



Research Article

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# Comparative Study of Copper Accumulation and Distribution in Soil of Selected Orchard and Non-Orchard Fields



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## Abstract

Nowadays the uses of copper based fungicides is increasing on orchards of peaches which is responsible for copper accumulation in soil and then it's up taken by the seasonal crops, cultivated in orchards. This research was conducted to study the copper content in soil and wheat crop grown under orchard and non-orchard fields with an objective to know about the effect of copper based fungicides applications and copper content in soil and different parts of wheat plant. 10 soil samples were collected from both fields (orchard and non-orchard) covering an area of about 50234.3m<sup>2</sup>. The collected soil samples were analyzed for total and available copper contents using Aqua-regia and Mehlich-3 extraction methods, respectively. Wheat plants were collected from both fields at maturity and were analyzed for copper contents. Results showed that total copper content in orchard soils was significantly high ( $p < 0.05$ ) in the range of 46.52 to 53.31mg kg<sup>-1</sup> and available copper contents were observed insignificantly low ( $p > 0.05$ ) as 5.16 to 8.06 mg kg<sup>-1</sup>. In non-orchard soils the range was 11.18 to 20.71mg kg<sup>-1</sup> and 1.1 to 4.41 mg kg<sup>-1</sup> for total and available copper contents respectively. Among different parts of wheat crop, significantly higher ( $p < 0.05$ ) copper content was observed in seed (23.11 to 37.1mg kg<sup>-1</sup>) with the maximum metal transfer factor (0.8) for orchard crop indicating a higher risk factor for consumption. Compared to non-orchard copper concentrations (5.02 to 8.03mg kg<sup>-1</sup>) and metal transfer factor (0.12) results concluded that higher copper content in orchard fields (total+available) arise from the use of copper based fungicides. It is therefore recommended to introduce the alternate source of copper based fungicides.

**Keywords:** Aqua-regia; Mehlich-3; Non-orchard field; Orchard field; Plant uptake; Soil

## Introduction

Human health is closely related to soil quality and the risks associated to soil pollution [1]. Soil is used to grow different types of crops/plants; therefore its fertility is an important factor which determines the plant growth. While high yield of crop depends upon the availability of nutrients in soil [2]. Soil serves as a sink for several elements where they stay for long time affecting the quality of crops produced [3]. The surface soil has greater accumulation of metals than sub-surface as the surface soil contributes a small fraction of metals to plants [4]. The availability of metals like Fe, Cu, Zn and Mn in optimum concentrations are essential for both plant and human nutrition but under the condition of very high concentration, these metals cause toxicity to both plants and animals [5]. Anthropogenic activities such as urbanization, industrial activities and agricultural practices (agrochemical uses) are the main sources of soil contamination [6], resulting in the introduction of metals

to soil in excessive quantities which indirectly get entered into human body through food chain [7].

Copper is an essential trace element for growth and development of plants and animals, required in minute quantities. It is toxic in high doses and affects food safety and human's health [8]. Higher concentrations of copper in soil effect the microbial population and their activities which cause harmful effects on nutrients cycle [9]. Humans are exposed to copper containing fungicides either through direct ingestion or consumption of contaminated food [10]. Health effects of excessive copper intake are intestinal cancer, nausea, vomiting, abdominal pain, respiratory problems and damage of liver [11]. World Health Organization recommended 1.4mg/day for 70Kg person daily intake of copper. Its permissible limit in soil is 40mg kg<sup>-1</sup> [12], while in plants the critical level of copper is 10mg kg<sup>-1</sup> suggested by WHO [13], Iqbal et al. [14]. Contaminated

source of water for irrigation purposes is another way for soil contamination. Industries discharge their untreated waste/effluents into water channels and thus degrade the water quality. Therefore, safe disposal of industrial discharges has become an ecological challenge all over the world [15].

Use of the agrochemicals (pesticides and fungicides) has been an attribute of conventional agricultural practice which increases the crop and fruit production [16]. Fungicides are used to control fungal diseases like grey mold, black spot and downy mildew. Each spray is done regularly throughout growing season whether or not the disease is present. But heavy uses of these agrochemicals cause toxic effects on agro-ecosystem [16]. The incidental contamination of horticultural soil with copper is due to prolonged use of copper containing chemicals such as fertilizers, fungicide and bactericide sprays. Among these compounds copper based fungicide is one of the major sources of soil contamination [17]. These chemicals add copper contents in upper soil layer where it stays permanently and cause toxicity to both plants and animals [18]. Such type of chemicals have protective value and are sparingly soluble in water which provide excessive concentrations of soluble copper up to toxic level.

