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Immobilization of Heavy Metals in Biochar Derived from Biosolids: Effect of Temperature and Carrier Gas

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Abstract: Slow pyrolysis was carried out in biosolids under three different temperatures (400, 500 and 600 °C) and two different carrier gases (CO_2 and N_2) on a fluidized bed reactor. The total concentration, chemical fractionation, and plant availability of the heavy metals in biochar were assessed by standard methods. The total concentration of Fe, Zn, Cu, Mn, Cr, Ni and Pb increased with the conversion of biosolids to biochar and with increasing pyrolysis temperature. The community's Bureau of Reference (BCR) sequential extraction identified the migration of metals from toxic and bioavailable to potentially stable available or non-available forms at higher pyrolysis temperatures. Diethylenetriamine penta-acetic acid (DTPA)-extractable metals (Cu, Zn, Cd, Cu, Fe and Pb) were significantly lower in biochar compared to biosolids. By replacing N_2 with CO_2, the total metal concentration of heavy metals was significantly different for Mn, Ni, Cd, Pb and As. There were larger amounts of metals in the residual and oxidizable fractions compared to when N_2 was used as a carrier gas. Consequently, the biochar produced at higher temperatures (500 and 600 °C) in the N_2 environment exhibited lower potential ecological risks than in CO_2 environments (69.94 and 52.16, respectively, compared to values from 75.95 to 151.38 for biochars prepared in N_2). Overall, the results suggest that the higher temperature biochar can support obtaining environmentally safe biochar and can be effective in attenuating the ecological risks of biosolids.

Keywords: biochar; biosolids; carrier gas; heavy metals; pyrolysis

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1. Introduction

Biosolids are the treated sewage sludge produced in wastewater treatment plants. The increasing human population results in a larger production of biosolids. In 2019, the production of biosolids in Australia was estimated at 371,000 tonnes, of which ~67% were used in agricultural land, and the rest was utilized in non-agricultural applications [1]. Biosolids are a source of organic matter and nutrients (N, P and K) and can potentially improve soil structure and fertility. Despite this, there could be many chemicals of concern in biosolids. For instance, heavy metals, pathogens, polycyclic aromatic hydrocarbons (PAHs), dioxins, furans and pesticides are often present and could limit land application [2–4]. These pollutants are associated with different environmental risks, including heavy metal accumulation in the human body via food chain contamination, which has the potential to lead to serious health

hazards [5]. Therefore, the land application of biosolids has been subject to stringent regulations in recent times. In Victoria, Australia, only the least contaminant (C1) and highest treatment (T_1) grades of biosolids have unrestricted application in agricultural soils [6]. A large proportion of biosolids do not meet the criteria for sustainable land application, and alternative management is required for these.

Pyrolysis of biomass is a thermochemical technique that produces biochar, a carbon-rich solid material, in a limited oxygen environment. Whilst pyrolysis degrades persistent organic contaminants and pathogens in biosolids, volatilizes light organic compounds and promotes condensation/dehydration reactions, the resulting biochar becomes enriched in heavy metals due to their high thermal stability [7]. The concentrations of Cu Zn, Pb, Cr, Mn and Ni are largely increased in biochars with increasing pyrolysis temperature [8,9]. However, the highly volatile (low boiling points) metals such as As, Hg and Cd can have reduced concentration in the biochar compared to the parent biosolids depending on the pyrolysis conditions. For instance, Zhang et al. [10] observed that Hg almost completely partitioned in the oil and gas product fractions during pyrolysis at 300 °C while Cd and As had less than 10% recovery in the biochar at 650 °C.

Besides the general increase in heavy metal concentration in biochar, there has been a strong interest in studying the heavy metal leachability and toxicity in biochar produced from biosolids [5,7]. Most of the heavy metals are converted into oxidizable and residual forms at higher pyrolysis temperatures, usually around 600 °C, which significantly decreases their bioavailability, leading to a very low environmental risk of biochars [5]. It has been demonstrated that the bio-available contents of DTPA-extractable metals are lower in biochar compared to biosolids and that the concentration of bioavailable heavy metals in biochar decreased with increasing pyrolysis temperature [7,11]. However, the elevated heavy metal content demands an assessment of the potential risk posed by the biochar when applied to the soil.

The pyrolysis of biosolids requires an oxygen-free atmosphere to minimize oxidation reactions by continuously flowing N_2 or other inert carrier gases such as CO_2 throughout the process. The use of different carrier gases during pyrolysis has been reported to impact the pyrolysis process and product characterization. Different studies [12–14] have used CO_2 as a carrier gas to produce biochar with a higher surface area and lower content of PAH and leachable metals compared to when the N_2 atmosphere was used. The higher surface area of biochar produced in a CO_2 atmosphere benefits metal (loid) immobilization in soil compared to that produced in an N_2 atmosphere [14,15]. Moreover, Gao et al. [16] reported that carrier gas (CO_2 or N_2) played a significant role in the physicochemical properties and level of the contaminants in biochar. Liu et al. [17] suggested that using CO_2 as a carrier gas during pyrolysis could produce biochar with superior adsorption capacity due to higher surface area and high pore volume, which could enhance heavy metal sorption [10].

In our previous work [18], we demonstrated that a careful selection of temperature and carrier gas can fine-tune the physico-chemical properties of biochar derived from biosolids. However, a detailed identification of the migration characteristics of heavy metals, their toxicity, and plant availability in different pyrolysis atmospheres and temperatures has not been explored. In addition to this, the study of biochars prepared at different temperatures and in different atmospheres can be considered novel, as evidenced by a very limited amount of articles on this topic. This study aims to investigate the role of pyrolysis temperature and carrier gas on migration characteristics, and the bioavailability of heavy metals in biochar derived from biosolids.

2. Materials and Methods

2.1. Sample Collection and Biochar Preparation

2.1.1. Biosolids Collection

The treated sewage sludge (biosolids) was collected from the Mount Martha Water recycle plant, Southeast Water Corporation, Melbourne (38°16′06″ S and 145°03′31″ E), Australia. Lagoon and aerobic digestion were used for the sewage treatment. The digested

sewage sludge was processed by dosing polymer, dewatered using a belt press filter, and finally dried in a solar dryer to reduce the moisture content to 60%. The samples used in this study were the solids collected from the solar dryer, then grounded using a laboratory mill and sieved through (0.5–1.0 μm) aperture. The prepared sample was oven-dried at 105 °C overnight before further use.

2.1.2. Biochar Production

A fluidized bed reactor constructed of a quartz tube was used in a slow pyrolysis mode for biosolids pyrolysis. Detailed descriptions of the reactor features and setup can be found in our previous work [1]. Forty grams of oven-dried biosolids were weighed and placed in the quartz tube reactor. Then, the reactor and its contents were purged with either N_2 or CO_2 flowing at 7.5 L min^{-1}. The reactor was sealed up under a continuous flow of carrier gas. The reactor was heated under atmospheric pressure, and the temperature was controlled in three zones by thermocouples. Three different pyrolysis temperatures (400, 500 and 600 °C) were selected in nitrogen (N_2) or carbon dioxide (CO_2) atmospheres. The reactor with the biosolids feed was initially heated from room temperature to the desired pyrolysis temperature and maintained for 60 min at the desired temperature and carrier gas. The heating ramp was set at ~35 °C min^{-1}. The pyrolysis oil was collected in a steel condenser. The temperature of the connecting tube at the reactor outlet to the condensing unit was maintained at 280 °C to prevent vapor condensation using an external heating coil. The gas was analyzed online using a micro-GC. The biochar samples were collected from the reactor after the experiments and labeled accordingly. The biochar samples were denoted as BC400, BC500, BC600, BN400, BN500 and BN600, where C and N represent the carrier gases CO_2 and N_2, respectively, and 400, 500 and 600 indicate the pyrolysis temperature. The produced biochar was stored in a fridge before further analysis. The iochar yield was calculated by Equation (1).

$$\text{Biochar yield (wt\%)} = W_2/W_1 \times 100 \quad (1)$$

where W_1 is the total dry weight of biosolids used, and W_2 is the total weight of the biochar after pyrolysis.

