Transformation of Zinc and Boron and their Availability to Rice, Wheat and Jute Crops in Ganges River Floodplain Soils

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Declaration

I hereby declare that the Thesis entitled “Transformation of Zinc and Boron and their Availability to Rice, Wheat and Jute Crops in Ganges River Floodplain Soils” has been composed by me and the works presented herein have been performed by myself in the Department of Soil, Water and Environment, University of Dhaka, and that it has not been presented in any previous application for a degree. All sources of information specifically acknowledged by references to the authors.

(Muhammad Sajidur Rahman)

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Certificate

This is to certify that the thesis entitled "Transformation of zinc and boron and their availability to rice, wheat and jute crops in Ganges river floodplain soils" submitted by Muhammad Sajidur Rahman in fulfillment of the requirement for the award of the degree of Doctor of Philosophy in Soil, Water and Environment of the Faculty of Biological Sciences, University of Dhaka, Dhaka, is a piece of original research work conducted under our joint supervision. This work has not been presented anywhere before for any diploma or degree.

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ABSTRACT

Deficiencies of micronutrients particularly, zinc (Zn) and boron (B), in the intensively cropped soils of Bangladesh has long been established. An in-depth knowledge of the forms of Zn and B, their transformation in soils and interaction with soil components is desirable to determine the effects of Zn and B fertilizers on crops and their fate in the deficient soils. Therefore, field and laboratory experiments were conducted to study the fractionation of Zn and B and their transformation under variable field and laboratory conditions, in soils of Low Ganges River Floodplain (Agro ecological zone, AEZ 12) that contain low available Zn and B. The cropping patterns of the study were Wheat-Jute-Transplanted Aman (T. Aman) rice (W-J-R) and Boro-Fallow-T. Aman rice (R-F-R). Responses of wheat, jute and rice crops to various rates of Zn and B and the relationship between crop uptake of Zn and B and their fractions in soil were also studied. In addition, the status of micronutrients, namely, iron (Fe), manganese (Mn), copper (Cu), Zn and B in the High and Low Ganges River Floodplain (AEZs 11 and 12) soils were studied.

A large number of soil samples from AEZs 11 and 12 contained low concentrations of plant available Zn and B. On the other hand, the average concentrations of plant available Fe, Cu and Mn in the Ganges River Floodplain soils were too high for plant growth.

In the W-J-R pattern, significant effect of Zn and B was observed in grain yield of wheat (BARI Gom 26). The Zn effect was dominant over B effect. However, straw yield of wheat was unaffected by Zn and B application. The stick and fiber yield of jute (JRO 524) and grain yield of T. Aman rice increased but not consistently according to the rate of Zn and B application. Similar trend of inconsistent yield response was also observed in Boro and T. Aman rice crops of R-F-R pattern. The residual effect of Zn and B applied in wheat was realized in the yields and nutrient uptake of jute and T. Aman rice crops, suggesting that all of the applied Zn and B are not utilized by the current crop. However, a fresh addition of the nutrients yielded more jute or rice grain than that of the residual nutrients. The positive response of T. Aman rice to B applied in jute indicates that B application should not be ignored in Low Ganges River Floodplain soils. A significant response of crops to Zn and B application in R-F-R soil with sufficient available Zn and B implied a decrease in their availability in the soil during the crop season caused by interactions with various soil components. Similar to grain yield, the effect of Zn and B on the uptake of Zn and B in

wheat, jute and rice crops were insignificant, although some remarkable variation was observed.

A marked re-distribution in the amorphous and crystalline Fe-oxide bound Zn and residual Zn was observed in the incubation study with added Zn indicating a transformation of the added Zn. In the incubation of the soil with added B, the readily soluble and specifically adsorbed B increased substantially and residual B, decreased greatly implying a shift of added B to plant available forms.

Fractionation of the field soil under W-J-R soil after two years of cropping revealed significant variations in the exchangeable, organic and Mn oxide-bound Zn forms (which are comparatively labile) due to application of Zn and B implying changes in the chemistry of native soil components. The increase in organically bound Zn in the native soil could be a contribution of the crop residue or the impact of applying N, P, K and S fertilizers. The fractionation of B in the same soil revealed that the concentration of B in the various soil fractions decreased from that of the initial soil and the added B could not be traced out in any of the B fractions practically.

