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## Article

# Sawdust Amendment in Agricultural and Pasture Soils Can Reduce Iodine Losses

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**Abstract:** Iodine loss is common in the soil of hilly regions due to higher precipitation rates and steeper slopes. Iodine deficiency in soil reduces iodine's bioavailability to fruits and vegetables and consequently may contribute to health complications. However, the iodine retention of soils after the addition of selected organic and inorganic amendments has not been studied. Therefore, a study was carried out to investigate iodine loss during surface runoff. For this purpose, a soil amendment (namely, sawdust, charcoal, wood ash, lime or gypsum) was applied separately to pasture and agricultural soils under natural rainfall conditions. The soil was fertigated with iodine in the form of potassium iodide (KI) at the rate of 200 ppm. Surface runoff was related to soil properties. Results showed that iodine content in surface runoff was linearly related with soil pH ( $R^2 = 0.89$ ,  $p < 0.05$ ) and inversely related with soil organic carbon ( $R^2 = -0.76$ ,  $p < 0.05$ ). Soils amended with sawdust had significantly reduced iodine content in runoff. A higher amount of iodine was lost via surface runoff from soil after inorganic amendment. Soil amendments were varied for iodine retention in soil in the order of sawdust > charcoal > wood ash > lime > gypsum. The study results indicated that organic amendments, especially sawdust, improved soil properties and increased the iodine retention capacity of soils.

**Keywords:** iodine losses; surface runoff; sawdust; charcoal; wood ash; lime; gypsum

## 1. Introduction

Iodine (I) is an essential micronutrient and its deficiency in food sources can cause severe iodine deficiency disorders (IDDs) [1]. IDDs have been a severe concern, especially in hilly areas. Iodine is reported to be deficient in the soils of hilly areas in Pakistan. The iodine is either washed away by heavy rainfall or lost via leaching through soils. The iodine content of soil reflects the balance between the input amount and the ability of soils to guard it against leaching. Though iodine loss is due to many factors, the use of amendments can enhance iodine retention in soils. Research on the retention of iodine in soils has been poorly studied [2].

In the 1990s, 70% of the world's population was supplied with iodized salt, but IDDs still exist despite the iodized salt program [3]. Despite employing various strategies for combating iodine deficiency, the problem persists in Australia, the United Kingdom, the

Himalayas, and the Alps and is also severe in third world countries [4,5]. Biofortification of crops with iodine has been studied, whereas prevention of iodine losses from soil has been given less consideration.

Generally, iodine in soil is incorporated from the atmosphere, fixation, and volatilization, resulting in a wide range of soil iodine concentrations (0.1 to 150 mg kg<sup>-1</sup>) [6,7]. Iodine is distributed unevenly in soils and its fate in soils is determined by its chemical forms and the soil's features [8,9]. It is supplied via atmospheric transfer and the degradation of plant tissues. Iodine from the atmosphere is delivered to the lithosphere during precipitation, whereas a large proportion is washed away by runoff [10]. Himalayan and Alps watershed regions are reportedly iodine deficient [11,12]. Iodine loss by runoff and volatilization also restrict iodine bioavailability [13–15] due to iodine biogeochemical changes in soil [16] and the low retention capacity of soils.

Soil erosion and runoff accelerates the loss of soil nutrients and biota due to low organic matter and water holding capacity [15,17]. Vegetation removal from the soil surface degrades soil aggregates and enhances sediment transport in runoff. Soil physicochemical parameters, especially soil's organic matter, influences iodine availability and immobilization [18–21]. The formation of covalent bonding between carbon atoms and iodine in humified soil is considered to reduce the rate of iodine dissipation [22]. Electrophilic substitution of H by iodine in a phenolic ring is the mechanism of iodine's interaction with organic substances [23]. Soil bacteria can speed up this process by using laccase enzymes to oxidise I to I<sub>2</sub> and HOI, which are adsorbed into organic matter [24,25].