General physicochemical properties of the biosolids and biochar, including the ultimate and proximate analysis, XRD analyses, and SEM, have been reported elsewhere [18].

2.2. Analysis of Heavy Metals

2.2.1. Determination of Total Concentration of Heavy Metals

The total concentration of heavy metals in the biosolids and the produced biochar was determined using the USEPA 3050B method [19,20]. Briefly, 1.0 g of biosolids or biochar sample was taken in a VELP thermal glass vessel, and 10 mL of 1:1 (*v*/*v*) HNO_3 was added. The mixture was heated at 95 °C for 2 h without boiling under reflux in a water bath. Then, 5 mL of concentrated HNO_3 was added to the mixture after cooling to below 70 °C. Heating was then continued for 30 min under reflux without boiling. This process was repeated until the samples gave no brown fumes, which indicated a complete reaction with HNO_3. After this process, the solution was evaporated to around 5 mL by heating for 2 h at 95 ± 5 °C without boiling. Following the complete digestion of the samples in HNO_3, 2 mL of 18-MΩ water was added, followed by 10 mL of 30% H_2O_2. The resulting solution was heated until the effervescence subsided, and the solution volume was reduced to ~5 mL by heating at 95 °C without boiling for 2 h. After cooling, the sample was diluted with 100 mL water, followed by filtration and centrifugation to remove the particulates. Finally, the diluted liquid samples were quantified for metal contents using an Inductive coupled plasma mass spectrometry (ICP-MS 7700 Series, Agilent Technologies, Santa Clara, CA, USA) instrument.

2.2.2. Sequential Extraction of Heavy Metals

The chemical speciation of heavy metals contents in biosolids and their biochar were determined by sequential extraction using a modified three-step BCR sequential extraction procedure. This method allows the chemical classification of heavy metal species into four fractions—exchangeable and acid-soluble (F1), reducible (F2), oxidizable (F3) and residual (F4) [21]. The procedure is briefly discussed below.

F1 (exchangeable and acid-soluble fraction): Briefly, 0.5 g of oven-dried samples (biosolids or biochar) and 20 mL of acetic acid (0.1 M) were added in a 50 mL Eppendorf tube and agitated at 180 rpm and 25 °C for 16 h. The slurry was separated into an aqueous stream and a solid residue by centrifugation at 4000 rpm for 20 min. The aqueous stream was further filtered through a 0.45 µm nylon membrane, and the solid residue was washed with deionized water. The clear aqueous phase contained the acid-soluble/exchangeable fraction related to exchangeable metals and carbonates, and their contents were quantified in ICP-MS.

F2 (reducible fraction): The solid residue obtained from F1 was added with 20 mL hydroxylamine hydrochloride solution (0.1 M, pH 2.0) and shaken for 16 h at 180 rpm and 25 °C to obtain the reducible oxides related to Fe and Mn oxides. Following centrifugation, the liquid phase was filtered, diluted and analyzed for metal contents in ICP-MS, and the solid residue was washed with deionized water.

F3 (oxidizable fraction): First, 5 mL of 30% H_2O_2 (pH 2.2) was added to the solid residue from F2 with intermittent agitation at 25 °C for 1 h. Then, 5 mL of H_2O_2 was added to the solution and heated to near dryness in a water bath at 85 °C for another 1 h. After cooling, 25 mL of 1 M ammonium acetate (NH_4Oac, pH 2.0) was added and stirred at 25 °C for 16 h to obtain the oxidizable metals fraction bound to organic matter.

F4 (residual fraction): The solid residue obtained in F3 was digested using the 3050B method described earlier. The recovered liquid stream contained the residual metal fraction and was measured in ICP-MS.

A portion of the extracted liquids in F1–F3 was digested to remove dissolved organics with a mixture of concentrated acid (H_2O_2: HNO_3 = 1:1, *v*/*v*) on a hot plate at 100 °C and then diluted to a constant volume (50 mL) with 2% HNO_3 added before ICP-MS analysis.

2.2.3. Evaluation of Risk Assessment Code

The environmental risk of heavy metals in biosolids and their biochar was determined using the Risk assessment code (RAC) in Equation (2), where F1 is the bioavailable fraction, and TC indicates the total concentration of heavy metals (mg kg^{-1}). There are five types of risk: no risk (NR), RAC < 1%, low risk (LR) 1% ≤ RAC <10%, medium risk (MR) 10% ≤ RAC < 30%, high risk (HR) 30% ≤ RAC <50% and very high risk (VHR), RAC ≥ 50% [22,23]. It will identify the environmental risk of toxic heavy metals associated with biosolids and their biochar. The potential ecological risk was calculated by using Equations (3)–(5):

$$RAC = F1/TC \times 100 \quad (2)$$

$$Cf = Ci/Cn \quad (3)$$

$$Er = Tr \times Cf \quad (4)$$

$$RI = \sum Er \quad (5)$$

where *Cf* is the individual heavy metals contamination factor (Table 1); Ci is the content of individual heavy metals distributed in bioavailable fractions (F1 + F2 + F3); Cn is the content of individual heavy metals distributed in F4; *Er* is the potential toxic factor of the individual heavy metal; and RI is the potential ecological risk index. The *Tr* values are the "toxic-response" factor for the given substance that was used for the calculation of the potential ecological index for individual metals are Cr (2), Cu (5), Ni (6), Zn (1), Pb (5), Cd (30), As (10) and Mn (1) [5,24]. The value of *RI* is the potential ecological risk caused by overall heavy metal contamination [25].

Table 1. Ecological risk assessment for biosolids and their produced biochar, where Cf = contamination factor and Er = potential ecological risk factor for the individual heavy metal, while *RI* is the sum of the potential ecological risk index (Er) of each heavy metal.

C_f	Metal Contamination	E_r	Potential Ecological Risk	*RI*	Biosolids/Biochar Contamination
$C_f \leq 1$	Clean	$E_r \leq 40$	Low	$RI \leq 150$	Low
$1 < C_f \leq 3$	Low	$40 < E_r \leq 80$	Moderate	$150 < RI \leq 300$	Moderate
$3 < C_f \leq 6$	Moderate	$80 < E_r \leq 160$	Considerate	$300 < RI \leq 600$	Considerate
$6 < C_f \leq 9$	Considerate	$160 < E_r \leq 320$	High	$RI > 600$	High
$C_f > 9$	High	$E_r > 320$	Very high	-	-

2.2.4. Determination of Bioavailability of Heavy Metals in Biochar Derived from Biosolids

The bioavailability of heavy metals in biosolids and biochar was determined by DTPA extracting solution as per method 12A1 [26]. A liter of DTPA extracting solution was prepared by dissolving 1.97 g of DTPA, 1.47 g of calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) and 14.92 g of triethanolamine in Milli Q water with pH adjusted to 7.3 using HCl. The biochar sample and extracting solution (1:10 g/mL) were equilibrated into a 50 mL polyethylene bottle and continuously agitated on a mechanical shaker for 2 h. The extracts were filtered and digested with 2% HNO_3. The extractable metal concentrations were measured by ICP-MS [27].

