agriculture

Article

The Synergetic Effect of Soil Amendments on Reducing Bioavailable Heavy Metals and Greenhouse Gas Emissions from Upland Soil

Young-Kyu Hong [1], Jin-Wook Kim [1], Hyuck-Soo Kim [2], Jae-E. Yang [2,*] and Sung-Chul Kim [1,*]

[1] Department of Bio-Environmental Chemistry, Chungnam National University, Daejeon 34134, Korea; hyk8895@cnu.ac.kr (Y.-K.H.); kin1888@cnu.ac.kr (J.-W.K.)
[2] Department of Biological Environment, Kangwon National University, Chuncheon 24341, Korea; khs25@kangwon.ac.kr
* Correspondence: yangjay@kangwon.ac.kr (J.-E.Y.); sckim@cnu.ac.kr (S.-C.K.)

Abstract: Heavy metal pollution and greenhouse gas (GHG) emissions from soil are two major detrimental sources in the agriculture environment because of concerns about crop safety and global warming. Applying amendments on site is a common technique used for heavy metal remediation and the reduction in GHG emissions. This study aims to evaluate the effect of different amendments on the reduction in both bioavailable heavy metals and GHG emissions from soil. Four different amendments, namely bottom ash (BA), sintered material (SM), sintered material combined with lime (SM + L), and FeO (SM + FeO) were applied to upland fields, followed by maize (*Zea mays* L.) cultivation from April to October. Subsequently, SM + FeO treatment demonstrated the highest bioavailability reduction efficiency for As at 79.1%, and SM + L treatment had a high efficiency for the reduction in Cd and Pb by 64.6% and 41.4%, respectively. SM + FeO treatment also reduced bioaccumulated As and Pb in maize grain by 59.3% and 66.2%, respectively. Furthermore, SM + FeO treatment demonstrated the highest reduction efficiency for cumulative N_2O emissions by 70.7%, compared to the control soil. Among the four different amendments, the efficiency of heavy metal and GHG emission reduction was in the following order: SM + FeO > SM + L > SM > BA. Overall, SM combined with FeO is a promising amendment for reducing and managing both heavy metal pollution and GHG emissions in soil.

Keywords: heavy metals; greenhouse gas; amendments; remediation; upland soil

Citation: Hong, Y.-K.; Kim, J.-W.; Kim, H.-S.; Yang, J.-E.; Kim, S.-C. The Synergetic Effect of Soil Amendments on Reducing Bioavailable Heavy Metals and Greenhouse Gas Emissions from Upland Soil. *Agriculture* **2022**, *12*, 246. https://doi.org/10.3390/agriculture12020246

Academic Editor: Vasileios Antoniadis

Received: 12 January 2022
Accepted: 7 February 2022
Published: 9 February 2022

1. Introduction

Heavy metal pollution and greenhouse gas (GHG) emissions present in arable soil have recently become a concern due to crop safety and the threat of global warming [1–5]. The main sources of heavy metal pollution include anthropogenic activities, such as urbanization, industrialization, and environmental over-development [6,7].

Mining, smelting activities, and compost made from sludge or waste are typical sources of heavy metal pollution in the environment [6–8]. Agricultural soil is also a major source of GHG emissions, including nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4). Nitrous oxide (N_2O) is of main concern as it has a 298 times greater global warming potential (GWP) than CO_2, with an increased ability to disrupt the atmospheric ozone layer [4,5,9].

Various remediation techniques have been applied to reduce both heavy metal concentrations and GHG emissions in agricultural soil. The application of amendments is a popular technique used to immobilize bioavailable heavy metals and reduce GHG emissions in soil because of its high efficiency, low cost, and ease of use [10–13]. The most commonly used amendments include organic materials (biochar, compost, and plant residuals), minerals (zeolite), and pH adjusters (lime, steel slag, and coal ash) [2,3,14,15].

Coal ash, including fly ash (FA) and bottom ash (BA), are used as a soil amendment for heavy metal remediation in agricultural fields. FA generally contains alkaline properties and a large surface area suitable for adsorbing bioavailable heavy metals in soil [16,17]. BA is a porous medium that can efficiently absorb soluble heavy metals in soil [18–20]. However, unprocessed FA and BA demonstrated decreased efficiency of heavy metal sorption in soil compared to other amendments, which were then modified to increase the sorption efficiency [2,21–23]. Representative methods include the hydrothermal method [24,25], synthesis of zeolite-type adsorbents [26], and sintering processes [2,22,23].

The potential risks associated with heavy metal pollution and GHG emissions in soil have not been thoroughly investigated. Heavy metal toxicity in soil can inhibit microbial activity, leading to biomass reduction, increased tolerance, and reduced biodiversity [27]. Greenhouse gas emissions may increase as microbial activity decreases, due to slower biological processes, including nitrification/denitrification or organic decomposition [5,11,27]. Other soil variables, including soil water content, nutrient availability, and soil pH, can affect heavy metal remediation and GHG emissions in soil [4,28].

Thus, this study aims to evaluate the efficiency of soil amendments in reducing bioavailable heavy metals and GHG emissions in upland soil. The synergetic effect of combined sintered material and lime or FeO is also evaluated.

2. Materials and Methods

2.1. Soil Amendments

Sintered material (SM) was manufactured using recycled materials, including bottom ash, low-quality unburned carbon, and dredging sand (ratio of 2:5:3 *w*/*w*/*w*) at a coal power plant in the Incheon province, Korea. Heating (550–600 °C), cooling (25 °C), and re-heating (1100–1200 °C) was conducted to generate the SM. The detailed manufacturing process and physicochemical properties of SM are described in our previous study [2]. Lime and iron oxide (FeO) were applied together with SM to investigate the combined effect on bioavailable heavy metal reduction and GHG in upland soil. The optimum application rate for heavy metal sorption efficiency was previously determined, and 10% SM and 0.5% combined lime or FeO (*w*/*w*) were subsequently added to the upland field assuming the total mass of the soil within 100 cm depth with density of 1.3 g/cm^3 [2]. Lime and FeO were obtained from a commercially available market (Sigma Aldrich, Seoul, Korea).