Bordeaux mixture ( $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$ ), Copper Oxchloride ( $3\text{Cu}(\text{OH})_2 \cdot \text{CuCl}_2$ ) and Copper Hydroxide ( $\text{Cu}(\text{OH})_2$ ) are common fungicides used on orchards against fungal diseases but their intensive uses contribute copper to soil and cause contamination [19]. These fungicides are used on pome (apple, pear, strawberry) and stone fruit orchards (peach and plum) for over 100 years but their foliar applications increase copper inputs in soils which significantly have an effect on soil and its biota [16]. Data has been reported on high concentrations of total copper in orchard soils from around the world especially in India (29-131mg kg<sup>-1</sup>), Australia (11-320mg kg<sup>-1</sup>) and France (100-1500mg kg<sup>-1</sup>). There is need to reduce this toxicity to its allowable level ranged from 36-60mg kg<sup>-1</sup> for different countries [17]. Since 2002, the maximum allowable level of total copper inputs in organic farms is 8kg ha<sup>-1</sup> year<sup>-1</sup> suggested by the International Federation of Organic Agriculture Movements (IFOAM).

This study was aimed to analyze the soil and wheat crop grown inside peach orchard for Cu toxicity. The experimental site was situated on main road near the junction point of River Swat and River Kabul in district Charsadda (KPK). The district lies between latitude of 34°-03', 34°-38' N and longitude of 71°-28', 71°-53' E Khan et al. [20]. The area is famous for horticultural crops including peach, plum, pear, strawberry and guava. The orchards growers extensively use agrochemicals such as fertilizer/compost and pesticides. Among pesticides, the most common one is copper based fungicide. As the trend of copper based fungicide is in high peak which is becoming a part of our food chain and is transferred to human body through inhalation of dust and ingestion of food. Therefore, it was felt important to monitor their potential effects on human's health for safety assessment.

As peach plant is deciduous, the land is therefore, conventionally used to grow wheat crop also. Since all peach orchards are heavily sprayed with copper based fungicides (Bordeaux mixture, Copper Oxchloride and Copper Hydroxide), there is likelihood of wheat grown as intercrop receiving excessive amounts of copper. This study is an attempt to analyze soil of peach orchards for Cu concentration as well as its uptake and accumulation in wheat crop.

### Materials and Methods

#### Field survey and sampling

To select sample site for in-depth study, reconnaissance survey was carried out at district Charsadda. The orchard owners and farmers were interviewed by asking few common questions such as:

- Total land under peach orchards and non orchard
- Types of fungicides used
- What type of crops are grown on orchard
- Quantity and Frequency of Fungicides application
- Uses of orchard field for crop cultivation
- Source of irrigation water
- Conventional method used for treatment of fungi
- Source of water used for irrigation

13 different orchards were surveyed by conducting interviews with their owners. In case of non-availability of owners, farmers/workers were interviewed. The selected points were 10 out of 13. During survey, two types of agricultural fields were selected for soil and wheat sampling, one with peach orchard while the other was non orchard field. The representative 10 (S1-S10) soil samples were collected randomly from selected sites of orchard and non-orchard fields with 0-25cm depth with the help of a spade. Each sample was taken in labeled polythene bag and brought to the laboratory of Environmental Sciences, University of Peshawar. The collected samples were mixed thoroughly, air dried, ground to pass through 2mm sieve and stored in labeled plastic jars for analysis. Eight representative water samples (W1-W8) were collected in plastic bottles from different spots of water channel from the experimental site and stored in laboratory. Wheat crop was sampled from each field in month of May 2013 when crop was ready to harvest and was dried in oven at 60-65°C for 10-15 minutes. The plant was divided into four parts, seed, leaf, stem and root and each part was ground in powdered form and stored for further analysis.