2.3. Data Analysis and Statistical Significance

Data resulting from all the metals analysis of biosolids and biochar were tested for normality using the Shapiro–Wilk test. Data were log-transformed when they did not meet the normality test. A two-way analysis of variance (ANOVA) was performed to identify the effects of temperature (400, 500 and 600 °C) and carrier gas (environment, N_2 or CO_2) and their interactions. A post hoc analysis was carried out for temperature using Tukey's test. All data were analyzed in the SPSS 26.0 version, and the significance level was set at $p < 0.05$.

3. Results and Discussion

3.1. Total Concentration of Heavy Metals

The total concentration of heavy metals in biosolids based on a dry mass, along with maximum allowable limits according to EPA Victoria biosolids guidelines [6] and international biochar guidelines [28], is presented in Table 2. The heavy metals content varied greatly in biosolids; the sequence was Zn > Cu > Mn > Cr > Ni > Pb > As > Co > Cd. The high contents of Zn (1424 mg kg^{-1}), Cu (1029 mg kg^{-1}) and Cd (1.37 mg kg^{-1}) would disqualify the biosolids from being classified as Grade C1. The higher concentration of Zn and Cu is likely related to massive utilization in galvanized pipelines for transporting wastewater, while Cu can be related to the high proportion of trade metals effluent, leading to a limitation to the direct application of biosolids in the land [10,29].

Pyrolysis temperature significantly increased the total concentration of Cr, Mn, Cu, Ni, Zn, Cd, and As (Figure 1) ($p < 0.05$), while Co and Pb did not show any significant difference ($p > 0.05$, Table 3). The increase in metal concentration with pyrolysis temperature was mainly associated with the loss of organic mass, resulting in an enrichment of heavy metals [30]. Additionally, heavy metals mainly exist in various metal salts such as carbonate, chlorate, phosphate and sulfate in sewage sludge, which is converted into oxide and sulfides with greater thermostability. As a result, the major portion of heavy metals is retained in biochar after pyrolysis [8].

Table 2. The total concentration of heavy metals (mg kg^{-1}) in biosolids and limits according to the Victoria Guidelines for the environmental management of biosolids (grade C1 and Grade C2) and the international biochar guidelines.

Heavy Metals	Biosolids	C1 Grade	C2 Grade	International Biochar Guidelines
Cr	72.21 ± 1.45	400	3000	93–1200
Co	3.65 ± 0.25	N/A	N/A	34
Mn	321.18 ± 4.98	N/A	N/A	N/A
Ni	33.01 ± 0.99	60	270	47–420
Cu	1029.19 ± 3.26	100	2000	143–6000
Zn	1424.36 ± 21.71	200	2500	416–7400
Cd	1.37 ± 0.01	1	10	1.4–39
Pd	17.51 ± 0.34	300	500	121–300
As	3.09 ± 0.64	20	60	13–100

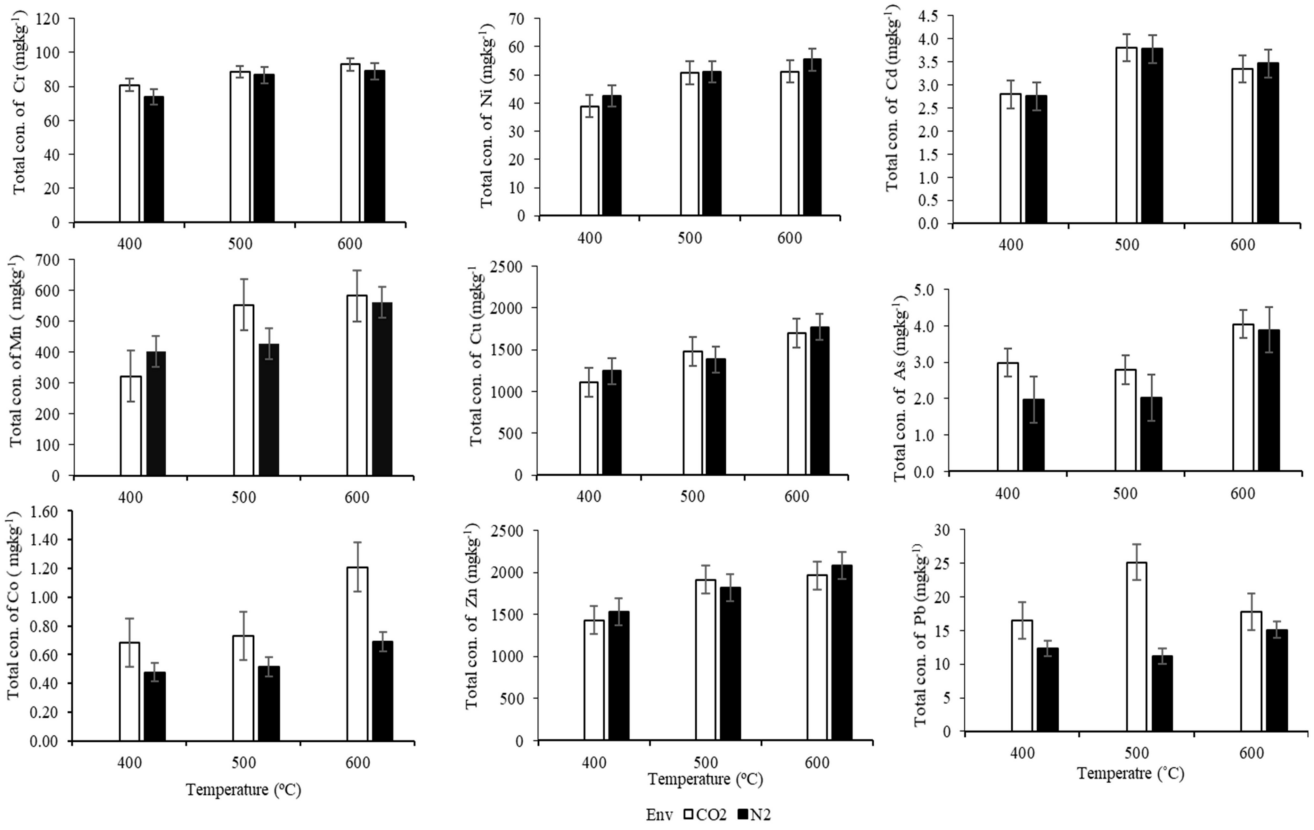

Figure 1. Total concentration of heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb and As mg kg^{-1}) in biochar produced from biosolids at three different temperatures (400 °C, 500 °C and 600 °C) in CO_2 and N_2 carrier gases. The error bars represent the standard deviation (n = 3).