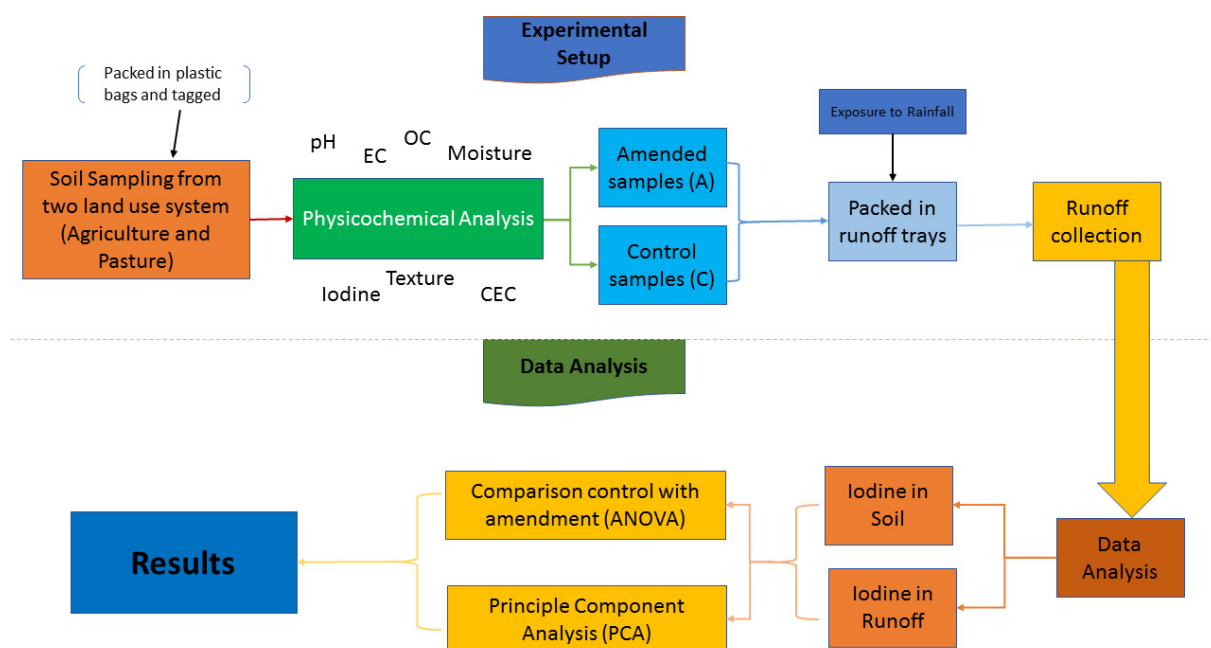
Previously, there was greater attention paid to the fractionation of iodine [26], its bioavailability, biofortification [27,28], and sorption and desorption of iodine in the soil [29–31], but little effort had been made to study its retention and loss via runoff in hilly areas of Pakistan. Furthermore, the application of amendments to reduce iodine via surface runoff is not well studied. Therefore, this study aimed to evaluate the effects of soil amendments on iodine content in soil runoff.

## 2. Materials and Methods

### 2.1. Experimentation

The soil for this experiment was collected (0–20 cm) from cultivated and pastured lands in the Abbottabad District, Pakistan. The Abbottabad District is situated in the lesser Himalayas region. The study area is situated 1260 m above sea level and located between 34°92' N and 73°13' E. The area has a steep to moderately steep slope. The lithology of the rock formation comprises dolomitic limestone. The upper rock formation is made up of sandstone, while the lower is made up of shale. Composite soil samples were collected from plots of 400 m<sup>2</sup> (20 × 20 m<sup>2</sup>) and then mixed thoroughly. Wooden trays (size: 0.5 m × 0.5 m × 0.1 m) were layered with a plastic sheet at the bottom and sides and were packed with 10 kg of soil. The schematic of the experiment's workflow is given in Figure 1.

Five discrete amendments, i.e., gypsum, slaked lime, fly ash, charcoal, and sawdust, were mixed in the surface soil at a rate of 20 t ha<sup>-1</sup> (based on 2 million kg soil per plow layer per ha). The material used in this research was screened through a 0.25 mm sieve. Potassium iodide was added at a rate of 200 mg iodine kg<sup>-1</sup>. The trays were placed at a 5% slope in an open field. The soils packed in the trays were moistened and incubated at field capacity for two days. The outlet of each tray was connected to a plastic bottle, through which the runoff was collected during rainfall events of 2 h. The runoff water was filtered using filter paper (Whatman 42). Water-soluble iodine in water samples was determined by the procedure reported previously [32]. The soil loss in the runoff collected was also determined by evaporating the water in an oven at 105 °C after which the dry soil sediments were weighed. Iodine concentrations in both collected runoff (µg L<sup>-1</sup>) and soil (µg kg<sup>-1</sup> or mg kg<sup>-1</sup>) were determined by the method described by Kesari et al. [33].



**Figure 1.** Schematic workflow of the experiment and data analysis.

## 2.2. Soil Analyses

Soil samples were air-dried, sieved via a 2-mm sieve, and characterised for physicochemical properties (Table 1). Soil moisture content was measured by the gravimetric method after drying the samples at 105 °C for 24 h. Soil bulk density was measured by sampling a known volume of soil using a metal ring that was pressed into the soil and weighed after drying [34]. The soil's water holding capacity was measured by comparing the water content of the sample versus the dry weight of the soil sample. The hydrometric method was used to determine soil texture [35]. A soil–water solution (1:5) was used for the determination of the pH and EC of the soil (Model: HANNA HI 8520). One molar ammonium acetate solution (NH<sub>4</sub>OAc) (pH 7) was used for extraction the exchangeable cations and the contents were determined using an atomic absorption spectrophotometer (Model: Analyst 700, Perkin Elmer). Total carbon was calculated by the loss-on-ignition method [36]. Approximately 100 g of soil sample was placed in the furnace for 2 h at 550 °C and then samples were cooled in a desiccator for 40 min. Total C was calculated based on weight-loss-on-ignition.