2.2. Site Description and Experimental Field Setup

The experimental site was an upland field located in Dan-yang, Chungbuk province, South Korea (37°02′19″N; 128°15′02″E). The abandoned metal mine, You-jin mine, was located within a 2 km radius and severe heavy metal soil pollution was reported by the Ministry of Environment in Korea. A total of 5 plots (10 m × 10 m, W × L) were installed in the randomized block design and named control (no amendment), BA (10%), SM (10%), SM+L (10% SM and 0.5% lime), and SM + FeO (10% SM and 0.5% FeO). Amendments were evenly distributed across the surface soil and thoroughly plowed to a depth of 40 cm to homogenize the soil. Each plot was then irrigated with groundwater and equilibrated for eight weeks without water. Organic fertilizers were added and equilibrated one week before cultivation. No heavy metals exceeded the groundwater and organic fertilizer threshold values set by the Ministry of Environment (MOE) and the Rural Development Agency (RDA) in Korea (data not shown).

Maize (*Zea. mays* L.) was then cultivated for 32 weeks and an adequate amount (160 kg/ha) of chemical fertilizer (30-8-8, N-P-K) was added to each field at end of April, according to RDA recommendations.

2.3. Soil and Plant Sampling

Top soil samples were collected from upland soil, using a hand auger, after harvesting the maize. Three sub-samples per plot were collected at a depth of 20 cm and added to a single sample bag to make 1 sample. The soil sample was thoroughly mixed by shaking for one minute and stored in a cooled box. Maize samples were collected from all three stands in each plot, followed by on-site separation of the root and edible parts. The separated parts were individually placed in plastic sample bags and stored in a cooled box.

The transported soil sample was completely air-dried at 35 °C and passed through a 2 mm and 0.15 mm sieve for chemical and heavy metal analysis. The root samples were washed with deionized water several times and sonicated for one minute to remove fine surface particles. The grain was separated from the kernel after thorough air drying at 20 °C. Every 100 grains were weighed for yield comparisons in each plot. Ground-up grain and root were used for heavy metal analysis.

2.4. Chemical and Heavy Metal Analyses of Soil and Plants

The soil pH and electrical conductivity (EC) were measured using a pH meter (MP220, Mettler Toledo, Columbus, OH, USA) and EC meter (S230, Mettler Toledo, Columbus, OH, USA), after shaking 10 g of soil with 50 mL of distilled water for 1 h. Organic matter (OM) and available P_2O_5 (Av. P2O5) were measured following the Walkley–Black and Bray No1 methods.

The total concentrations of As, Cd, and Pb were prepared by digesting the soil sample with aqua regia (HNO_3: HCl (*v*/*v*) = 1:3) in a heating block (block heating sample preparation system, Ctrl-M Science). The bioavailable heavy metal fraction in the soil was extracted using Mehlich-3 extractant.

Maize grain and roots were digested using a heating block for 2 h, after 24 h stagnation in a HNO_3 solution. Heavy metal concentrations were measured using an inductively coupled plasma-optical emission spectrometer (ICAP 7000series, THERMO FISHER, Waltham, MA, USA). For quality assurance and quality control (QA/QC) purposes, blank and spiked samples were measured every 50 samples. The certified reference material (CRM) for heavy metal contaminated soil (BAM, Berlin, Germany) was also analyzed. The mean recovery ratios for As, Cd, and Pb were 102%, 97%, and 98%, respectively. All glassware and polyethylene bottles were soaked overnight in a 0.5% HNO_3 solution and rinsed with deionized water before the experiment.

2.5. Monitoring Greenhouse Gas Emissions

Monthly N_2O and CO_2 flux monitoring was conducted every third week from April 2018 to October 2018. A static opaque closed chamber, made of a PVC column with a 24.8 cm diameter and 17 cm height, was installed at the center of each plot. Gas was sampled for 2 h at a time (10:00 a.m.–12:00 p.m.) [11]. Weeds and plant residuals were removed from the surface soil before installing a chamber. The chamber lid was left open for one hour to allow ventilation. The chamber lid was closed at the start of the sampling procedure, followed by sample collection every 20 min using a 20 mL polypropylene syringe. The gas sample was then transferred into a 12 mL evacuated glass vial (Exetainer, Labco, Ceredigeon, UK), as previously described [10,11]. N_2O and CO_2 concentrations were measured using a gas chromatography-mass spectrometer (GC/MS, OP2020, Shimazu, Kyoto, Japan). GC/MS conditions were maintained during the analysis, including a column temperature of 60 °C, heating temperature of 330 °C, and N_2 gas as a carrier [10,11]. For the calculation of gas flux, only 20 and 40 min gas sample concentrations were used because of asymptotic problems [10,29]. In addition, the linear interpolation between days was considered for the calculation of cumulative GHG emissions. The information about air temperature and rainfall was collected at the nearest weather station from the sampling site. The daily gas flux and cumulative gas flux were calculated using Equations (1) and (2):

$$\text{Daily gas flux (g/ha/day)} = (\Delta g/\Delta t) \times d \times (273/T) \times (V/A) \times k \times a \tag{1}$$

$$\text{Cumulative gas flux (kg/ha/yr)} = \sum(\text{Ri} \times \text{Di}) \tag{2}$$

where $\Delta g/\Delta t$ is the rate change in the gas concentration inside the chamber ($g/m^3/min$), d is the gas density (g/m^3) at 273 K and 0.101 MPa, and T is the chamber air temperature. V is the volume of the chamber (m^3), A is the surface area of the chamber (m^2), k is the time conversion factor (min/day), and a is the area conversion factor (10,000 m^2/ha). For the cumulative gas flux, the mean value of the daily gas flux (R_i) was multiplied by the length of the period (D_i) and added to the previous cumulative amount for the total calculation.

2.6. Statistical Analysis

The means of the triplicate measurements for soil chemical properties, heavy metal concentration, crop yield, and gas flux analysis were used throughout the study. The differences between the varied treatments were compared using the analysis of variance (ANOVA) test at a significance level of $p < 0.01$ or $p < 0.05$, with SPSS software (version 20.0). Correlation analyses among the soil chemical properties, heavy metal concentrations, and GHG emissions were also conducted with SPSS software using multiple correlation analysis.