The pyrolysis environment had a significant effect ($p < 0.05$, Table 3) on Mn, Ni, Cd, Pb and As. The results showed that the total concentration of Mn, Pb and As were slightly higher in a CO_2 atmosphere, while the concentration of Ni and Cd were higher under N_2. A previous study [14] reported similar results where higher metal concentrations were observed in biochar produced in CO_2 resulting from the higher feedstock mass loss during pyrolysis in an atmosphere of CO_2 compared to N_2. A higher pyrolysis temperature resulted in more loss of feedstock mass, which aggravated the effect of increased metal concentration. There was a significant interaction for temperature * environment ($p < 0.05$,

Table 3) for Mn, Cu, Zn, Cd and Pb, showing a complicated interplay between temperature and carrier gas.

Table 3. Two-way ANOVA study of the total concentration of heavy metals in biochar produced at different temperatures (400 °C, 500 °C and 600 °C) in two (CO_2 and N_2) atmospheres. Significance was set at $p < 0.05$.

Source	Variable	Mean Square	F-Value	*p*-Value
Temperature	Cr	403.452	10.640	0.001
	Mn	90,135.494	245.138	<0.001
	Co	0.329	1.590	0.231
	Ni	359.825	81.367	<0.001
	Cu	623,198.247	229.409	<0.001
	Zn	627,775.130	96.969	<0.001
	Cd	3.414	8.899	0.002
	Pb	28.254	2.716	0.093
	As	6.212	27.544	<0.001
Environment	Cr	111.083	2.930	0.104
	Mn	2860.507	7.780	0.012
	Co	0.589	2.849	0.109
	Ni	43.113	9.749	0.005
	Cu	7594.857	2.796	0.112
	Zn	10,085.836	1.558	0.228
	Cd	3.414	8.899	0.008
	Pb	289.140	27.799	<0.001
	As	2.512	11.138	0.004
Temperature × Environment	Cr	13.829	0.365	0.699
	Mn	21,376.306	58.136	<0.001
	Co	0.065	0.315	0.734
	Ni	8.663	1.959	0.170
	Cu	27,649.237	10.178	0.001
	Zn	27,618.833	4.266	0.030
	Cd	3.414	8.899	0.002
	Pb	74.942	7.205	0.005
	As	0.386	1.711	0.209

3.2. Chemical Fractionation of Heavy Metals

3.2.1. Effects of Pyrolysis Temperature and Carrier Gases

The bio-availability and eco-toxicity of heavy metals in the environment depend on the fractionation of heavy metals in the biochar, following the sequence F1 > F2 > F3 > F4. Most of the Zn and Mn (over 30%) in biosolids were in the bioavailable (F1 + F2) fractions, while most Pb remained in the stable fraction (98%). The high percentage of Pb in biochar and biosolids (around 98%) can be explained by the formation of stable Pb phosphate in sewage sludge [31]. Cu, Cr, Ni, Co and As were mainly distributed in the potential bioavailable fraction (F3).

Pyrolysis temperature converted the bioavailable or potential bioavailable fraction to a stable fraction with an increase in temperature (Figure 2). For example, the major portion of Cu was in oxidizable fraction (F3) (average value 55%) in biochar prepared at 400 °C, which

decreased to 23% at 600 °C. In contrast, the stable fraction (F4) increased from 43% to 75% from 400 °C to 600 °C. Pyrolysis temperature had significant effects on F1 and F3 ($p < 0.05$) for Cu (Table 4). Higher pyrolysis temperature may reduce Cu bound with organic matter to lower valence, Cu (I), or stable crystal, Cu (0), during pyrolysis [32]. A similar distribution was observed for Cr, Co and As at higher pyrolysis temperatures (600 °C), where the major fraction of heavy metals was in residual fraction (F4) compared to 400 °C. The reason for converting bioavailable fraction to stable fraction with increasing pyrolysis temperature could be that metals in biosolids were trapped and formed organometallic complexes or bound with mineral and crystal lattices to form insoluble inorganic forms like metal-phosphate and metal-silicate [33]. Pyrolysis temperature had a statistically significant effect on F3 and F4 ($p < 0.05$) for Cr, Ni and Co. The majority of Ni was in the stable fraction (94%) at 400 °C, which was slightly reduced at 600 °C (82%). The reason for this decrease could be related to the volatilization of Ni compounds at these temperatures, which may lead to fluctuations in the stable fraction [34]. A similar distribution was obtained for Zn in the stable fraction, where the value decreased from 87% to 80% from 400 °C to 600 °C, indicating the formation of less volatile Zn_2SiO_4 and $ZnAl_2O_4$ at higher temperatures, which will trap the Zn and occluded into the carbon matrix of biochar as organometallic [35]. Pyrolysis temperature significantly ($p < 0.05$) transformed bioavailable fractions of Cd regardless of atmospheric condition, indicating pyrolysis temperature improved Cd stability by forming carbon matrix as organometallic compounds or Cd oxides.

Table 4. Two-way analysis of variance (ANOVA) of the fractionation of metals in biochars at (400 °C, 500 °C and 600 °C) and in two (CO_2 and N_2) atmospheres. BC—Biochar produced in CO_2; BN—Biochar produced in N_2 carrier gas under three different temperatures (400 °C, 500 °C and 600 °C).

	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb
Temperature									
F1	10.08 (0.000)	17.16 (0.000)	13.99 (0.000)	0.87 (0.429)	70.75 (0.000)	11.00 (0.000)	26.33 (0.000)	16.65 (0.000)	01.21 (0.314)
F2	3.008 (0.064)	05.60 (0.009)	01.98 (0.155)	2.25 (0.123)	4.41 (0.021)	2.38 (0.110)	30.42 (0.000)	37.72 (0.000)	1.86 (0.173)
F3	32.53 (0.000)	7.81 (0.002)	08.03 (0.002)	34.13 (0.000)	33.73 (0.000)	26.17 (0.000)	0.98 (0.389)	2.06 (0.145)	2.06 (0.144)
F4	4.49 (0.020)	39.77 (0.000)	118.96 (0.000)	105.68 (0.000)	43.39 (0.000)	9.91 (0.000)	49.55 (0.000)	22.34 (0.000)	38.48 (0.000)
Environment									
F1	0.07 (0.792)	1.07 (0.309)	0.42 (0.521)	0.09 (0.927)	106.13(0.000)	1.02 (0.031)	0.05 (0.831)	5.17 (0.030)	1.63 (0.212)
F2	6.33 (0.017)	0.48 (0.493)	0.61 (0.441)	1.55 (0.223)	1.157 (0.291)	1.344 (0.255)	3.28 (0.083)	2.27 (0.142)	3.25 (0.081)
F3	0.83 (0.371)	00.33 (0.570)	06.08 (0.020)	00.14 (0.709)	03.87 (0.050)	0.22 (0.640)	2.48 (0.126)	8.99 (0.005)	35.47 (0.000)
F4	28.33 (0.000)	16.98 (0.000)	59.83 (0.000)	60.09 (0.000)	50.40 (0.000)	11.07 (0.002)	34.98 (0.000)	0.36 (0.555)	17.27 (0.000)
Temperature × Environment									
F1	11.19 (0.000)	05.52 (0.009)	07.78 (0.002)	06.43 (0.005)	66.99 (0.000)	08.15 (0.001)	04.15 (0.026)	5.78 (0.008)	4.67 (0.017)
F2	7.82 (0.002)	1.25 (0.302)	0.41 (0.672)	0.46 (0.637)	6.72 (0.004)	2.45 (0.104)	01.32 (0.283)	2.36 (0.112)	0.32 (0.733)
F3	1.85 (0.174)	4.68 (0.017)	1.43 (0.256)	0.07 (0.994)	1.12 (0.341)	3.01 (0.065)	0.12 (0.890)	5.16 (0.012)	14.06 (0.000)
F4	15.78 (0.000)	3.15 (0.057)	6.41 (0.005)	7.06 (0.003)	7.04 (0.003)	13.35 (0.000)	8.45 (0.001)	15.95 (0.000)	7.47 (0.002)