**Table 1.** Physicochemical Properties of soils used in the study.

Soil Sample	C	Iodine	Ca	K	CE	EC	pH	Moisture	Sand	Silt	Clay
	g kg <sup>-1</sup>			mg kg <sup>-1</sup>		µS/cm			%		
Agric.	21.6 <sup>a</sup>	0.42 <sup>b</sup>	76.3 <sup>b</sup>	156 <sup>b</sup>	324 <sup>b</sup>	125 <sup>a</sup>	7.6 <sup>a</sup>	18.2 <sup>b</sup>	75.6 <sup>a</sup>	16.6 <sup>a</sup>	7.8 <sup>b</sup>
Pasture	15.6 <sup>b</sup>	0.54 <sup>a</sup>	149 <sup>a</sup>	171 <sup>a</sup>	388 <sup>a</sup>	92 <sup>b</sup>	7.8 <sup>b</sup>	21.2 <sup>a</sup>	69.2 <sup>a</sup>	9.2 <sup>a</sup>	21.6 <sup>a</sup>

The same lettering showing no significant difference.

For iodine determination, the method proposed by Kesari et al. [33] was used, in which iodine was extracted from the soil, oxidation of iodide to iodate was carried out by bromine water, and free iodine was liberated from iodate by the addition of KI in an acidic medium. The iodine was then reacted with leuco crystal violet and the pH of the medium was adjusted to between 4.5–5.5. The solution was left for 30 min for color development and iodine content was determined by UV-spectrophotometer at 591 nm. The physicochemical properties of the soil are given in Table 1. The pasture soil has higher

iodine content ( $0.54 \text{ mg kg}^{-1}$ ), CEC ( $388 \text{ mg kg}^{-1}$ ), pH (7.8) and moisture content (21.2%) than agricultural soil.

### 2.3. Statistical Analyses

The mean difference between groups was measured using a one-way analysis of variance (ANOVA) with least significance difference (LSD) test ( $p < 0.05$ ). Multivariate analyses, such as principal component analysis (PCA) and cluster analysis, were used to understand the factors impacting iodine retention in the soil because they are more thorough and precise than univariate analyses [37]. PCA is widely used for data summarisation and determination of linear relationships between variables. PCA divides data into tiny groups with substantial effects, which are represented as linear combinations and can preserve a lot of information about the original data set [37,38].

## 3. Results

### 3.1. Iodine Removal in Surface Runoff

Agricultural soil had higher iodine concentrations in runoff after amendment with lime and gypsum as compared to the control (Figure 2). Sawdust-amended soil had the lowest iodine concentrations in surface runoff, followed by charcoal and wood ash. Pasture soil amended with gypsum released significantly more iodine in surface runoff than the control. Soil amended with sawdust showed significantly less iodine loss. Both gypsum and lime amended soils showed an increase in the iodine contents of their runoff by 5% and 3.1%, respectively, as compared to the control. Sawdust reduced iodine content in surface runoff by 24.9%, charcoal reduced iodine content by 19.6%, and wood ash reduced iodine content by 14.9%. Pasture soil also showed a change in the iodine content of runoff after adding soil amendments. All of the amendments, except lime and gypsum, decreased iodine loss during surface runoff. Like agricultural soil, sawdust amendment in pasture soil was superior to other amendments.

