whole vegetation period of the year when soil and plant material were sampled for analyses. Generally the set of retorts was operating for minimum of 5 years.

The soil material was collected in points by means of Egner's stick from the top layer of the soil cover (0–10 cm) in September 2011, from 4 cardinal directions (north, east, south and west) at the distance of 10.20 and 30 meters from the retort set. Approximately 1 kg of soil was collected as an average sample from the area of about 0.5 m^2 at a given distance. The directions of sample collection were established according to compass, where the reference point was the extreme retort to the given geographical direction. The soil material was dried in natural conditions and sifted through a sieve with 1mm mesh. Plant material from grass communities was collected into linen bags at the same time as the soil material. It was gathered from four cardinal directions, at the distance of 10, 20 and 30 meters from the retort set, in the area of about $1m^2$. The material was dried and then ground.

Granulometric composition, pH in soil and water and soil with 1 $mol \cdot dm^{-3}$ KCl

solution suspension, electrolytic conductivity and total content of heavy metals were assessed in the soil material with methods commonly applied in environmental chemistry. Heavy metal concentrations were determined in the plant material [Ostrowska et al. 1991]. The paper presents average values from two replications and four geographical directions (n = 8) depending on the distance from the extreme retort.

RESULTS AND DISCUSSION

The soil material from the area under the influence of charcoal calcination sites was mostly classified to medium and heavy loams. Proportion of floatable particles in the soils classified to medium loams ranged from 41% to 69%, while in heavy loams from 53% to 70%.

The soil reaction of the material collected closest to the retorts ranged from 4.03–6.71 in soil and water suspension and from 3.34–6.01 in soil and KCl suspension (Table 1). The changes of maximum and minimum values and values of mean pH in the investigated area may evidence an alkalinizing effect of charcoal calcination in field conditions on the soil environment in the immediate retort vicinity, however the factor varies widely. In the research of Rzadkowski et al. [1999], the soil revealed the highest pH at the distance of 25 m from the active retorts and the value was decreasing with increasing distance from the installation. This distribution of soil pH values is caused by dispersion in the environment of one of pyrolysis side-effects (ash). The best raw material for charcoal production are deciduous trees, which after burning contain about 0.34–05.2% of ash (data for beech and oak tree) and reveal pH from 11.47–11.71, therefore, wood ash causes soil alkalinization [Ciesielczuk et al. 2011]. According to Arvidsson, Lundkvist [2003] and Park and others [2005] ash which comes from the burned trees is contributing to a large extent to the alkalinization of soil and it influences the amount of alkaline cations in the soil. Changeability of pH with the distance may result from the frequency of works around the retorts together with ash granulometric fraction translocation with ash fallout.

Changes occurred in the minimum, maximum and mean value of electrolytic conductivity in the soil material originating from the distance of less than 20 m from the installation in relation to the value characterizing the material collected at 30 meters from the retorts (Table 1). Average value of electrolytic conductivity ranged from 0.071– 0.114 mS·sm^{-1}.