The pyrolysis environment had a significant effect on F4 ($p < 0.05$) for Cr, Mn, Co, Ni, Cu, Zn, As and Pb. By replacing N_2 with a CO_2 environment, the distribution of Cu was

15% lower in stable fraction (F4) in the CO_2 atmosphere than in N_2 [36]. The stable fraction of Cr had ~5% lower levels of biochar in the CO_2 atmosphere than the N_2. The results demonstrated that pyrolysis improved the transformation of Cr from a bioavailable fraction to an oxidizable and stable fraction due to the decomposition of organic materials, and Cr may be volatilized during pyrolysis [37]. Similarly, the stable fraction (F4) of As, Mn, Cd, Pb and Zn was slightly lower in biochar produced in CO_2 than N_2, indicating CO_2 may promote volatilization of stable metals compared to N_2. Therefore, the results indicated that the pyrolysis environment had a significant influence on metal fraction during pyrolysis. There was a significant interaction for temperature * environment ($p < 0.05$) for both F1 and F4 fractions for all metals. Therefore, the above results indicate that both pyrolysis temperature and carrier gases could significantly transform the weakly bonded metals into stable fractions, which may be related to the complexation of heavy metals with the crystal lattices of the residual solid phase.

3.2.2. Environmental Risk Assessment

The environmental risk assessment code of biosolids and their derived biochar was identified by measuring the risk assessment code (RAC) and potential ecological risk index (RI). The RAC results are shown in Table 5 and the level of significance in Table 6. Pyrolysis temperature had a significant effect ($p < 0.05$) for all metals except for Pb. The RAC values for As (35), Ni (43), Mn (34), Cr (32) and Co (32) were high risk: 30% $\leq$ RAC <50% in biosolids, indicating potentially high environmental toxicity, while Pb (10), Cd (22) and Zn (15) showed medium risk (10%$\leq$ RAC < 30%). Additionally, the RAC value of Cu was very low in biochar after pyrolysis, while Co possessed a very high risk (VHR), RAC $\geq$ 50%, after pyrolysis. Pyrolysis temperature could significantly reduce the RAC value at the higher temperature. On the other hand, the pyrolysis environment had only a significant effect ($p < 0.05$, Table 6) for Cu, Cd and Pb. Biochar produced in a CO_2 environment had a lower risk for Pb, while biochar prepared in an N_2 environment had a lower risk for Cd. There was a significant interaction for temperature * environment ($p < 0.05$, Table 3. 6) for Cr, Mn, Cu, Ni, Zn and Cd. For example, the highest RAC values for Cr, Mn, Ni, Zn and Cd were achieved in BC400. Therefore, the risk assessment codes (RAC, Table 5) value was lower under biochar produced in a CO_2 than in an N_2 environment at a higher pyrolysis temperature.

Table 5. Risk assessment codes (RAC) of biosolids and biochars with (±) standard deviation.

Heavy Metals	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb	As
Biosolids	32 ± 6/HR	34 ± 2/HR	32 ± 5/HR	43 ± 5/HR	3 ± 4/LR	15 ± 1/MR	25 ± 5/MR	10 ± 2/MR	35 ± 5/HR
BC400	31 ± 9/HR	20 ± 2/MR	77 ± 20/VHR	33 ± 6/MR	2 ± 1/LR	12 ± 4/MR	36 ± 15/MR	11 ± 3/MR	16 ± 6/MR
BC500	16 ± 3/MR	12 ± 1/MR	68 ± 21/VHR	13 ± 4/MR	1 ± 1/LR	5 ± 1/LR	5 ± 1/LR	5 ± 1/LR	8 ± 3/LR
BC600	20 ± 3/MR	4 ± 2/LR	34 ± 23/HR	20 ± 8/MR	1 ± 1/LR	4 ± 2/LR	4 ± 1/LR	7 ± 1/LR	3 ± 1/LR
BN400	26 ± 2/MR	10 ± 6/MR	62 ± 27/VHR	20 ± 2/MR	1 ± 1/VLR	6 ± 1/LR	5 ±1/LR	11 ± 1/MR	14 ± 1/MR
BN500	22 ± 1/MR	17 ± 5/MR	91 ± 25/VHR	27 ± 11/MR	4 ± 1/LR	11 ± 5/MR	5 ± 1/LR	22 ± 10/MR	13 ± 2/MR
BN600	19 ± 2/MR	7 ± 3/LR	39 ± 7/HR	14 ± 1/MR	2 ± 1/LR	3 ± 1/LR	3 ± 1/LR	13 ± 9/MR	4 ± 1/LR

LR—low risk; MR—medium risk; HR—high risk; very high risk—VHR.

Table 6. Two-way ANOVA for RAC of heavy metals in biochar produced at different temperatures (400 °C, 500 °C and 600 °C.) under two (CO_2 and N_2) atmospheres. Significance was set at $p < 0.05$.

Source	Variable	Mean Square	F-Value	*p*-Value
Temperature	Cr	223.735	12.377	<0.01
	Mn	219.543	18.662	<0.01
	Co	4912.652	4.984	0.02
	Ni	193.000	4.442	0.03
	Cu	5.574	27.444	<0.01
	Zn	67.019	7.747	<0.01
	Cd	681.079	6.238	0.01

Table 6. *Cont.*

Source	Variable	Mean Square	F-Value	*p*-Value
	Pb	21.134	0.398	0.68
	As	281.775	11.212	<0.01
Environment	Cr	0.002	0.000	0.99
	Mn	1.311	0.111	0.74
	Co	338.411	0.343	0.57
	Ni	21.889	0.504	0.49
	Cu	5.618	27.661	<0.01
	Zn	0.132	0.015	0.90
	Cd	631.968	5.788	0.03
	Pb	364.051	6.849	0.02
	As	5.614	0.223	0.64
Temperature × Environment	Cr	65.831	3.642	0.05
	Mn	125.412	10.661	<0.01
	Co	1224.309	1.242	0.31
	Ni	381.372	8.778	<0.01
	Cu	8.773	43.191	<0.01
	Zn	63.500	7.340	<0.01
	Cd	637.366	5.837	0.01
	Pb	155.907	2.933	0.08
	As	23.610	0.939	0.41