3. Results and Discussion

3.1. Properties of Amendments and Upland Soil

The chemical properties and total heavy metal concentrations of the amendments without soil mixing are summarized in Table 1. All amendments were alkaline with pH ranging from to 8.02–9.00. The main material, BA, is alkaline on its own, but the pH increased more after sintering. In fact, SM had a significantly higher pH than BA. A previous study reported that the formation of a crystal phase during the sintering process can increase pH because of the dissolution of silicate (SiO_2) and aluminum (Al), which contain certain minerals. Additionally, calcium (Ca)-containing materials are re-precipitated under alkaline conditions [2,25,30]. The highest pH (9.00) was observed when lime was added to SM. A similar trend was observed for the EC, OM, and Av. P_2O_5, showing significantly higher values for SM, SM + L, and SM + FeO, except for the combination of Av. P_2O_5 and SM + FeO.

Table 1. Physicochemical properties of amendments.

	pH	EC	OM	Av. P_2O_5	Total Heavy Metal Concentration As	Cd	Pb	Cu	Zn	Ni
	(1:5)	dS/m	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
BA	8.02 ± 0.61 [b]	0.19 ± 0.05 [c]	0.05 ± 0.01 [c]	30.04 ± 3.2 [b]	1.26 ± 0.61	0.22 ± 0.02	7.41 ± 3.37	5.13 ± 0.05	14.52 ± 4.49	15.22 ± 0.27
SM10	8.68 ± 0.11 [a]	1.29 ± 0.03 [b]	0.25 ± 0.10 [b]	117.9 ± 11.2 [a]	10.4 ± 0.96	0.66 ± 0.14	4.23 ± 0.22	17.23 ± 0.72	31.45 ± 1.41	13.43 ± 1.03
SM10 + L	9.00 ± 0.04 [a]	1.25 ± 0.07 [b]	0.35 ± 0.01 [a]	102.2 ± 1.1 [a]						
SM10 + FeO	8.15 ± 0.05 [b]	1.62 ± 0.05 [a]	0.21 ± 0.10 [b]	36.90 ± 11.9 [b]						

Different letters indicate that the value is significantly different at $p < 0.05$.

The initial physicochemical properties of the upland soil before the application of the amendments are listed in Table 2. The soil texture was silt loam and three out of four chemical properties were out of range for the optimum range of crop cultivation set by RDA, Korea. The soil pH was alkaline, which was higher than the optimum range and exceeded the concentrations of OM. Av. P_2O_5 was also observed. The soil samples were collected in April, just before the maize season, and compost was generally applied before crop growth. We can assume that the OM and Av. P_2O_5 concentrations exceeding the optimum range were due to the application of compost fertilizer.

Table 2. Physicochemical properties and total heavy metal concentration in the soil.

	Sand	Silt	Clay	Texture	pH	EC	OM	Av. P_2O_5	Total Heavy Metal Concentration		
									As	Cd	Pb
	%	%	%			dS/m	%	mg/kg	mg/kg	mg/kg	mg/kg
Soil	36.2	50.4	13.4	Silt loam	7.23 ± 0.31	1.46 ± 0.12	3.66 ± 0.87	1131.8 ± 26.31	94.9 ± 4.28	4.2 ± 1.01	338.5 ± 22.5
Optimum range/ threshold value					6.0–6.5	<2.0	2.0–3.0	300–500	25	4	200

3.2. Effect of Amendments on Soil Chemical Properties

Soil chemical properties were measured after harvesting (32 weeks after sowing) and are summarized in Table 3. Although no significant difference was observed for soil pH in the BA and SM treatments compared to the control, the application of amendments increased the soil pH in all treatments. The highest soil pH increase was observed with SM+FeO treatment (12.2%), followed by SM + L treatment (9.0%). Increased EC values were also observed in all treatments, except BA. For OM and Av. P_2O_5, the values were decreased in all treatments compared to the control. The applied amendments were porous media with an increased surface area, which may have contributed to the sorbing of Av. P_2O_5 and complexation with OM [2]. In addition, P_2O_5 sorption could occurred when calcium (Ca) containing materials are applied in the soil by increasing the soil pH [31].

Table 3. Soil chemical properties in the upland field after harvesting the maize.

Treatment	pH	EC	OM	Av. P_2O_5
	(1:5)	dS/m	%	mg/kg
Control	7.30 ± 0.01 ^{c}	0.51 ± 0.01 ^{b}	3.49 ± 0.22 ^{a}	1246.8 ± 46.1 ^{a}
BA	7.60 ± 0.06 ^{bc}	0.40 ± 0.01 ^{c}	2.86 ± 0.44 ^{bc}	844.1 ± 42.2 ^{b}
SM	7.37 ± 0.08 ^{c}	0.61 ± 0.20 ^{a}	3.03 ± 0.25 ^{b}	1110.2 ± 31.8 ^{a}
SM + L	7.96 ± 0.19 ^{ab}	0.66 ± 0.04 ^{a}	1.94 ± 0.06 ^{d}	857.4 ± 46.2 ^{b}
SM + FeO	8.19 ± 0.36 ^{a}	0.64 ± 0.01 ^{a}	2.44 ± 0.06 ^{c}	1170.6 ± 64.7 ^{a}

Different letters indicate that the value is significantly different at $p < 0.05$.

3.3. The Effect of Amendments on Reducing the Bioavailable Heavy Metals in Soil

We evaluated the reduction efficiency of the bioavailable fractions of As, Cd, and Pb using amendment application in upland soil, and the M3 extracted heavy metal concentrations are summarized in Table 4. Significantly lower concentrations of bioavailable As were measured in all treatments compared to the control at 32 weeks after application. When calculating the reduction efficiency by comparing the bioavailable concentrations at 0 and 32 weeks, the highest reduction efficiency of As was observed with SM + FeO treatment (79.1%), followed by BA treatment (47.7%). This corresponds with previous investigations, in which the fate and mobility of As was highly impacted on iron oxide, and can be sorbed onto amorphous FeO (α-γ-Fe_2O_3), crystalline iron hydroxide (α-γ-FeOOH), or other forms of FeO minerals, reducing bioavailable As in the soil [32,33].