#### Chemical Analysis

Soil pH and electrical conductivity (EC) were measured as 1:5 suspensions of soil and water with the help of pH meter and conductivity meter respectively [21]. Soil organic matter was determined by following the Walkely and Black procedure as

1g soil was taken in 500ml flask then added 10ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, 20ml of H<sub>2</sub>SO<sub>4</sub> and shaken for a minute then heated it for 5 minutes on hot plate and then allowed to stand for 30 minutes. After 30 minutes it was diluted up to 200ml with distilled water then added 10ml of H<sub>3</sub>PO<sub>4</sub>, 0.2g of NaF and 3-4 drops of o-phenanthroline indicator and titrated against Fe(NH<sub>4</sub>)<sub>2</sub> (SO<sub>4</sub>)<sub>2</sub> solution (0.5M). Blank without soil was also run and noted the readings till its color changed from greenish blue to reddish brown [22]. Organic Carbon was calculated with the help of formula:

$$\text{Organic Carbon (\%)} = (\text{mLblank} - \text{mLsample}) (\text{M Fe}^{2+}) (0.3)$$

Wight of dry soil

Copper was analyzed by two digestion methods

i) Aqua-regia extraction method for total metals in soil and plants being efficient, safe and rapid digestion method which prevent the loss of volatile metals.

ii) Mehlich-3 extraction method was used for total available metals to plant. In aqua-regia extraction method 1g of soil was digested in 15ml of aqua-regia (5:1:1 mixture of HNO<sub>3</sub>: H<sub>2</sub>SO<sub>4</sub>: HClO<sub>4</sub>) at 180°C and 120°C until the solution become transparent. The solutions were filtered and diluted up to 50ml with de-ionized water and subjected to atomic absorption spectrophotometer [23]. For bioavailability of copper, 2g soil from each sample was extracted with 20ml of Mehlich-3 solution. It is a solution of five different chemicals ie. Acetic Acid, Ammonium Nitrate, Ammonium Fluoride, Nitric Acid and Ethylene-Diamine-Tetra-Acetic acid (0.2N CH<sub>3</sub>COOH+0.25N NH<sub>4</sub>NO<sub>3</sub>+0.015N NH<sub>4</sub>F+0.013N HNO<sub>3</sub>+0.001M ETDA). The solutions were shaken for 5 minutes and then analyzed by atomic absorption spectrophotometer after filtration [24].

Water temperature was measured with the help of thermometer on the spot. Water pH and EC were measured with the help of pH meter and conductivity meter. Total Dissolved Solids (TDS) were observed by oven dry method at 105°C. The acidified water samples were analyzed for copper content in Central Resource Laboratory (University of Peshawar), using atomic absorption spectrophotometer model AAS-700 [25].

For extraction of copper in wheat crops 0.5g of crop sample was digested with 15ml of aqua-regia (5:1:1 mixture of HNO<sub>3</sub>: H<sub>2</sub>SO<sub>4</sub>: HClO<sub>4</sub>) at varying temperature (180-120°C) till the solution become transparent. Solution was cooled, filtered and diluted up to 50ml with de-ionized water and subjected to atomic absorption spectrophotometer.

### Metal transfer factor (MTF)

Metals transfer factor from soil to crop was calculated as the ratio of metal concentration in crop to metal concentration in corresponding soil as

$$\text{MTF} = \text{Ccrop} / \text{Csoil}$$

Where C<sub>crop</sub> and C<sub>soil</sub>, show metal concentrations in crop and soil samples respectively [26].

### Statistical Analysis

The average, standard deviation and correlation (R<sup>2</sup>) of copper in water, soil and plant were calculated using MS Excel 2007. An unpaired t-test (showed as P (2-tail)) was applied for comparative study of two different field's samples using SPSS software with 95% of confidence interval. Statistically significant differences were determined in mean concentrations of copper among groups of soils and crops.

### Results and Discussion

#### Soil parameters

**Table 1:** Pre-sowing soil Samples analysis for pH, EC and organic matter.

Orchard		Non-Orchard		
pH				
Sample	Avg	Sample	Avg	P (2- tail)
S1	7.5	S6	7.1	0.251
S2	7	S7	7.8	0.211
S3	6.5	S8	8.4	0.061
S4	6.2	S9	7.2	0.124
S5	6.6	S10	8	0.062
Electrical Conductivity $\mu\text{S}/\text{cm}$				
Sample	Avg	Sample	Avg	P (2- tail)
S1	139	S6	129	0.01
S2	135	S7	124	0.01
S3	128	S8	133	0.071
S4	137	S9	138	0.13
S5	125	S10	123	0.069
Organic Matter %				
Sample	Avg	Sample	Avg	P (2- tail)
S1	1.7	S6	0.8	0.131
S2	1.6	S7	0.4	0.08
S3	1.9	S8	0.4	0.076
S4	1.6	S9	0.5	0.068
S5	1.4	S10	0.7	0.062