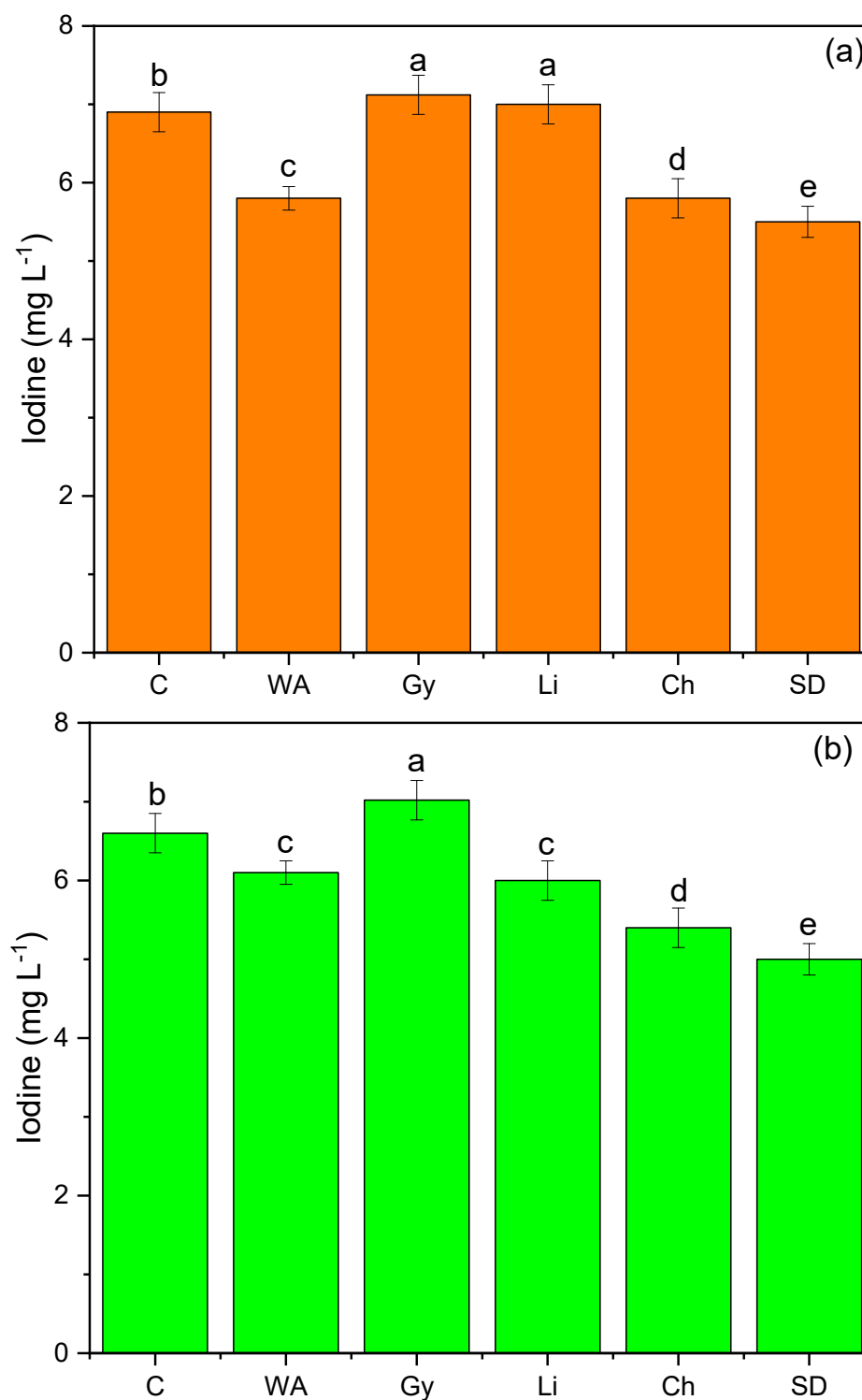
### 3.2. Iodine Retention in Soils

Figure 3a represents iodine retention in the soils of two land use systems. In both land use systems, all of the amendments significantly enhanced iodine retention except for the gypsum amendment, and sawdust amended soil significantly enhanced iodine retention in comparison to the control. All of the amendments, in both soils, retained iodine in the order of sawdust > charcoal > wood ash > lime > gypsum.

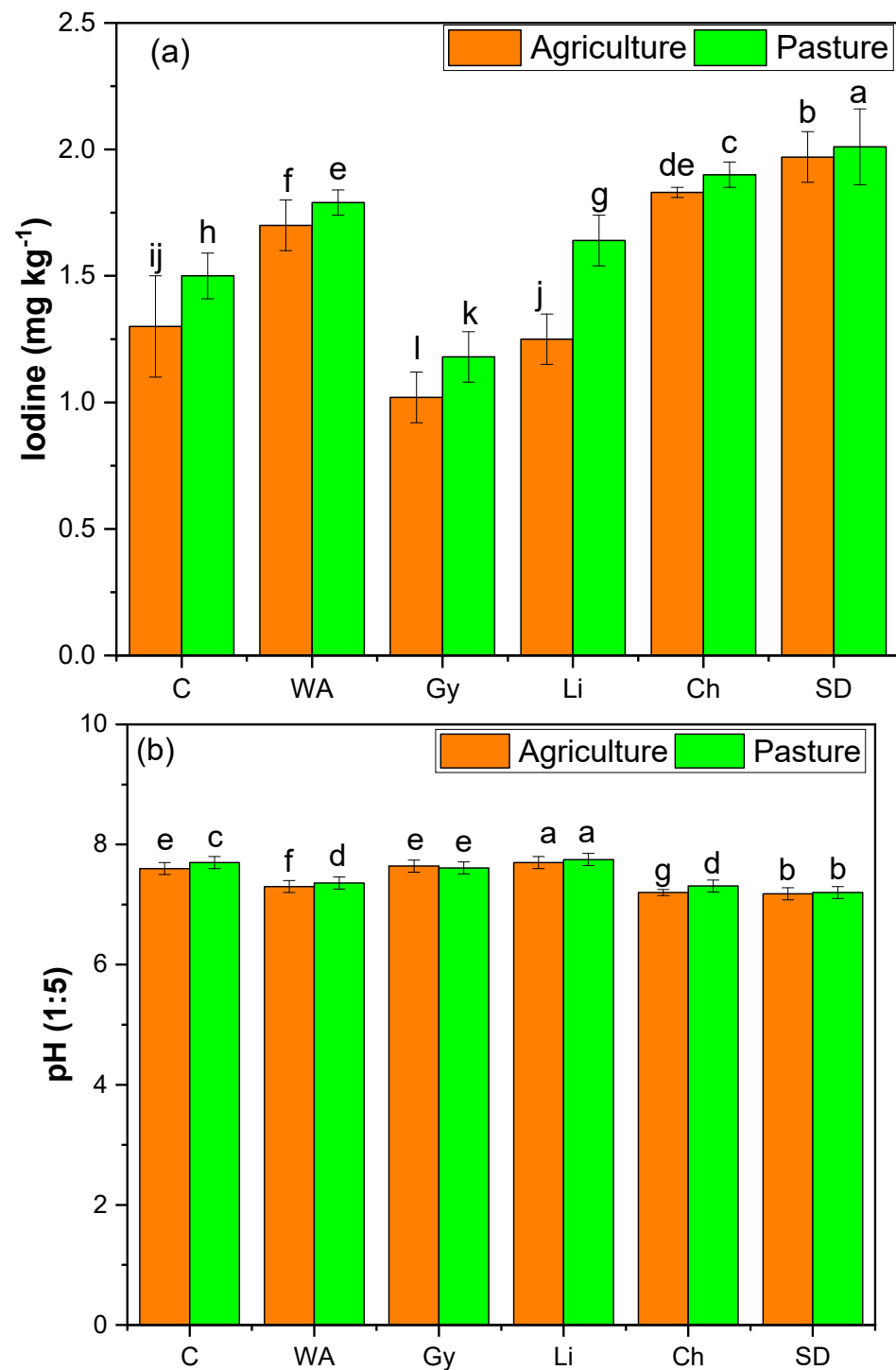
Except gypsum, all types of amendments retained iodine in agricultural soil against runoff. Sawdust retained the most iodine content in agricultural soil, followed by charcoal and wood ash. Compared with the control, the pH value of the amended soils varied substantially. The soil amendments, namely sawdust, charcoal, and wood ash, reduced the pH of the soil, while lime and gypsum increased the soil pH when compared with the control. In agricultural soil, gypsum retained less iodine and had higher soil pH. Sawdust-amended soil retained  $1.97 \text{ mg kg}^{-1}$  of iodine at pH 7.18 when compared with the control (no amendment). Charcoal- and wood ash-amended agricultural soil retained  $1.8 \text{ mg kg}^{-1}$  and  $1.7 \text{ mg kg}^{-1}$  iodine at pH 7.2 and 7.3, respectively. Both gypsum and lime increased the pH of soil (7.64 and 7.70) and retained  $1.0 \text{ mg kg}^{-1}$  and  $1.3 \text{ mg kg}^{-1}$  of iodine, which was lower than the iodine retained by the control soil. More iodine (52.3%) was retained by the sawdust-treated soil, followed by charcoal (41.3%), and wood ash (31.4%), while soils with added lime and gypsum retained 3.5% and 21.3% less iodine, respectively, compared to the control.