For Cd and Pb soil concentrations, a significantly higher reduction efficiency than the control was observed with the SM + L and SM + FeO treatments, with reduction efficiencies of 64.6% and 55.4% for As, respectively, and 41.4% and 35.5% for Pb, respectively. Various researchers have pointed out that soil pH is a major factor influencing the decrease in the bioavailable fraction of the cationic form of heavy metals in soil [1,34–36]. In our study, soil pH was significantly increased when SM was combined with lime, compared to the control (Table 3). Soil liming decreases its zeta potential and consequently increases soil pH [37]. As the soil pH increases, the cationic forms of Cd^{2+} or Pb^{2+} cause precipitation as an insoluble form of $Cd(OH)_2$, $CdCO_3$, or $2PbCO_3 \cdot Pb(OH)_2$ at the surface of the material, or in soil [13,38].

Table 4. Bioavailable concentration of heavy metals before and after cultivation in upland soil.

	Heavy Metals								
	As mg/kg			Cd mg/kg			Pb mg/kg		
	Before	**After**	**Reduction Efficiency (%)**	**Before**	**After**	**Reduction Efficiency (%)**	**Before**	**After**	**Reduction Efficiency (%)**
Control	2.12 ± 0.11 ^{a}	3.45 ± 0.06 ^{a}		0.35 ± 0.03 ^{a}	0.41 ± 0.01 ^{a}		55.53 ± 3.09 ^{b}	60.04 ± 0.89 ^{a}	
BA	2.66 ± 0.06 ^{a}	1.39 ± 0.17 ^{c}	47.7	0.36 ± 0.01 ^{a}	0.44 ± 0.01 ^{a}	−22.2	70.40 ± 0.55 ^{a}	63.76 ± 0.92^a	9.4
SM	2.29 ± 0.06 ^{a}	1.93 ± 0.05 ^{bc}	15.7	0.31 ± 0.01 ^{a}	0.41 ± 0.01 ^{a}	−32.3	52.36 ± 1.32 ^{b}	46.00 ± 0.84 ^{b}	12.1
SM + L	2.61 ± 0.07 ^{a}	2.15 ± 0.08 ^{b}	17.6	0.37 ± 0.03 ^{a}	0.08 ± 0.01 ^{b}	64.6	64.63 ± 4.98 ^{a}	37.88 ± 0.31 ^{b}	41.4
SM + FeO	2.20 ± 0.04 ^{a}	0.46 ± 0.03 ^{d}	79.1	0.31 ± 0.01 ^{a}	0.36 ± 0.01 ^{a}	55.4	55.49 ± 1.53 ^{b}	35.77 ± 2.85 ^{b}	35.5

Different letters indicate that the value is significantly different at $p < 0.05$.

Although less reduction efficiency was observed with SM + FeO than with SM+L treatment for bioavailable Cd and Pb in soil, FeO also had a higher reduction efficiency than BA and SM (Table 4). Yao et al. examined X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) analyses to verify the sorption mechanism of heavy metals with various sorbents, and concluded that the interaction between FeO and Cd or Pb in soil was affected more by a combination of multi-metal precipitation, or specific chemisorption, than by organic chelation [13]. Thus, we could assume that the ionic form of Cd can precipitate with FeO and form $CdFe_2O_4$ under alkaline conditions.

3.4. The Effect of Amendments on Heavy Metal Bioaccumulation

The heavy metal concentrations in maize corn and roots are summarized in Table 5. No significant reductions in heavy metals were observed for As and Cd with all treatments, except for the As concentrations in corn with SM + FeO treatment. Significantly lower maize corn Pb concentrations were observed in all the treatments, while no reductions were measured in the maize roots with all treatments. The highest reduction efficiency of As and Pb in corn was observed in the SM + FeO treatment of 59.3% and 66.2%, respectively.

Cao et al. examined 39 different maize cultivars to determine the bioconcentration factor (BCF) of As and Cd and reported that the BCF of As and Cd was ordered: root > stems > grain, for all 39 cultivars [39]. The average root concentrations of As and Cd were 5.5–52 and 1.2–13.5 times higher than those in straw or grain, respectively. Similar results were observed in our study, with 23.0–173.5, 32.0–78.0, and 10.5–38.2 times higher concentrations of As, Cd, and Pb observed in roots than in grains, respectively. The main reason for the higher accumulation of heavy metals in roots is that heavy metals are generally immobilized by complexation with iron oxide plaques or thiol ligands in roots, which inhibits heavy metal translocation to grain [40]. We therefore observed a markedly higher reduction efficiency of As and Pb in corn when FeO was combined with SM.

Table 5. Heavy metal concentration in corn and root of maize.

	Heavy Metals					
	As mg/kg		**Cd mg/kg**		**Pb mg/kg**	
	Corn	**Root**	**Corn**	**Root**	**Corn**	**Root**
Control	0.32 ± 0.04 ^{ab}	9.18 ± 1.46 ^{b}	0.01 ± 0.01 ^{a}	0.64 ± 0.10 ^{b}	3.02 ± 0.06 ^{a}	19.68 ± 1.51 ^{b}
BA	0.40 ± 0.20 ^{a}	18.01±1.72 ^{a}	0.02 ± 0.01 ^{a}	0.94 ± 0.05 ^{a}	1.63 ± 0.24 ^{b}	34.38 ± 3.29 ^{a}
SM	0.46 ± 0.16 ^{a}	10.59 ± 0.60 ^{b}	0.02 ± 0.01 ^{a}	0.64 ± 0.04 ^{b}	1.89 ± 0.16 ^{b}	19.89 ± 1.31 ^{b}
SM + L	0.31 ± 0.10 ^{ab}	17.88 ± 3.38 ^{a}	0.01 ± 0.01 ^{a}	0.78 ± 0.10 ^{ab}	1.15 ± 0.06 ^{c}	34.89 ± 5.69 ^{a}
SM + FeO	0.13 ± 0.07 ^{b}	22.55 ± 2.17 ^{a}	0.02 ± 0.01 ^{a}	1.23 ± 0.04 ^{a}	1.02 ± 0.06 ^{c}	38.98 ± 3.52 ^{a}