The pH values of both orchard (6.2 to 7.5) and non-orchard soils (7.1 to 8.4) were found slightly alkaline with insignificant P values (>0.05) as given in Table 1. The low pH of orchard field can possibly be attributed to high soil organic matter content compared to non- orchard [27]. Organic matter content was high in orchard fields (1.4 to 1.9%) as compared with non-orchards (0.4 to 0.8%) having insignificant difference (p>0.05), shown in Table 1. This high organic content in orchard fields can be attributed to tree residues like leaves, twigs and other biomass such as use of compost. The highest value of Electrical conductivity (EC) was 139 $\mu\text{S}/\text{cm}$  for orchard field and 138 $\mu\text{S}/\text{cm}$  for non-orchard field, showing a significant difference (p<0.05), (Table 1). By comparing EC values with national guidelines

standard of 2000 $\mu$ S/cm, all samples, orchard and non-orchard, were within the safe limits [28] and there is a little or no likelihood of salinity. Physiochemical Parameters of Water The physiochemical parameters of water are listed in Table 2. The pH of water samples varied from 7.8 to 8 and EC ranged as 266 to 289 $\mu$ S/cm. The average concentration of Total Dissolved solids (TDS) in eight water samples was 147.7mg/L while average copper concentration was observed as 0.15mg/L in waste samples used for irrigation (Table 2). This copper content is the contribution of water channel carrying industrial effluents (River Kabul) and joins the irrigation source of water. The lacking of industrial waste water treatment plants the industries discharge their wastes into River Kabul and thus making its water unfit for

agricultural sector [29]. The discharges of industrial effluents into fresh water damage its water quality and put negative effects on agricultural soil and aquatic organisms. As the water quality is very important for crop yield therefore irrigation water under this study is one of the minor contributory factors for copper availability to soil and then crop. In comparison with soil, all water samples showed pH values within permissible limits and may have no contribution in decreasing soil pH. By comparing copper concentration with WHO [30], National Standards for Drinking Water Quality [31] and Irrigation water guidelines (2007) for Pakistan, water used for irrigation was within the permissible limit of 2mg/L [32]. Copper Content in Soil.

**Table 2:** Concentrations of Physiochemical Parameters of Water.

Samples	Temperature (°C)	pH	EC uS/cm	TDS mg/L	Cu mg/L
W1	17.5	8	265.5	133.5	0.1
W2	11	7.8	273	136.5	0.2
W3	11.2	7.4	289	144.5	0.1
W4	11	7.9	276	176	0.06
W5	11.8	7.1	266	121.5	0.09
W6	15.3	8	259	168	0.2
W7	12.1	7.2	275	145	0.07
W8	15.4	6.9	270	157	0.4
Min	11	6.9	265.5	121.5	0.06
Max	17.5	8	289	176	0.2
Average	13.2	7.5	271.7	147.7	0.15
S.D	2.524	0.443	8.987	1.24	0.113
WHO standards	30-45	6.5-8.5	1400	1400	2
NSDWG	40	6.5-8.5	1000	1000	2
Irrigation water standards for Pakistan	-	6.5-8.4	-	1000	0.2

**Table 3:** Total and Available Contents of Copper in Soil Samples (mg kg<sup>-1</sup>).

Extraction Method	Orchard			Non- Orchard			
	Sample	Avg	S.D	Sample	Avg	S.D	P (2- Tail)
Aqua-regia	S1	53.3	0.04	S6	15.6	0.06	0
	S2	52.6	0.01	S7	15.6	0.06	0
	S3	52	0.05	S8	20.7	0.01	0
	S4	47.6	0.01	S9	10.4	0.08	0
Mehlich-3	S5	46.5	1.01	S10	11.2	0.75	0
	S1	8.1	2.71	S6	1.1	0.39	0
	S2	8.1	0	S7	2.9	0	0.024
	S3	7.8	0	S8	2.7	0	0.031
	S4	7.4	0	S9	2.2	0	0.011
	S5	5.2	0	S10	1.4	0	0.052