The pH of pasture soils (with or without amendment) ranged between 7.20 and 7.75. Sawdust reduced pH of pasture soil more than other soil amendments.  $2.1 \text{ mg kg}^{-1}$  of iodine was retained by the sawdust and maintained a soil pH of 7.2. Charcoal and wood ash retained iodine up to  $1.9 \text{ mg kg}^{-1}$  and  $1.79 \text{ mg kg}^{-1}$  at pH 7.31 and 7.36, respectively. Sawdust retained 34% more iodine in pasture soil, followed by charcoal (26.7%), wood ash (19.3%), and lime (9.3%), respectively. Gypsum reduced the iodine retention capacity of soil

(<21.3%) more than the control soil (Figure 3). During this study, an inverse relationship was found between iodine retention and soil pH. The retention of iodine decreased with increasing soil pH. Lime and gypsum increased the pH of the soil; therefore, lower iodine retention was achieved with these amendments. Sawdust, charcoal, and wood ash reduced the pH of the soils and higher retention of iodine was noted in soils with these amendments.



**Figure 2.** Iodine in surface runoff of agricultural soil (a) and pasture soil (b) applied with soil amendments (C = control, WA = wood ash, Gy = gypsum, Li = lime, Ch = charcoal, SD = sawdust). The same lettering showing the no significant difference.



**Figure 3.** Iodine concentration retained by the soil (a) and pH (b) after application of amendments (C = control, WA = wood ash, Gy = gypsum, Li = lime, Ch = charcoal, SD = sawdust). The same lettering showing the no significant difference.

The pH of the amended soils varied after application of both organic and inorganic amendments. Although the pH of some amendments did not differ significantly, soils amended with gypsum, lime, and sawdust had significantly different pH levels when compared with the control.

### 3.3. Soil Losses

The addition of amendments to the soils reduced soil losses, except for the gypsum and lime amendments. In agricultural soil, there was a 45.9% decrease in soil loss after amendment with sawdust, followed by charcoal (40.1%), and wood ash (36.7%). Gypsum and lime increased topsoil loss by 5.6% and 1.4%, respectively, in comparison with the control. In pasture soil, all amendments decreased soil losses up to 41.0% when compared with the control, except gypsum. Sawdust reduced soil loss by 41.0%, followed by charcoal (22.5%), wood ash (10.7%), and lime (3.6%). Gypsum increased soil loss by 9.5%.