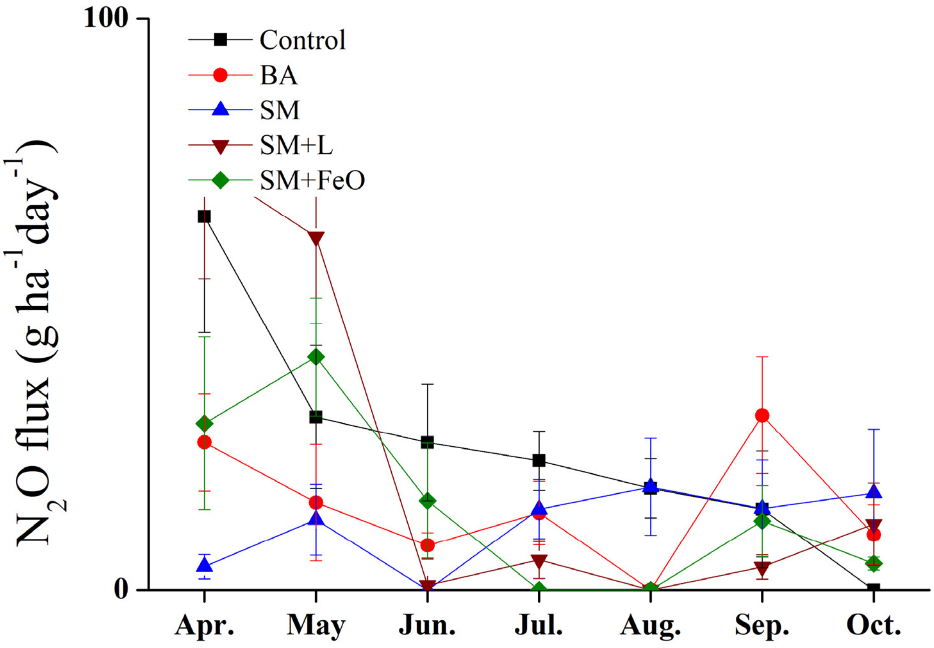
Different letters indicate that the value is significantly different at $p < 0.05$.

3.5. The Effect of Amendments on Greenhouse Gas Emission Reduction and Crop Yield

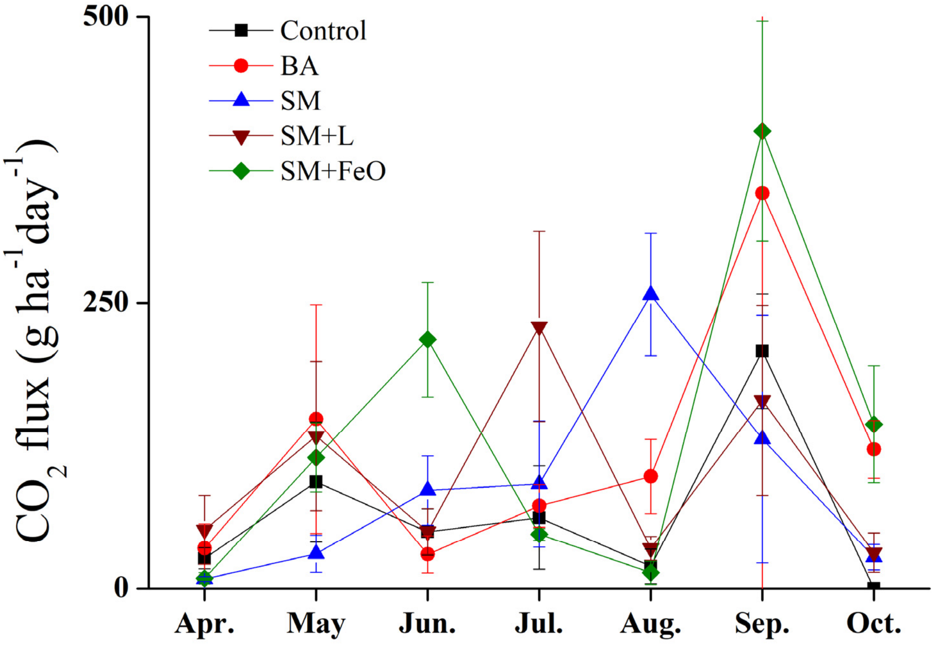
The temporal changes in N_2O and CO_2 fluxes with monthly measurements are shown in Figure 1. The high initial N_2O flux was stabilized 2 months after sowing in all the amendments. The highest peak of N_2O flux was observed in August at SM treatment, and again in September at SM + FeO treatment. For the CO_2 flux, a fluctuation was observed in all the treatments throughout the experimental period. The highest peak was observed in September with all treatments. The increased GHG emissions in August and September can likely be linked with the moisture content of the soil. When soil moisture reaches approximately 60% water-filled pore space (WFPS), N_2O emission is the greatest, with an exponential increase observed when WFPS is above 80% [9,41]. Rainfall data during the experimental period indicated that heavy rainfall frequently occurred at the end of July and the beginning of September (Figure 2). Therefore, we could assume that increased WFPS in upland soil may have enhanced GHG emissions [11,29]. In addition, drying and rewetting cycle can cause the high peak of N_2O and CO_2 in Figure 1. Kim et al. (2012) reported that the GHG emission peak occurred after soil rewetting and the throwing cycle [42]. Increased soil temperatures can also enhance GHG emissions in soil due to enzymatic reactions [43]. We did not measure the soil temperature, but the air temperature increased from July. The highest air temperature was observed in August (31.8 °C), which then gradually decreased in September. Assuming that the soil temperature also increased as the air temperature increased, the increased soil temperature may have contributed to the reduction in soil N_2O emissions. Other factors, such as soil Eh and soil ammonium contents, can effect GHG emissions.

The application of amendments significantly reduced cumulative N_2O-N soil emissions (Table 6). The highest reduction efficiency was observed with SM + FeO treatment (70.7%), followed by SM treatment (70.6%). No significant reductions were observed for cumulative CO2-C emissions. However, lower emissions were observed in all amendment treatments, ranging from 5.3% to 17.1%. SM+FeO treatment showed the highest reduction efficiency for both N_2O-N and CO_2-C emissions.