Total copper content extracted with Aqua-regia was found high in soils of peach orchards with average range of being 46.5 to 53.3mg kg<sup>-1</sup> and all samples were above the permissible limit (40mg kg<sup>-1</sup>) in soil. The non-orchard fields were low in copper content with average range of 11.2 to 20.7mg kg<sup>-1</sup> (Table 3). The difference in total Cu content between orchard and non-orchard fields was significant (p<0.05). In orchard soils high copper content can be attributed to the use of copper based fungicides spray on peach orchard and to high organic matter content. Moreover, some contribution of copper comes from irrigation source of water.

Soil samples extracted with Mehlich-3 for available copper to plant showed copper content with average concentrations of 5.2 to 8.1mg kg<sup>-1</sup> in orchard fields. While in non-orchard fields the range was 1.1 to 4.4mg kg<sup>-1</sup> (Table 3). Results were found highly significant for available copper in soil samples (p<0.05). It was observed that one spray of copper based fungicides ranged from 20-25Kg per hectore of land area (10000m<sup>2</sup>) and was applied at the rate of 10-12 sprays per annum (self-observation). Results showed that pH of orchard soil were low as compared with non-orchard soils that might have enhanced copper uptake. Studies revealed that organic matter and low pH are closely related to copper availability and its uptakes by plant [33]. In agricultural fields the uptakes of heavy metals by plants may be low as these metals are non-reactive and have low mobility but the risk of

food chain contamination exists by heavy metals and particularly for copper [34]. Heavy applications of copper based fungicides are harmful for soil flora and fauna as the microbial activities are depressed and soil fertility is significantly affected [35].

**Copper in wheat crops**

Among different parts of wheat plant significantly high level of copper was observed in wheat seeds/grains of orchard field (p<0.05) with average concentrations of 23.1 to 37.1mg kg<sup>-1</sup>. In non-orchard fields the concentrations were significantly low with 5 to 8mg kg<sup>-1</sup>. Copper content was observed in order of seed>leaf>stem>root (Table 4). The content was high in crop seed of orchard fields when compared with WHO-1996 standard (10mg kg<sup>-1</sup>) for crop. Comparative study of orchard and non-orchard fields showed significant results for seed and stem (p<0.05) and non-significant results for crop root and leaves (p>0.05), (Table 4). High level of copper in soil contaminates food chain. The WHO (1996) suggested safe intake of copper for humans regarding age and sex as; 0.6mg/day in infancy, 0.75mg/day for children (6-10 years), 1.15mg/day for an adult female and 1.35mg/day for an adult male [11]. The highest level of copper 10-12mg/day is considered safe for an adult by WHO [35]. Cereals and meat are the important sources of copper which are consumed by humans and contribute copper contents to their bodies.

**Table 4:** Copper Content in Different Parts of Wheat Crops (mg kg<sup>-1</sup>).

Plant Part	Orchard			Non- Orchard			
	Sample	Avg	S.D	Sample	Avg	S.D	P(2- Tail)
Seed	S1	37.1	1.03	S6	8	0.59	0
	S2	34.5	0.01	S7	6.9	0.01	0
	S3	32.8	0	S8	7.6	0.01	0
	S4	24.3	0.05	S9	5.1	0	0
	S5	23.1	0.08	S10	5	0.01	0
Leaf	S1	4.4	1.58	S6	3.9	1.24	0.524
	S2	5.1	0	S7	3.7	0	0.055
	S3	4.3	0	S8	3.9	0	0.517
	S4	2.2	0	S9	1.9	0	0.456
	S5	2.4	0	S10	1.4	0	0.101
Stem	S1	3.8	1.39	S6	1.9	0.78	0.008
	S2	1.7	0.01	S7	1.1	0	0.022
	S3	2.5	0.01	S8	1.1	0	0.051
	S4	1.7	0	S9	0.9	0	0.063
	S5	2	0.1	S10	0.7	0.02	0.021
Root	S1	2.4	1.1	S6	1.4	0.69	0.103
	S2	1	1.00E-04	S7	0.2	0.01	0.5
	S3	0.3	0	S8	0.2	0.01	0.65
	S4	1.8	5.00E-04	S9	1.2	0.01	0.553
	S5	0.4	0.03	S10	0.2	0.02	0.541