### 3.4. Multivariate and Correlation Analysis

Multivariate analyses were performed using cluster analysis (CA) and principal component analysis (PCA) in order to incorporate factors affecting the iodine retention in soil. Origin software (ORIGIN 2021) was used for CA and PCA and the two main clusters are shown in Figure 4. These clusters were identified on the basis of the distribution of iodine retention and surface runoff in the soils. Two main clusters were identified: factors affecting iodine in runoff and factors affecting iodine retention in soil. The first cluster was divided into two sub clusters: (1) soil loss-I (runoff) and (2) soil loss-I (runoff)-pH. The second cluster was divided into three subclusters; (1) iodine (retained)-carbon, (2) sand-silt, and (3) EC. PCA is extensively used in determining the factors affecting iodine runoff after the application of amendments. Mean values of soil physicochemical properties, along with the soil's iodine retention and loss, was treated by PCA using Varimax rotation with Kaiser Normalization to find their compositional pattern. In Figure 5, solid points represent amendment and the solid line is representative of the approximate correlations between soil properties and soil amendments. The length of the line indicates the overall contribution of soil properties to the soil amendments. The direction of each line indicates its correlation with each axis, since the vector lines parallel to an axis are highly correlated with that axis, while angles between the vector lines demonstrate correlations between the amendments.

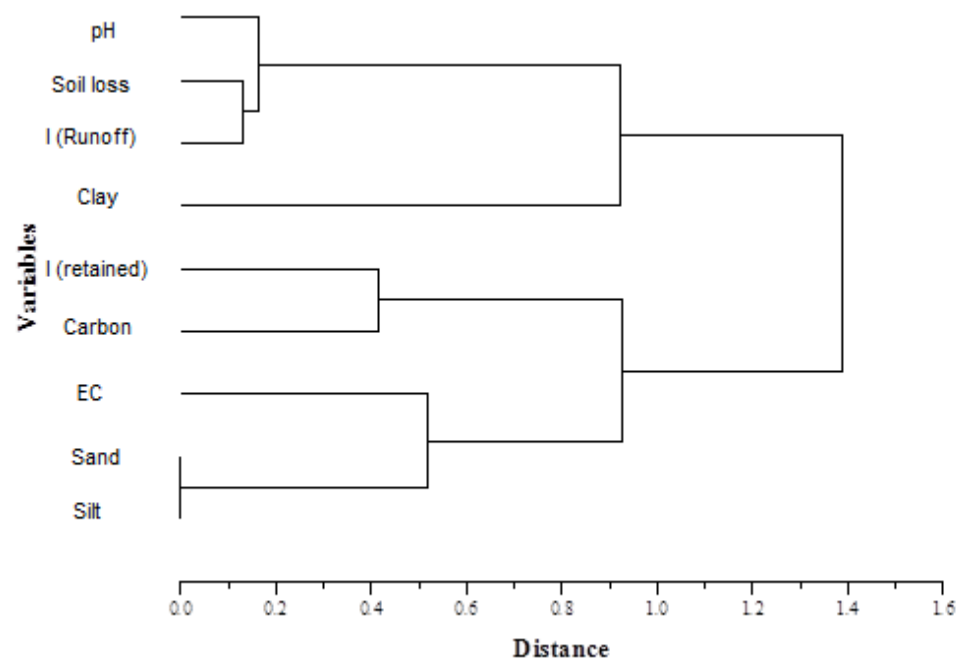
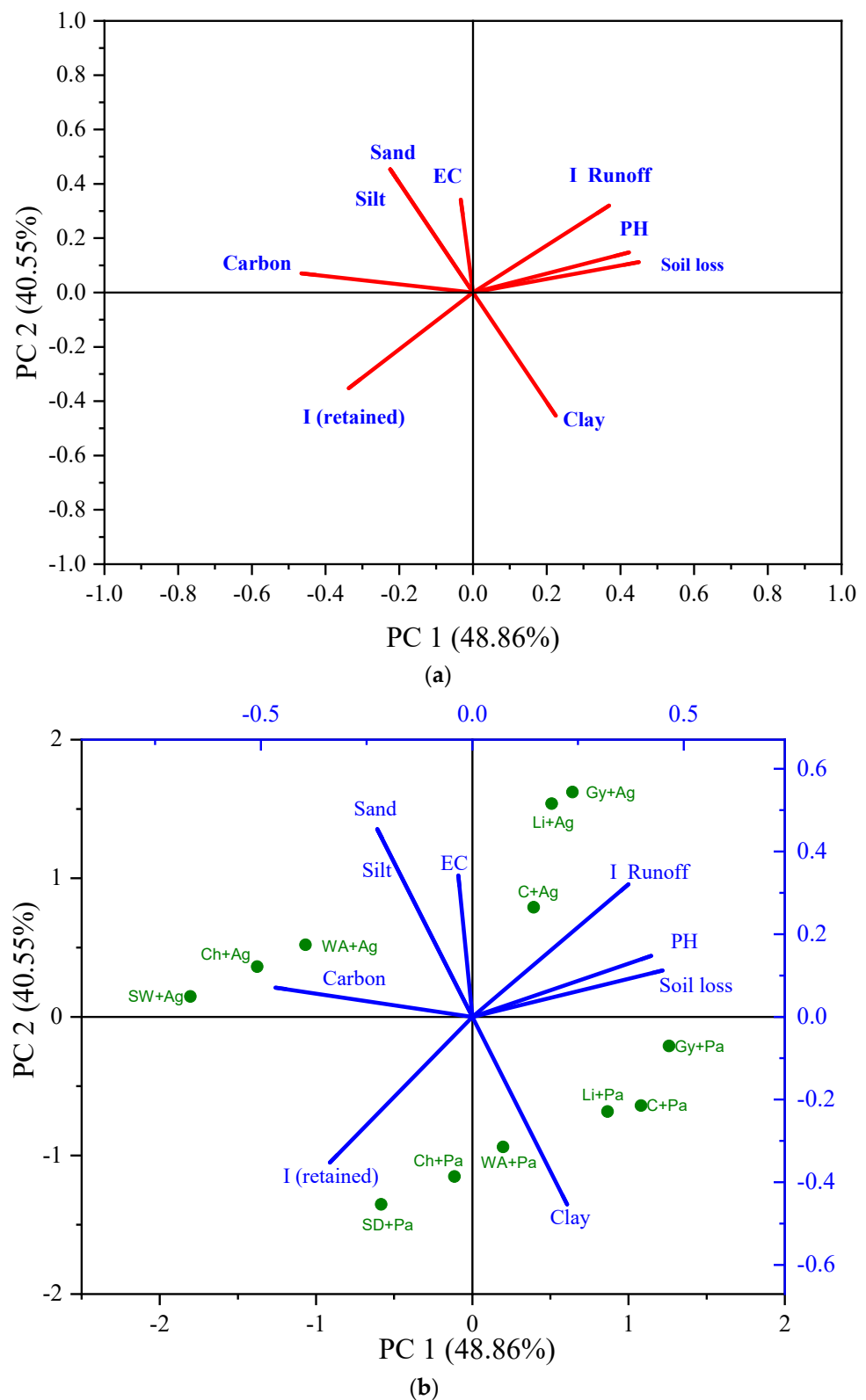