Greenhous gas (GHG) emissions in soil can be affected by various factors, such as soil pH, Eh, and ammonium nitrogen concentrations [10,11,29,44]. Soil acidification increases GHG emissions [5,45]. The microbial structure or functioning can be altered as the soil pH decreases [46]. When the soil pH is low, N_2O reduction rates can be reduced because of the inhibition of denitrification or production of enzymes [44,47]. The soil pH in our study increased with the application of amendments compared to the control. A significantly higher soil pH can be observed with the SM+L and SM + FeO treatments (Table 3). Increased soil pH might promote the reduction of N_2O to N_2 during denitrification. However, increased soil pH has a controversial effect on reducing CO_2 emissions [46]. Microbial activity and respiration generally increase as the soil pH increases, causing CO_2 production. This could explain the minimal effect of soil amendments on the reduction in CO_2 emissions in our study.



(**a**)



(**b**)

Figure 1. Monthly GHG flux, (**a**) N_2O flux, and (**b**) CO_2 flux.

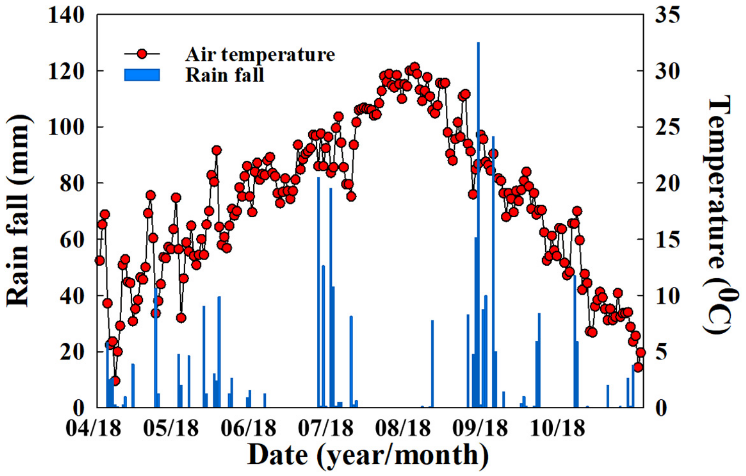


Figure 2. Air temperature and precipitation during the cultivation period.

Table 6. Cumulative N_2O-N and CO_2-C emission amounts based on a monthly measured gas emission flux.

	N_2O-N	CO_2-C
	kg/ha/yr	ton/ha/yr
Control	46.97 ± 9.33 ^{a}	35.19 ± 3.49 ^{a}
BA	20.34 ± 3.25 ^{b}	29.82 ± 0.84 ^{a}
SM	13.80 ± 3.81 ^{b}	33.33 ± 1.76 ^{a}
SM + L	16.64 ± 8.91 ^{b}	33.02 ± 1.74 ^{a}
SM + FeO	13.77 ± 7.91 ^{b}	29.20 ± 2.43 ^{a}

Different letters indicate that the value is significantly different at $p < 0.05$.

4. Conclusions

The application of SM, combined with lime (SM + L) and FeO (SM + FeO), was evaluated for the reduction in bioavailable heavy metals and greenhouse gas emissions in upland soil. When SM was combined with lime or FeO, bioavailable heavy metals and GHG emissions were significantly reduced. The highest reduction efficiency of As in soil was observed in the SM + FeO treatment (79.1%), and in the SM+L treatment for Cd and Pb by 64.6% and 41.4%, respectively. A reduction in bioaccumulated As and Pb in maize grain was also observed with SM + FeO by 59.3% and 66.2%, respectively, compared to the control. A GHG reduction was observed for all treatments, where a markedly greater reduction was measured for N_2O emissions than for CO_2. The greatest N_2O reduction was also observed in the SM + FeO treatment (70.7%). Overall, SM combined with FeO was the most efficient treatment for reducing both bioavailable heavy metals and N_2O emissions in upland soil. Thus, combinations with FeO might be necessary to enhance the efficiency of heavy metal remediation and GHG emission reduction in heavy metal-polluted soils.