Charcoal calcination in field conditions influences heavy metal content in soil material (Table 2). Average content of Mn, Cd, Ni and Cd in the soil material decreases with the distance from the retort set. Mn concentration decreases from 822.8 to 506.88 mg·kg^{-1} of soil. Cd content fluctuates from 0.25 to 0.07 mg·kg^{-1} of oil, whereas Ni ranges from 40.98 to 26.94 mg·kg^{-1} of soil. Cu concentration diminishes from 22.39 to 17.35 mg ·kg^{-1} of soil. An opposite tendency than in previously noted for pH and electrolytic conductivity was observed for Fe, Zn, Pb and Cr, because at 20 m from the set of operating retorts an increase in heavy metal concentrations occurred in relation to their content in the soil material collected at 10 and 30 m from the operating retorts. Obtained results did not corroborate the relationships observed by Rzadkowski [1999]. In his research charcoal calcination most probably affected Fe concentrations, because with growing distance from the retorts its content in the top layer of the soil material decreased up to the distance of about 50 m. In the research of the same author Mn and Zn content was gradually increasing to the distance of 50 m. Pb content declined to 25 m, then grew to the distance of 50 m and again decreased at longer distances. Considering Cu, its slight increase to the distance of 25 m was followed by the decline of its content in the soil material collected 50m from the retorts. Increasing content of this element was observed in material collected at longer distances. Heavy metal concentrations in the soil material might have been also affected by the ash from wood burning, since it contains great amount of these metals. According to Ciesielczuk, Kusz and Nemś [2001] ash from beech tree contains 45197 mg·kg^{-1} Mn, 1284.2 mg·kg^{-1} Zn, 231.8 mg·kg^{-1} Cu, 187.2 mg·kg^{-1} Ni, 52,40 mg·kg^{-1} Pb, 24.45 mg·kg^{-1} Cr and 1.30 mg·kg^{-1} Cd. Such high amounts of heavy metals in the ash, which is freely emitted outside the installation during retort unloading, may to a great extent affect the direct vicinity. On the other hand, the above mentioned authors state, after Wirsz and Matwiejew [2005] that the literature data reveal

Table 1. Minimum, maximum and man values of pH and electrolytic conductivity

Distance from retorts [m]	pH						Electrolytic conductivity [mS · cm^{-1}]		
	H_2O			KCl					
	minimum	maximum	mean ± SD	minimum	maximum	mean ± SD	minimum	maximum	mean ± SD
10	4.37	6.71	5.21±1.03	3.34	6.01	4.20±1.22	0.048	0.131	0.088±0.03
20	3.99	4.81	4.48±0.35	3.07	3.57	3.35±0.21	0.041	0.114	0.071±0.03
30	4.02	6.50	5.42±1.09	3.00	5.73	4.25±1.13	0.068	0.239	0.114±0.08

Explanation: SD – standard deviation.

Table 2. Content of total forms of elements in the soil material from the topsoil (0–10 cm) collected at 10, 20 and 30 m from the set of retorts

Element	Distance from retorts [m]								
	10			20			30		
	Content [mg · kg^{-1} d.m.]								
	minimum	maximum	mean ± SD	minimum	maximum	mean ± SD	minimum	maximum	mean ± SD
Fe	15900.0	21187.5	19025.0±2379.8	17900.0	22537.5	20090.6±3141.9	13800.0	21518.8	18817.2±3452.7
Mn	568.88	995.25	822.80±202.50	317.50	929.75	724.38±270.44	167.63	1181.63	506.88±463.93
Zn	54.94	73.52	65.26±9.11	67.19	80.51	71.06±8.06	40.81	73.59	55.25±13.20
Cd	0.04	0.49	0.25±0.26	0.05	0.34	0.13±0.18	0.05	0.09	0.07±0.04
Pb	13.60	25.26	18.67±4.59	18.26	26.14	22.07±6.62	15.84	23.59	22.02±6.94
Ni	34.81	46.87	40.98±6.34	22.23	46.41	37.77±12.26	21.19	37.29	26.94±7.37
Cu	19.96	25.19	22.39±3.06	13.02	28.75	22.04±7.40	9.90	23.66	17.35±5.77
Cr	15.92	22.66	20.50±3.06	19.36	22.71	21.10±1.99	17.11	22.33	19.25±4.04

Explanation: SD – standard deviation.

a higher content of chromium (30.8–133.3 mg/kg d.m.) but much lower manganese concentrations (68.7–398.0 mg/kg d.m.) in ash from wood briquettes. Also lower Zn concentration was registered, on the level of 9.75–47.7 mg/kg d.m. In the presented investigations, the material from the charcoal calcination site had the highest contents of Fe and Mn, then Zn, Ni, Pb, Cu and Cr but much lower quantities of Mn and Cd.