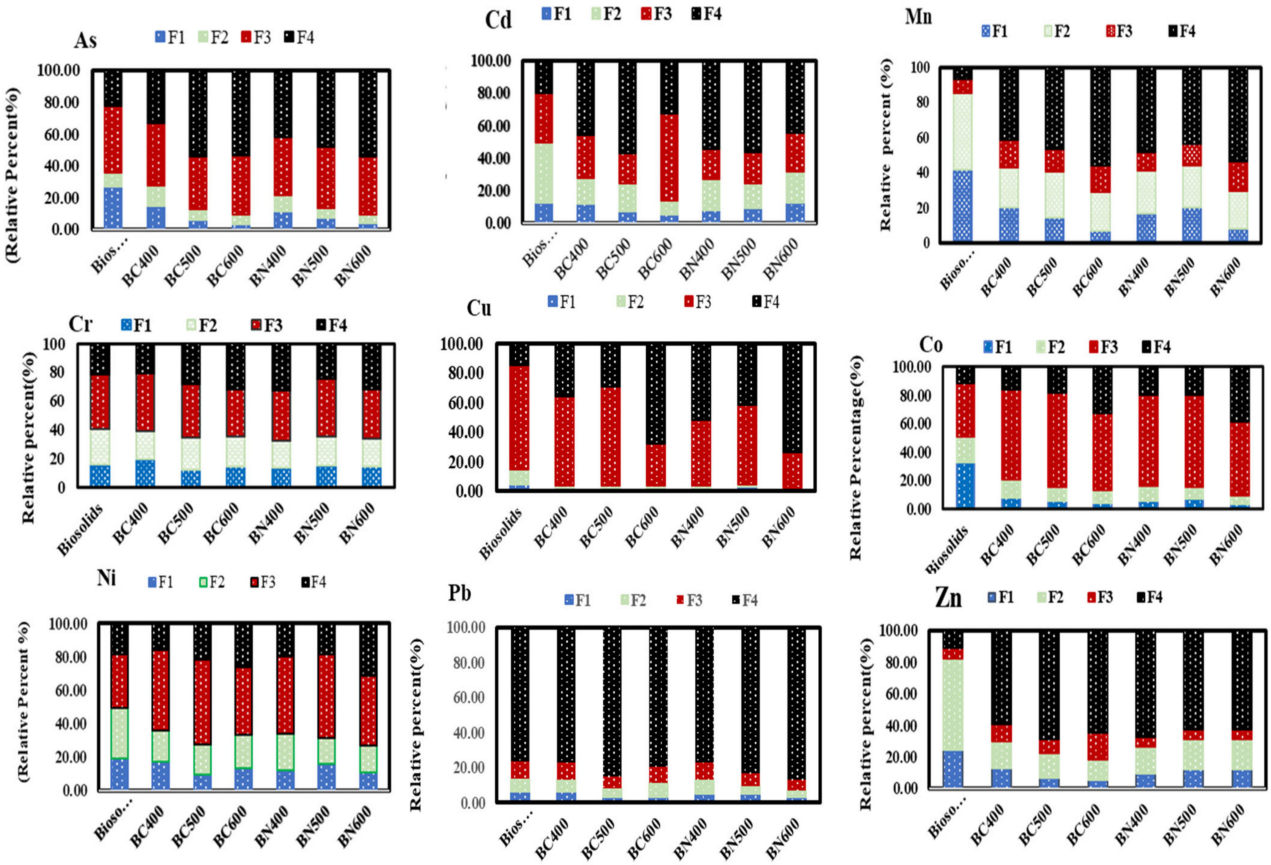

Figure 2. The percent distribution of various heavy metals in biosolids sample and biochar derived from biosolids, where F1—exchangeable; F2—reducible; F3—oxidizable; F4—residual fraction BC—Biochar produced under CO_2; BN—Biochar produced under N_2 carrier gas at 400 °C, 500 °C and 600 °C.

The results of metal contamination (Cf), potential environmental risk (Er) and biosolids/biochar contamination (RI) of different heavy metals were presented in Table 7, and the level of significance was presented in Table 8. Biosolids represent the highest contamination where the RI value (316.3) is equivalent to considering potential ecological risk if directly applied in soils. The value of RI in biochar was greatly reduced from 400 °C to 600 °C after pyrolysis. Pyrolysis temperature, environment, and the interaction for temperature * environment had a significant effect ($p < 0.05$, Table 8) on the RI value of biochar. Biochar produced in a CO_2 environment exhibited a slightly higher RI value compared to the N_2 environment. Similarly, there was a gradual decrease of RI value from 400 to 500 °C in the CO_2 environment and a slight increase at 600 °C. On the other hand, the RI value gradually decreased from 74.84 to 52.16 at 400 °C to 600 °C in the N_2 environment, indicating lower potential ecological risk at higher pyrolysis temperatures. Therefore, biochar produced in the N_2 environment had a lower potential ecological risk (RI value, Table 7) evaluation. In particular, BN500 and BN600 had the lowest RI values compared to the other treatments.

Table 7. Potential ecological risk assessment of the heavy metals in biosolids and their biochar.

Heavy Metals	Tr	Cf							Er						
		Biosolids	BC400	BC500	BC600	BN400	BN500	BN600	Biosolids	BC400	BC500	BC600	BN400	BN500	BN600
Cr	2.00	4.07	4.56	2.74	2.24	1.71	2.93	1.69	8.13	9.12	5.47	4.48	3.43	5.86	3.38
Mn	1.00	17.15	2.27	1.20	0.79	1.02	1.19	0.69	17.15	2.27	1.20	0.79	1.02	1.19	0.69
Ni	6.00	5.03	6.60	4.07	2.79	3.99	3.93	1.72	30.20	39.63	24.44	16.76	23.94	23.59	10.32
Cu	5.00	5.54	1.80	1.88	0.44	1.02	1.08	0.26	27.68	9.01	9.38	2.20	5.11	5.38	1.30
Zn	1.00	6.13	0.25	0.21	0.15	0.02	0.20	0.17	6.13	0.25	0.21	0.15	0.02	0.20	0.17
As	10.00	6.56	3.33	0.92	0.84	1.43	1.05	0.66	65.62	33.27	9.19	8.36	14.32	10.51	6.59
Cd	30.00	5.29	1.84	0.84	1.92	0.85	0.74	0.97	158.64	55.30	25.08	57.58	25.59	22.14	29.12
Pb	5.00	0.55	0.51	0.19	0.26	0.28	0.21	0.12	2.75	2.54	0.97	1.29	1.42	1.07	0.58
RI									316.30	151.38	75.95	91.61	74.84	69.94	52.16

Tr—toxic response factor of the individual heavy metal; Er—a potential ecological risk factor for the individual heavy metals, and RI—the sum of the potential ecological risk index (Er) of each heavy metal. Biosolids, BC—Biochar produced in CO_2; BN—Biochar produced in N_2 carrier gas under 400 °C, 500 °C and 600 °C.

Table 8. Two-way ANOVA study for potential ecological risk of heavy metals (HM) in biochar produced at different temperatures (400 °C, 500 °C and 600 °C) in two (CO_2 and N_2) atmospheres. Significance was set at $p < 0.05$.