Author Contributions: S.-C.K., conceptualization and supervision; J.-E.Y., funding acquisition and supervision; Y.-K.H., writing—original draft preparation and formal analysis; J.-W.K., methodology, validation and formal analysis; H.-S.K., formal analysis. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Korean Ministry of Environment, grant number 2019002820004.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: This subject is supported by the Korean Ministry of Environment as "The surface soil conservation and management" project, 2019002820004.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bolan, N.; Kunhikrishnan, A.; Thangarajan, R.; Kumpiene, J.; Park, J.; Makino, T.; Kirkham, M.B.; Scheckel, K. Remediation of heavy metal(loid)s contaminated soils–to mobilize or to immobilize? *J. Hazard. Mater.* **2014**, *266*, 141–166. [CrossRef] [PubMed]
2. Hong, Y.K.; Kim, J.W.; Kim, H.S.; Lee, S.P.; Yang, J.E.; Kim, S.C. Bottom Ash Modification via Sintering Process for Its Use as a Potential Heavy Metal Adsorbent: Sorption Kinetics and Mechanism. *Materials* **2021**, *14*, 3060. [CrossRef] [PubMed]
3. Lee, D.S.; Lim, S.S.; Park, H.J.; Yang, H.I.; Park, S.I.; Kwak, J.H.; Choi, W.J. Fly ash and zeolite decrease metal uptake but do not improve rice growth in paddy soils contaminated with Cu and Zn. *Environ. Int.* **2019**, *129*, 551–564. [CrossRef]
4. Chapuis-Lardy, L.; Wrage, N.; Metay, A.; Chotte, J.-L.; Bernoux, M. Soils, a sink for N2O? A review. *Glob. Chang. Biol.* **2007**, *13*, 1–17. [CrossRef]
5. Feng, Z.; Zhu, L. Impact of biochar on soil N2O emissions under different biochar-carbon/fertilizer-nitrogen ratios at a constant moisture condition on a silt loam soil. *Sci. Total Environ.* **2017**, *584–585*, 776–782. [CrossRef] [PubMed]
6. Farrell, M.; Perkins, W.T.; Hobbs, P.J.; Griffith, G.W.; Jones, D.L. Migration of heavy metals in soil as influenced by compost amendments. *Environ. Pollut.* **2010**, *158*, 55–64. [CrossRef] [PubMed]
7. Rosen, V.; Chen, Y. Effects of compost application on soil vulnerability to heavy metal pollution. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 35221–35231. [CrossRef]
8. Kumarathilaka, P.; Seneweera, S.; Meharg, A.; Bundschuh, J. Arsenic speciation dynamics in paddy rice soil-water environment: Sources, physico-chemical, and biological factors—A review. *Water Res* **2018**, *140*, 403–414. [CrossRef] [PubMed]
9. Oertel, C.; Matschullat, J.; Zurba, K.; Zimmermann, F.; Erasmi, S. Greenhouse gas emissions from soils—A review. *Geochemistry* **2016**, *76*, 327–352. [CrossRef]
10. Lee, H.H.; Kim, S.U.; Han, H.R.; Hur, D.Y.; Owens, V.N.; Kumar, S.; Hong, C.O. Mitigation of global warming potential and greenhouse gas intensity in arable soil with green manure as source of nitrogen. *Environ. Pollut.* **2021**, *288*, 117724. [CrossRef]
11. Ruangcharus, C.; Kim, S.U.; Yoo, G.Y.; Choi, E.J.; Kumar, S.; Kang, N.; Hong, C.O. Nitrous oxide emission and sweet potato yield in upland soil: Effects of different type and application rate of composted animal manures. *Environ. Pollut.* **2021**, *279*, 116892. [CrossRef]
12. Wu, Y.; Zhou, X.-y.; Lei, M.; Yang, J.; Ma, J.; Qiao, P.-w.; Chen, T.-b. Migration and transformation of arsenic: Contamination control and remediation in realgar mining areas. *Appl. Geochem.* **2017**, *77*, 44–51. [CrossRef]
13. Yao, A.; Ju, L.; Ling, X.; Liu, C.; Wei, X.; Qiu, H.; Tang, Y.; Morel, J.L.; Qiu, R.; Li, C.; et al. Simultaneous attenuation of phytoaccumulation of Cd and As in soil treated with inorganic and organic amendments. *Environ. Pollut.* **2019**, *250*, 464–474. [CrossRef]
14. Derakhshan Nejad, Z.; Jung, M.C.; Kim, K.H. Remediation of soils contaminated with heavy metals with an emphasis on immobilization technology. *Environ. Geochem. Health* **2018**, *40*, 927–953. [CrossRef]
15. Huang, J.H.; Hsu, S.H.; Wang, S.L. Effects of rice straw ash amendment on Cu solubility and distribution in flooded rice paddy soils. *J. Hazard. Mater.* **2011**, *186*, 1801–1807. [CrossRef]
16. Kobayashi, Y.; Ogata, F.; Nakamura, T.; Kawasaki, N. Synthesis of novel zeolites produced from fly ash by hydrothermal treatment in alkaline solution and its evaluation as an adsorbent for heavy metal removal. *J. Environ. Chem. Eng.* **2020**, *8*, 103687. [CrossRef]
17. Xu, D.; Ji, P.; Wang, L.; Zhao, X.; Hu, X.; Huang, X.; Zhao, H.; Liu, F. Effect of modified fly ash on environmental safety of two soils contaminated with cadmium and lead. *Ecotoxicol. Environ. Saf.* **2021**, *215*, 112175. [CrossRef]
18. Alam, Q.; Dezaire, T.; Gauvin, F.; Delsing, A.C.A.; Brouwers, H.J.H. Valorization of bottom ash fines by surface functionalization to reduce leaching of harmful contaminants. *J. Environ. Manag.* **2020**, *271*, 110884. [CrossRef] [PubMed]
19. Chindaprasirt, P.; Jaturapitakkul, C.; Chalee, W.; Rattanasak, U. Comparative study on the characteristics of fly ash and bottom ash geopolymers. *Waste Manag.* **2009**, *29*, 539–543. [CrossRef]
20. Levandowski, J.; Kalkreuth, W. Chemical and petrographical characterization of feed coal, fly ash and bottom ash from the Figueira Power Plant, Paraná, Brazil. *Int. J. Coal Geol.* **2009**, *77*, 269–281. [CrossRef]
21. Bethanis, S.; Cheeseman, C.R.; Sollars, C.J. Properties and microstructure of sintered incinerator bottom ash. *Ceram. Int.* **2002**, *28*, 881–886. [CrossRef]
22. Geetha, S.; Ramamurthy, K. Properties of sintered low calcium bottom ash aggregate with clay binders. *Constr. Build. Mater.* **2011**, *25*, 2002–2013. [CrossRef]
23. Giro-Paloma, J.; Mañosa, J.; Maldonado-Alameda, A.; Quina, M.J.; Chimenos, J.M. Rapid sintering of weathered municipal solid waste incinerator bottom ash and rice husk for lightweight aggregate manufacturing and product properties. *J. Clean. Prod.* **2019**, *232*, 713–721. [CrossRef]
24. Luo, H.; Wu, Y.; Zhao, A.; Kumar, A.; Liu, Y.; Cao, B.; Yang, E.-H. Hydrothermally synthesized porous materials from municipal solid waste incineration bottom ash and their interfacial interactions with chloroaromatic compounds. *J. Clean. Prod.* **2017**, *162*, 411–419. [CrossRef]