Figure 4. Cluster analysis.





**Figure 5.** Principal component analysis of soil applied with amendments. (a) without amendments and landuse systems; (b) with amendments and landuse system.

### 3.5. Principal Component Analysis

Two principal components, PCA 1 and PCA 2, were extracted based on eigenvalue (>1). The accumulated variance accounted for 89.41% of the total variation (Table 2). The first component contributed 48.86% of the total variation with a maximum loading of four

soil parameters: pH, soil loss, carbon, and iodine content in runoff, with a percent variance of 0.42, 0.44,  $-0.46$  and  $0.36$ , respectively. The contribution of the second component was 40.5% of the cumulative variation and had maximum loading of iodine retained ( $-0.35$ ), EC ( $0.34$ ), sand ( $-0.46$ ), silt ( $-0.44$ ), and clay ( $-0.49$ ).

**Table 2.** Principal component analysis (PCA) of the soil applied with amendments.

Variables	PC 1	PC 2
Total variance	48.86%	40.55%
Cumulative variance	48.86%	89.41%
Eigenvalue	4.3970	3.6499
pH	0.4228	0.1473
I retention	$-0.3369$	$-0.3524$
Soil loss	0.4498	0.1117
EC	$-0.0329$	0.3416
Sand	$-0.2245$	0.46
Silt	$-0.2245$	0.44
Clay	0.2245	$-0.49$
OC	$-0.4653$	0.0706
I in runoff	0.3693	0.3204

Figure 5 shows the distribution of the variables in PCA 1 and PCA 2. The results showed that EC has the lowest contribution compared to rest of the variables. Clay is inversely related to silt and sand, while positively related to carbon and iodine retention. The iodine in runoff was closely related to pH and soil loss. In Figure 5b, charcoal, wood ash, and sawdust affected the carbon content of agricultural soil, while more iodine was retained by the pasture soil amended with charcoal, sawdust, and wood ash. The lime- and gypsum-amended soil increased the iodine content of the runoff.

## 4. Discussion

### 4.1. Iodine Retention and Runoff after Amendments

Iodine loss varied among amendments as gypsum > lime > wood ash > charcoal > sawdust. Jourgholami & Abari [39] reported a 72% decrease in runoff when soil was amended with a sawdust and straw mulch. In this study, gypsum and lime amendments did not reduce iodine loss in surface runoff. Speciation, pH, redox potential, organic carbon (C), and clay content influenced the mobility of iodine in soil [40]. The iodine was supplied in the form of iodide and has a low affinity for alkaline soil. The absorption of iodide by granitic minerals such as calcite, chlorite, epidote, goethite, gypsum, hematite, kaolinite, muscovite, and quartz was low [41,42].