Correlation between plant tissue Zn and the soil Zn fractions varied with plant type, season and soil properties. The Zn fractions that are positively correlated with wheat tissue Zn was negatively correlated with rice tissue Zn. Concentration and uptake of grain B in wheat and rice were significantly correlated with exchangeable and specifically adsorbed B implying that crops absorbed B from these B pool in the soil.

The concentration of exchangeable-Zn of the soils from different AEZs decreased with the increase in soil pH. The reactivity of MnOx was reflected proportionately with the increase in available Zn of the soils, impliying that MnOx-bound Zn acts as an important source of available Zn in Bangladesh soils. Higher residual Zn was observed in Ganges River Floodplain soils indicating fixation by clay minerals. Likewise greater quantity of specifically adsorbed B in Ganges River Floodplain indicates adsorption of B by smectite type clay minerals.

Further investigations of the factors that interact with the fractions of Zn and B can reveal the details about the fate of the fertilizers applied under flooded and upland soil conditions. Development of appropriate soil management practices can make use of the potential sources in soil (e.g., labile pool) of these micronutrients for increased crop yield and increased levels of Zn and B in the food crops.

CHAPTER I

INTRODUCTION

Intensification of agricultural land use with high yielding crop varieties and unbalanced fertilizer application in Bangladesh has led to mining out the native soil nutrients. Consequently, new nutrient deficiency, especially micronutrient deficiency arises. Traditionally, in fertilizer practices an emphasis has been given to macronutrients, especially nitrogen, phosphorus and potassium considering that the requirement of micronutrient by crops is small compared to that of macronutrients. This situation creates an unbalanced condition in soil fertility (Rijpma and Jahiruddin, 2004).

In many parts of Bangladesh, deficiency of micronutrients like Zn, B, Mn, Cu and Mo in crops has been reported along with the identified deficiencies of major nutrients (Mondal *et al.*, 1992; Jahiruddin *et al.*, 1995; Quamruzzaman *et al.*, 2006; Islam, 2008; Sarker *et al.*, 2019).

At present, Zn deficiency is the most visible micronutrient deficiency in crops in Bangladesh. This element deficiency in the country was identified in late 1970s (Jahiruddin *et al.*, 1981) and now more than 70% of cultivated soils are deficient in Zn (Jahiruddin and Islam, 2014). The major soil types that are frequently associated with Zn deficiency are calcareous soil, sandy soil, weathered tropical soil, saline soil, waterlogged soil and heavy cracking clay soil (Alloway, 2009). Zinc deficiency is prominent in calcareous and wetland rice soils across Bangladesh (Jahiruddin *et al.*, 2000). Crops are intensively cultivated in calcareous soils which lie in two AEZs – High and Low Ganges River Floodplains, covering 1.32 and 0.797 m ha area, respectively.

Next to zinc, deficiency of boron is frequently reported on crops, particularly, wheat, mustard, chickpea and mungbean (Bhuiya *et al.*, 1981; Mondal *et al.*, 1992; Jahiruddin *et al.*, 1995; Islam *et al.*, 1997; Ferdous *et al.*, 2003). In wheat, remarkable yield increases was recorded due to application of B (Jahiruddin *et al.*, 1995). Adequate B replenishment is essential to achieve maximum yield and crop quality even in high fertility soils, as natural soil B reserves are rapidly mined in heavily cropped systems (Gupta, 1993).

All crops or varieties are not equally sensitive to Zn and B deficiency or responsive to micronutrient fertilizers. Efficient genotypes are able to acquire Zn and other micronutrients from the soil more effectively and achieve higher yields (Graham, 1984). If the soil is poor in Zn, wheat crop can't show their full potential to absorb Zn (Cakmak and Kutman, 2018). Supplementary applications of Zn, Cu and Mo to crops have been shown to increase levels of these micronutrients in rice and wheat grain (Johnson *et al.*, 2005).