25. Pena, R.; Guerrero, A.; Goni, S. Hydrothermal treatment of bottom ash from the incineration of municipal solid waste: Retention of Cs(I), Cd(II), Pb(II) and Cr(III). *J. Hazard. Mater.* **2006**, *129*, 151–157. [CrossRef]
26. Chiang, Y.W.; Ghyselbrecht, K.; Santos, R.M.; Meesschaert, B.; Martens, J.A. Synthesis of zeolitic-type adsorbent material from municipal solid waste incinerator bottom ash and its application in heavy metal adsorption. *Catal. Today* **2012**, *190*, 23–30. [CrossRef]
27. Ipsilantis, I.; Coyne, M.S. Soil microbial community response to hexavalent chromium in planted and unplanted soil. *J. Environ. Qual.* **2007**, *36*, 638–645. [CrossRef]
28. Linn, D.M.; Doran, J.W. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Sci. Soc. Am. J.* **1984**, *48*, 1267–1272. [CrossRef]
29. Kim, S.U.; Lee, H.H.; Moon, S.M.; Han, H.R.; Hong, C.O. Nitrous oxide emissions and maize yield as influenced by nitrogen fertilization and tillage operations in upland soil. *Appl. Biol. Chem.* **2021**, *64*, 18. [CrossRef]
30. Luo, H.; He, D.; Zhu, W.; Wu, Y.; Chen, Z.; Yang, E.H. Humic acid-induced formation of tobermorite upon hydrothermal treatment with municipal solid waste incineration bottom ash and its application for efficient removal of Cu(II) ions. *Waste Manag.* **2019**, *84*, 83–90. [CrossRef]
31. Reddy, K.R.; Vardanyan, L.; Hu, J.; Villapando, O.; Bhomia, R.K.; Smith, T.; Harris, W.G.; Newman, S. Soil phosphorus forms and storage in stormwater treatment areas of the Everglades: Influence of vegetation and nutrient loading. *Sci. Total Environ.* **2020**, *725*, 138442. [CrossRef] [PubMed]
32. Aftabtalab, A.; Rinklebe, J.; Shaheen, S.M.; Niazi, N.K.; Moreno-Jimenez, E.; Schaller, J.; Knorr, K.H. Review on the interactions of arsenic, iron (oxy)(hydr)oxides, and dissolved organic matter in soils, sediments, and groundwater in a ternary system. *Chemosphere* **2022**, *286*, 131790. [CrossRef]
33. Stopelli, E.; Duyen, V.T.; Mai, T.T.; Trang, P.T.K.; Viet, P.H.; Lightfoot, A.; Kipfer, R.; Schneider, M.; Eiche, E.; Kontny, A.; et al. Spatial and temporal evolution of groundwater arsenic contamination in the Red River delta, Vietnam: Interplay of mobilisation and retardation processes. *Sci. Total Environ.* **2020**, *717*, 137143. [CrossRef] [PubMed]
34. Cao, X.; Ma, L.; Liang, Y.; Gao, B.; Harris, W. Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. *Environ. Sci. Technol.* **2011**, *45*, 4884–4889. [CrossRef]
35. Li, H.; Xu, H.; Zhou, S.; Yu, Y.; Li, H.; Zhou, C.; Chen, Y.; Li, Y.; Wang, M.; Wang, G. Distribution and transformation of lead in rice plants grown in contaminated soil amended with biochar and lime. *Ecotoxicol. Environ. Saf.* **2018**, *165*, 589–596. [CrossRef] [PubMed]
36. Wang, Z.; Liu, G.; Zheng, H.; Li, F.; Ngo, H.H.; Guo, W.; Liu, C.; Chen, L.; Xing, B. Investigating the mechanisms of biochar's removal of lead from solution. *Bioresour. Technol.* **2015**, *177*, 308–317. [CrossRef] [PubMed]
37. Tan, Z.; Yuan, S.; Hong, M.; Zhang, L.; Huang, Q. Mechanism of negative surface charge formation on biochar and its effect on the fixation of soil Cd. *J. Hazard. Mater.* **2020**, *384*, 121370. [CrossRef] [PubMed]
38. He, L.L.; Huang, D.Y.; Zhang, Q.; Zhu, H.H.; Xu, C.; Li, B.; Zhu, Q.H. Meta-analysis of the effects of liming on soil pH and cadmium accumulation in crops. *Ecotoxicol. Environ. Saf.* **2021**, *223*, 112621. [CrossRef]
39. Cao, X.; Gao, X.; Zeng, X.; Ma, Y.; Gao, Y.; Baeyens, W.; Jia, Y.; Liu, J.; Wu, C.; Su, S. Seeking for an optimal strategy to avoid arsenic and cadmium over-accumulation in crops: Soil management vs cultivar selection in a case study with maize. *Chemosphere* **2021**, *272*, 129891. [CrossRef]
40. Cao, X.; Bai, L.; Zeng, X.; Zhang, J.; Wang, Y.; Wu, C.; Su, S. Is maize suitable for substitution planting in arsenic-contaminated farmlands? *Plant Soil Environ.* **2019**, *65*, 425–434. [CrossRef]
41. Davidson, E.A.; LKeller, M.; Erickson, H.E.; Verchot, L.V.; Veldkamp, E. Testing a conceptual model of soil emissions of nitrous and nitric oxides. *Bioscience* **2000**, *50*, 667–680. [CrossRef]
42. Kim, D.G.; Vargas, R.; Bond-Lamberty, B.; Turetsky, M.R. Effects of soil rewetting and thawing on soil gas fluxes: A review of current literature and suggestions for future research. *Biogeosciences* **2012**, *9*, 2459–2483. [CrossRef]
43. da Silva Cardoso, A.; Junqueira, J.B.; Reis, R.A.; Ruggieri, A.C. How do greenhouse gas emissions vary with biofertilizer type and soil temperature and moisture in a tropical grassland? *Pedosphere* **2020**, *30*, 607–617. [CrossRef]
44. Hu, J.; Inglett, K.S.; Wright, A.L.; Reddy, K.R. Nitrous Oxide Production and Reduction in Seasonally-Flooded Cultivated Peatland Soils. *Soil Sci. Soc. Am. J.* **2016**, *80*, 783–793. [CrossRef]
45. Tarin, M.W.K.; Khaliq, M.A.; Fan, L.; Xie, D.; Tayyab, M.; Chen, L.; He, T.; Rong, J.; Zheng, Y. Divergent consequences of different biochar amendments on carbon dioxide (CO_2) and nitrous oxide (N_2O) emissions from the red soil. *Sci. Total Environ.* **2021**, *754*, 141935. [CrossRef]
46. Abalos, D.; Liang, Z.; Dörsch, P.; Elsgaard, L. Trade-offs in greenhouse gas emissions across a liming-induced gradient of soil pH: Role of microbial structure and functioning. *Soil Biol. Biochem.* **2020**, *150*, 108006. [CrossRef]
47. Nobile, C.; Denier, J.; Houben, D. Linking biochar properties to biomass of basil, lettuce and pansy cultivated in growing media. *Sci. Hortic.* **2020**, *261*, 109001. [CrossRef]