		Temperature			Environment			Temperature × Environment		
HM		Mean Square	F-Value	*p*-Value	Mean Square	F-Value	*p*-Value	Mean Square	F-Value	*p*-Value
Cr	*Cf*	4.43	14.96	<0.01	10.27	34.68	<0.01	7.51	25.38	<0.01
	Er	17.71	14.96	<0.01	41.06	34.68	<0.01	30.05	25.38	<0.01
Mn	*Cf*	2.45	12.29	<0.01	1.84	9.22	<0.01	1.41	7.09	<0.01
	Er	2.45	12.29	<0.01	1.84	9.22	<0.01	1.41	7.09	<0.01
Ni	*Cf*	27.95	65.3	<0.01	14.65	34.23	<0.01	4.68	10.93	<0.01
	Er	1006.22	65.3	<0.01	527.53	34.23	<0.01	168.4	10.93	<0.01
Cu	*Cf*	4.8	55.38	<0.01	3.1	35.69	<0.01	0.37	4.29	0.02
	Er	120.07	55.38	<0.01	77.39	35.69	<0.01	9.31	4.29	0.02
Zn	*Cf*	0.01	2.29	0.12	0.05	7.79	0.01	0.06	9.49	<0.01
	Er	0.01	2.29	0.12	0.05	7.79	0.01	0.06	9.49	<0.01
As	*Cf*	9.33	18.73	<0.01	3.77	7.56	0.01	3.58	7.19	<0.01
	Er	932.66	18.73	<0.01	376.65	7.56	0.01	357.88	7.19	<0.01
Cd	*Cf*	1.51	3.92	0.03	4.15	10.73	<0.01	0.76	1.97	0.16
	Er	1363.11	3.92	0.03	3733.61	10.73	<0.01	684.45	1.97	0.16
Pb	*Cf*	0.16	16.38	<0.01	0.12	12.23	<0.01	0.05	4.76	0.02
	Er	4.04	16.38	<0.01	3.02	12.23	<0.01	1.17	4.76	0.02
	RI	6628.88	9.3	<0.01	14883.24	20.88	<0.01	3733.76	5.24	0.01

Cf—the individual heavy metals contamination factor; *Er*—potential environmental risk; *RI*—potential ecological risk caused by overall heavy metal contamination.

The metal contamination (Cf) value was the highest in biosolids and decreased significantly in biochar after pyrolysis at 400 °C and further reduced at 600 °C (Table 7). The results indicated a lower potential ecological risk (Er $\leq$ 40, Table 7) for all metals. Pyrolysis temperature and environment had a significant effect ($p < 0.05$, Table 8) on Cf and Er values of biochar. Both Cf and Er values were slightly lower in N_2 than in CO_2. There was a significant interaction for temperature * environment ($p < 0.05$, Table 8) for Cf and Er. Biochar showed a slightly higher environmental risk at 400 °C in CO_2, which was greatly reduced at 600 °C, indicating that using higher pyrolysis temperatures in biochar appeared to have low environmental risks when applied to land. Therefore, the production of biochar at 500 and 600 °C was effective in attenuating the ecological risks of biosolids. Similar conclusions have been reached in previous works [37].

3.3. Bioavailable Heavy Metals in Biosolids and Biosolids Derived Biochar

The total content of heavy metals in biochar does not show their availability for plant uptake. The DTPA-extractable method was used to measure the readily available heavy metals for plant uptake, as it has the capacity to chelate a wide range of metallic elements. In the current study, biosolids contained the highest concentration of DTPA-extractable metals (Cu, Fe, Zn, Cd, Cu and Pb, which was drastically reduced in biochar after pyrolysis. The content of bioavailable metals in biochar was always lower than the raw biosolids, suggesting that the pyrolysis process could prevent the release of these elements in DTPA extracts [7]. Similar results were reported by Lu et al. [8], showing that the DTPA-extractable and soluble fractions of heavy metals were significantly decreased in biochar compared to sewage sludge. Pyrolysis temperature had a significant effect ($p < 0.05$, Table 9) on DTPA-Fe, DTPA-Cu and DTPA-Zn. Biochar produced at a lower pyrolysis temperature (400 °C) significantly reduced all DTPA-extractable metal concentrations, while it was slightly increased at a higher pyrolysis temperature (600 °C). The lowest extractable metal concentrations (Fe, Cu and Zn) were found in biochar prepared under 400 °C (an average value ranging from Fe: 77 mg kg^{-1}, Cu: 14 mg kg^{-1} and Zn: 11 mg kg^{-1}), which was gradually increased at 600 °C (Fe: 162 mg kg^{-1}, Cu: 36 mg kg^{-1} and Zn: 20 mg kg^{-1}). The results indicated that pyrolysis could reduce the bioavailability of many trace elements at a lower temperature (400 °C) [11], while higher pyrolysis temperature could increase metal concentration for Cu and Fe. Moreover, biochar produced under lower temperatures contains abundant surface functional groups (carboxyl and hydroxyl), enhancing the formation of organometallic complexes with biochar organic structures [29]. Yang [38] reported that pyrolysis temperature increases the decomposition of organic matter in resulting biochar; as a result, heavy metals bound with organic matter may precipitate as carbonate and phosphate, which exhibit lower bioavailability.

Comparing the two carrier gases, the pyrolysis environment had a significant effect only for Cu ($p < 0.05$). Biochar produced in CO_2 contained slightly higher Cu concentration (average value 37 mg kg^{-1}) than in an N_2 environment (average value 34 mg kg^{-1}). Moreover, the effect of temperature, atmosphere and interaction was significant only for Cu ($p < 0.05$). Biochar produced at 600 °C in CO_2 had the highest Cu concentration (62 mg kg^{-1}) compared to all other pyrolysis conditions, while extractable Fe enrichment was slightly higher (Table 10) at 600 °C in an N_2 environment (193 mg kg^{-1}) than in a CO_2 environment (BC600: 132 mg kg^{-1}). The change in the concentration of trace elements in biochar obtained using CO_2 could be associated with different physicochemical properties that were different from the N_2 environment. For example, the biochar produced in CO_2 contained more aromatic carbon and higher surface area [18], which could increase the immobilization of heavy metals.

Table 9. Two-way analysis of variance (ANOVA) of plant-available metals in biochars obtained at different pyrolysis temperatures (400 °C, 500 °C and 600 °C) in two (CO_2 and N_2) atmospheres. Significance was set at $p < 0.05$.

Variable	Mean Square	F	*p*
Temperature			
DTPA- Mn	1.196	0.147	0.864
DTPA-Fe	14,690.169	6.391	*0.008*
DTPA-Cu	1047.919	29.354	*<0.001*
DTPA-Zn	180.698	12.117	*<0.001*
DTPA-Cd	0.000	1.714	0.208
DTPA-Pb	0.088	0.831	0.452
Environment			
DTPA- Mn	5.955	0.733	0.403
DTPA-Fe	6557.385	2.853	0.108
DTPA-Cu	3715.281	104.071	*<0.001*
DTPA-Zn	0.033	0.002	0.963
DTPA-Cd	9.20	0.730	0.404
DTPA-Pb	0.169	1.588	0.224
Temperature × Environment			
DTPA-Mn	7.931	0.977	0.396
DTPA-Fe	1910.851	0.831	0.452
DTPA-Cu	1040.548	29.147	*<0.001*
DTPA-Zn	24.786	1.662	0.218
DTPA-Cd	0.001	5.416	*0.014*
DTPA-Pb	2.00	0.200	1.886

Table 10. DTPA-extractable metals (mg kg^{-1}) of biosolids and their biochar at 400 °C, 500 °C and 600 °C in N_2 and CO_2 carrier gases. BC represents CO_2, and BN represents the N_2 environment.