All amendments retained more iodine in agricultural and pasture soils against runoff, except gypsum. In agricultural soil, sawdust retained the most iodine, followed by charcoal, and wood ash. When compared with the control soil, the pH value of the amended soil varied substantially. Soil amendments such as sawdust, charcoal, and wood ash reduced soil pH, while lime and gypsum increased soil pH compared with the control. In agricultural soil, gypsum showed less iodine retention and higher soil pH. Iodide is known to be relatively soluble in anoxic soils and iodide absorption has been reported to decrease with increasing pH [43]. Soils with comparatively more organic matter content have demonstrated enhanced iodine retention [26]. It has been reported that the sawdust caused changes in the bulk density and air spaces found in soil [44]. Bulmer [45] reported that the effects of sawdust and wood chips on forest soil indicated a beneficial effects on trees, the soil's organic matter, and moisture retention. An important principle of land use management is to maintain a neutral to slightly basic or acidic soil pH, due to its relationship to soil fertility and plant growth. Nutrient availability is commonly highest between pH 6 and 7. Sawdust decomposition has also contributed to a temporary increase in soil acidity [46]. Both lime and gypsum amendments contributed to weak iodine retention in

soils and increased soil losses. Kaplan et al. [40] reported few interactions of iodide and iodate ions with minerals (i.e., biotite, calcite, gypsum, muscovite, and vermiculite).

#### 4.2. Factor Affecting Iodine Retention and Surface Runoff

Figure 5 shows that iodine retention is inversely related to soil pH. Thus, by increasing the pH, the soil's ability to retain iodide significantly decreases [31]. Gypsum and lime increased the pH of the soil and lower iodine content was retained in soils mixed with the gypsum and lime [47]. Iodide retention in the soil is pH-dependent and a slight change in the pH of the soil medium may alter the iodide behaviour. The factors that significantly affect iodine retention in soils are organic carbon and clay content. The results of this study indicated improved iodine retention in soils with organic amendments, compared to inorganic material. The provision of organic carbons not only enhanced iodine retention but also affected the physicochemical properties of soil, especially pH [48]. Clay content was positively correlated with the iodine retention of the soil. It has also been reported that soil properties, such as cation exchange capacity, organic matter, and clay minerals, affected the iodine retention of soil [49,50].

The iodine content of soil runoff was affected by soil loss. Soil loss reduced the concentration of iodine, while carbon content reduced a soil's iodine loss. Organic carbon can retain iodine content at higher concentrations, as reported by Shetaya et al. [3]. The contribution of these factors showed that pH, soil loss, and iodine runoff were directly related to each other, while carbon content inversely affected the iodine retention of soil. Iodide retention is weaker at higher pH levels ( $\text{pH} > 6$ ), but organic matter plays an important role for the retention capacity of soil [31].

#### 4.3. Relationship of Iodine Retention with Soil Properties

The interrelation between the different variables in amended and unamended soils was investigated using a Pearson's correlation matrix (Table 3). The iodine retained in soil showed a strong correlation with total carbon ( $R^2 = 0.84$ ) and reflected a strong negative relationship with pH ( $R^2 = -0.90$ ) and soil loss ( $R^2 = -0.83$ ), respectively. Iodine retention in soil was poorly related with soil particles. At  $\text{pH} < 6$ , most of the iodine content was retained by oxides of Fe/Al and clay minerals [30,51]. Hence, higher adsorption can be seen in acidic soil environments. Most of the iodine was accumulated in soil because of higher amounts of organic matter. Soil humus is considered a major iodine source [29,41]. Biogeochemical transformations of iodine in soil [16] and iodine losses via volatilization may limit its bioavailability, however [13,14]. The availability of iodine and its translocation depend mainly on iodine interactions with other soil components [28,52].

**Table 3.** Correlation coefficient matrix of soil parameters analysed.

	PH	I (Retained)	Soil Loss	EC	Sand	Silt	Clay	Carbon	I Runoff
PH	1								
I (retained)	−0.907 **	1							
Soil loss	0.849 **	−0.826 **	1						
EC	0.079	−0.243	0.039	1					
Sand	−0.153	−0.097	−0.253	0.481	1				
Silt	−0.153	−0.097	−0.253	0.481	10.000 **	1			
Clay	0.153	0.097	0.253	−0.481	−10.000 **	−10.000 **	1		
Carbon	−0.952 **	0.837 **	−0.849 **	−0.006	0.359	0.359	−0.359	1	
I Runoff	0.821 **	−0.939 **	0.870 **	0.306	0.169	0.169	−0.169	−0.761 **	1

\*\* significant at  $p < 0.001$ .

## 5. Conclusions

This study revealed that all amendments, except gypsum, significantly reduced the iodine losses from soils via runoff. Multivariate analysis and PCA tests showed that

physicochemical properties of the soils and the carbon content of the organic amendments affected iodine retention. Among the treatments, sawdust significantly reduced soil loss and iodine content in the runoff. Therefore, such a material can be used to enhance iodine retention in soil. Iodine retention in the soils varied between sawdust > charcoal > wood ash > lime > gypsum. Application of amendments in the soil of mountainous areas aids iodine retention and improves soil quality.

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