Copper is used in agriculture and horticulture in many formulations of copper bearing fungicides which are considered effective against fungal diseases but the major consequence of its high content in soil is its toxicity to plants and microbial organisms. Wheat is an important staple food crop in Pakistan with average grain yield of 2.71 tons ha<sup>-1</sup> [36]. The consumption of wheat grains is a direct way of copper intake and its stem and leaves are used as fodder for animals which are then taken indirectly by humans in the form of meat and milk [37]. Therefore food chain is contributing copper contents to humans and if this uptake is above the required limit (10-12mg/day) then it will cause health problems. In humans the high intake of copper leads to several disorders like gastro-intestinal problems and Wilson disease (a genetic disorder due to copper accumulation in liver) reported by Goyer et al. [38]. The main targeting organ of copper is liver where it accumulates in high concentrations and causes toxicity.

The use of alternative fungicides such as Fluazinam and Pristine (pristine is a combination of pyraclostrobin and boscalid) are considered effective as copper based fungicides. When fluazinam is applied with di-1-p-methen, it shows

good efficiency and is protective for skin [39]. Similarly the application of neem oil/jajoba oil is much effective for all types of fungal and bacterial attacks [40]. Moreover it was reported that fungicides like captan, ziram, ferbam and benomyle can be used for treatment of fungal diseases due to their minimum toxicity and good efficiency [41]. So, there is need to protect soil contamination with chemicals (fungicides) which are toxic for soil micro-organisms and its productions may become toxic to human after entering into food chain.

### Correlation of copper between soil and Crop

Correlation between soil Cu contents and its accumulation in different parts was measured with both total and available copper contents for orchard and non-orchard fields. Available copper content showed strong correlations with crop seed, stem and root of orchard field with observed R<sup>2</sup> of 0.621, 0.790 and 0.927 respectively (Table 5). Total copper contents in soils showed weak correlations with wheat crops in comparison to available copper (Table 5). While in non-orchard fields R<sup>2</sup> values expressed weak co-relations of copper accumulation from soil to plants (Table 5). This difference is because of enrichment of orchard soils with copper contents [41-47].

**Table 5:** Correlation (R<sup>2</sup>) of Copper in Crop, Soil and water Samples.

Sample Name	R <sup>2</sup> with Aqua-Regia Extracted Soil		R <sup>2</sup> with mehlich-3 Extracted Soil		R <sup>2</sup> with Water Samples		Metal Transfer Factor for Total Cu Contents	
	Orchard	Non-Orchard	Orchard	Non-Orchard	Orchard	Non-Orchard	Orchard	Non-orchard
Seed	0.574	0.318	0.621	0.022	0.342	0.074	0.8	0.12
Leaf	0.192	0.078	0.31	0.244	0.112	0.002	0.08	0.01
Stem	0.388	0.231	0.79	0.109	0.149	0.036	0.12	0.05
Root	0.346	0.178	0.967	0.341	0.7	0.57	0.03	0.02

### Correlation of copper between water and crops

The concentrations of copper in crop and water samples were also analyzed for R<sup>2</sup>. Copper contents in water showed strong correlation with crop root of orchard field (0.700). Other parts of wheat plant were weakly correlated with R<sup>2</sup> ranged from 0.002 to 0.570 (Table 5). Results showed that water is involved in minor contribution of copper to crops. The major contribution of copper in wheat crops comes from contaminated soils.

### Metal transfer factor

The highest value of metal transfer factor (MTF) was observed in crop seed of orchard field with MTF value of 0.80 and 0.12 for non-orchard field respectively (Table 5). The results of present investigations showed that the use of copper based fungicides increase the uptake of copper by crops along with a risk factor for consumption of crops.

### Conclusion and Recommendations

The study showed a high concentration of copper in soil and wheat crop grown on orchard fields. This high copper content is a potential threat for human's health as the MTF was high for seed. It is therefore recommended to regulate the use of

fungicides by using the alternate fungicides like Fluazinam and Pristine or Neem oil.

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### Contribution of Authors

Nazish Huma Khan (PhD scholar) is the original author who worked on this study as M.Phil research, under the supervision of Dr. Muhammad Nafees (professor at university of Peshawar).

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