	Biosolids	BC400	BC500	BC600	BN400	BN500	BN600
DTPA-Mn	83.96	6.31	5.99	5.08	5.20	6.75	6.43
DTPA-Fe	463.21	60.94	122.33	117.15	76.01	122.47	218.62
DTPA-Cu	494.26	18.52	24.92	49.98	11.18	17.61	11.48
DTPA-Zn	444.90	22.10	20.25	16.39	13.85	18.10	16.83
DTPA-Cd	0.86	0.03	0.02	0.02	0.02	0.04	0.02
DTPA-Pb	3.65	0.57	0.85	0.72	0.39	0.61	0.90

3.4. Principal Component Analysis (PCA) of Biochar Quality

The principal component analysis was measured for the total concentration of heavy metals (Figure 3) and bioavailable heavy metals (Figure 4). Two main components of the principal component analysis (PC1 and PC2) explained 71.5% of the total variation in the total concentration of heavy metals in biochar and 61.6% in the bioavailable heavy metals. Both PC1 and PC2 showed a significant relationship between the pyrolysis condition and the physicochemical properties of the biochar, as well as the HM content in biochar. The variation in PCA indicates the possible reason for the reduction in available HM content in the biochar. There was a gradual increase in specific surface area (SSA) and ash content at 600 °C, which increased the retention capacity as well as HM availability [18]. The other important factor is the pH of the biochar which has direct effects on the availability of heavy metals. Most of the heavy metals, including Zn, Mn, Pb and Cu, tend to precipitate in the form of carbonate, hydroxide, sulfates, or phosphates at higher pH and become unavailable [39]. There was a decrease in acidic surface functional groups due to the decomposition of oxygen-containing functional and increased aromaticity at high pyrolysis temperatures [32]. Biochar produced at 600 °C showed a lower H/C ratio that promoted

aromaticity and increased sorption of heavy metals and became less available compared to biochar produced at 400 °C [18]. These physicochemical characteristics, separately or interactively, contributed to reductions of 31.0% and 26.0% for bioavailable heavy metals.

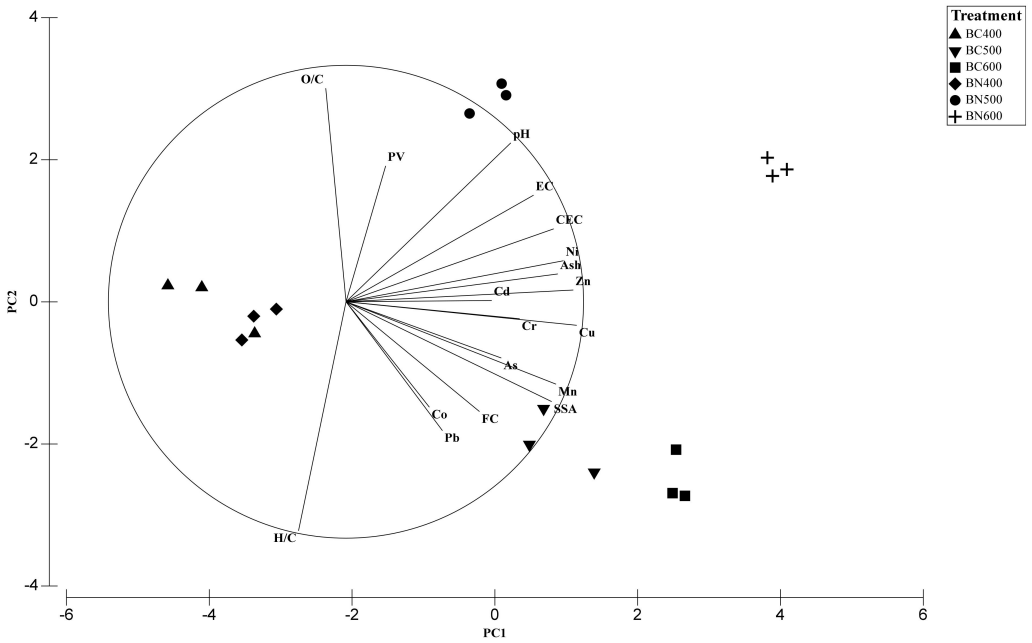

Figure 3. Principal component analyses (PCA) of total concentration heavy metal indicating 49.5% variation in PC1 and 22% variation in PC2 values were grouped according to pyrolysis conditions.

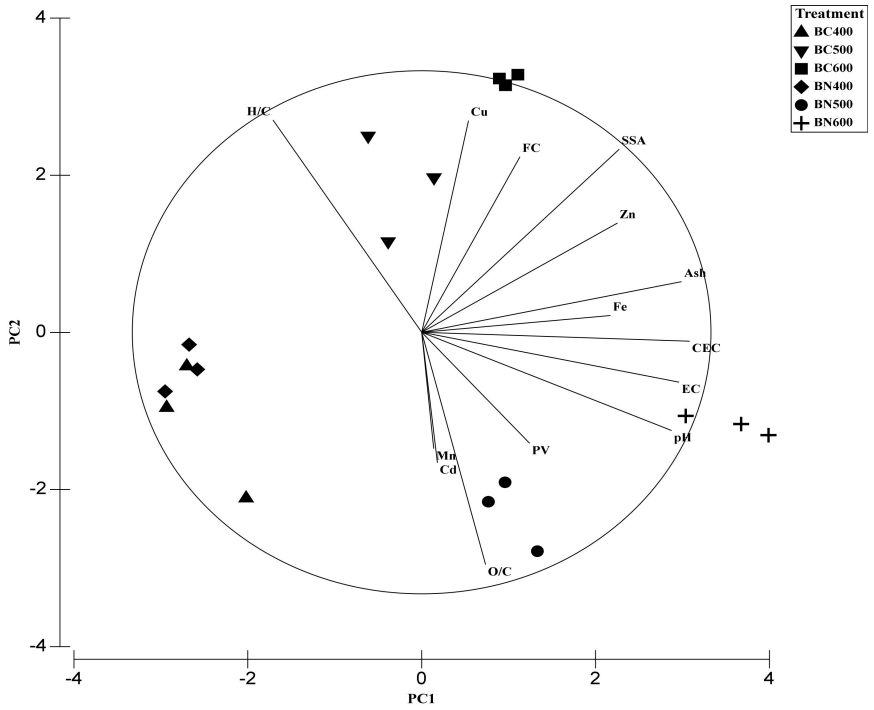

Figure 4. Principal component analyses (PCA) of bioavailable metal concentration indicated a 34.5% variation in PC1 and a 27.1% variation in the PC2 values grouped according to pyrolysis condition.

4. Conclusions

The production of biochar in a fluidized bed reactor carried out in a slow pyrolysis process at three temperatures (400, 500 and 600 °C) and two atmospheres (CO_2 and N_2)

had various influences on heavy metal concentrations, chemical fractionation, bioavailability and potential eco-toxicity. Higher pyrolysis temperatures significantly increased the total metal concentration in biochar. Changing the atmosphere led to changes in the bioavailability and chemical fractionation of different metals. The bioavailable fractions were transformed into immobilized fractions due to precipitation in crystalline lattice or reduced to a stable fraction. Overall, biochar produced at higher temperatures (500 and 600 °C) in N_2 environments exhibited lower potential ecological risks than biochar produced in CO_2 environments. Studying the effects of pyrolysis temperature and carrier gases on the ecological risk assessment of heavy metals in biochar indicated that the biochar produced at higher temperatures in both carrier gases is more effective in reducing environmental toxicity.

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