High values of standard deviation evidence a considerable diversification in the content of the analyzed elements in the soil material collected at the same distance from the operating retorts set. It is due to the specificity of the research object, because field experiments favour a considerable diversification of elements in soil. It may additionally testify an unequal effect of charcoal calcination in field conditions. It is most probably also caused by specific character of the terrain and possible tunnel effect, but also by prevalence of northern and southern winds [Michnia and Paczos 1972].

Charcoal calcination also influences heavy metal concentrations in the plant material from the immediate neighbourhood (Table 3). For Fe, Zn, Cd, Pb, Ni, Cu and Cr a tendency for their content diminishing was noted in the plant material collected 20 meters from the retorts in comparison with the contents in plants gathered at 10 and 30 meters. Only for Mn a tendency for its increasing concentration in the plant material became visible with increasing distance from the calcination site and it is opposite to the relationship noted for this element content in the soil material. In case of Fe, Ni, Cu and Cr the highest concentrations were registered in the soil material from the immediate vicinity of the retorts. On the other hand, the highest contents, as compared with the other sampling places, were assessed at the distance of 30 meters from the installation for Zn, Cd and Pb. The tendency observed for a majority of selected metals, i.e. their decreased content in the material collected at 20 m from the installation, has not been confirmed by a generally accepted principle that the lower pH, the more heavy metal forms available to plants. Soil reaction is one of the main factors conditioning the form in which heavy metals occur in the soil environment and therefore their availability to the local vegetation [Kabata-Pendias and Pendias 1999]. Decreasing pH of the soil material from slightly acid and acid, such as in this case to 4.48 and 3.35 should cause an increase in bioavailable metal forms in soil [Kwiatkowska-Malina, Maciejewska 201]. However, no such pH effect was observed. The situation might have been affected by organic matter content in soil, since it influences the strength of impact on heavy metal solubility. In soil enriched with organic matter (in this case charcoal) bioavailability of heavy metal forms and their toxicity to plants decrease [Kwiatkowska-Malina, Maciejewska 2009, 2011]. Confirmation of this thesis requires additional investigations of the area.

CONCLUSIONS

1. Charcoal calcination in field conditions had an alkalinizing effect and caused a decrease in electrolytic conductivity value in soil material in the immediate vicinity – 10 meters from the installation.

Table 3. Content of total forms of elements in the plant material collected at 10, 20 and 30 m from the set of retorts

Element	Distance from retorts [m]								
	10			20			30		
	Content [mg · kg^{-1} d.m.]								
	minimum	maximum	mean ± SD	minimum	maximum	mean ± SD	minimum	maximum	mean ± SD
Fe	1310.50	7358.50	3918.00±2592.59	538.85	2905.00	1328.61±1041.66	675.85	7616.50	3171.66±3024.65
Mn	196.90	399.50	287.26±79.22	264.70	554.25	399.94±111.92	292.80	1181.50	664.58±358.18
Zn	37.68	51.54	44.16±5.41	24.39	45.28	35.43±9.59	38.49	78.39	49.99±18.39
Cd	0.20	0.54	0.33±0.14	0.11	0.26	0.17±0.07	0.32	1.15	0.73±0.52
Pb	1.24	4.69	2.89±1.32	0.80	2.43	1.37±0.75	1.28	10.89	4.18±4.22
Ni	4.02	15.53	9.24±4.47	3.44	7.20	4.90±1.55	5.78	16.84	8.77±5.05
Cu	8.43	11.84	10.03±1.47	3.02	9.91	6.05±2.69	5.14	6.73	6.11±1.30
Cr	3.57	14.53	7.86±4.75	2.51	5.71	3.65±1.36	3.43	10.63	6.47±3.25

Explanation: SD – standard deviation.

2. Calcination process influences an increase in the content of total forms of Mn, Cd, Ni and Cu in the soil material in the close proximity of the retorts.
3. It cannot be unanimously stated if charcoal calcination immediately affects heavy metal concentrations in plants.

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