Apart from yield advantage due to Zn fertilization, zinc-enriched foods are also very important on the point of human health benefit (Jahiruddin, 2020) and better seed health, seedling vigor and higher stress tolerance on potentially Zn-deficient soils (Cakmak, 2008). Plants emerged from seeds with low concentration of Zn could be highly sensitive to biotic and abiotic stresses (Obata *et al.*, 1999). Zinc enriched seeds can perform better in respect to seed germination, seedling health, crop growth and finally yield advantage (Cakmak *et al.*, 1996a; Cakmak, 2005). Thus, the prevailing situation makes micronutrient research a promising area of study in meeting the demand for higher food production with enhanced mineral nutritional value in this millennium.

Deficiencies of micronutrients in the soils of Bangladesh are reported to have been favoured mainly by intensive cultivation with HYV crops, depletion of soil organic matter, unbalanced use of fertilizers, minimum use of manure, increasing cropping intensity, high soil pH (e.g., calcareous soils), nutrient leaching and light textured soils (FAO, 2006; Jahiruddin and Islam, 2014). Rice-wheat sequential cropping system in parts of India, Pakistan and Bangladesh combines a number of soil chemical factors causing severe Zn deficiency (Timsina and Connor, 2001). The factors include reducing conditions of soil, high bicarbonate concentration and possibly salts in the flooded soil causing Zn deficiency in lowland rice. High pH and chemisorption on calcareous soils during free-draining periods when wheat is grown can also create Zn deficiency (Timsina and Connor, 2001). With the passage of time, the deficiency of micronutrients is arising in new areas of the country due to intensive cropping with modern HYVs. Hence, in addition to correcting deficiencies, the application of the nutrients has become much important to maintain their levels in the soils.

Distribution of different fractions of Zn and B as influenced by different management practices and environmental conditions and their contribution to plant uptake is fundamental to an understanding of soil chemistry. Fractionation research has provided some insight into the distribution of the forms of Zn and B among the solid and liquid phases and relates these forms with the factors controlling their distribution, transformation and bioavailability (Shuman, 1985; Jin *et al.*, 1987; Mandal *et al.*, 1988; Hou *et al.*, 1994). Physico-chemical properties of the soil like pH, cation exchange capacity, oxides of Fe, Al and Mn and $CaCO_3$ controls the transformations of the fractions of Zn and B and their availability to plants (Shuman, 1991; Goldberg, 1997; Mandal *et al.*, 2000; Slaton *et al.*, 2005). Thus, fractionation study helps devising management practices to correct nutrient deficiency, toxicity and improve soil fertility. Also, fractionation study has important implications to understand the fate of the applied Zn and B, and its residual effects. The applied nutrients may not be readily taken up by the standing crops due to transformation to unavailable forms by various fixation reactions.

Sequential extraction technique is applied to study the amount of soil micronutrients in various forms (Beckett, 1989; Shuman, 1991). The fractionation scheme attempts to selectively remove discrete fractions usually in order of decreasing reactivity. This technique has become increasingly popular leading to understanding of the fractionations that are supplying micronutrients to the plants (Shuman, 1986). Selective sequential extraction also provides indications on agronomic problems (e.g., deficiency or toxicity of nutrients), geochemistry and environmental science.

It is evident that enormous studies have been conducted on the chemistry of soil Zn and B throughout the world. Also, studies related to factors affecting their availability, their fractionation and transformation into various chemical forms, and crop response to Zn and B fertilization has been done. However, in the context of Bangladesh, the information available on the transformation of Zn and B is still limited, particularly in the Ganges River Floodplain soils, that are known as generally Zn and B deficient due to high soil pH, presence of $CaCO_3$ and some other factors.

Some specific research is, therefore, needed to generate information on the fractionation and transformation of Zn and B as well as the response of Zn and B fertilization on the growth, yield and nutrient uptake of wheat, jute and rice crops in the Ganges River Floodplain soils. The study would help update the fertilizer recommendation as well as management of Zn and B in the Gangetic alluvial soils of Bangladesh. The present investigation was, therefore, undertaken with the following specific objectives:

I. Delineation of micronutrients status (Fe, Zn, Cu, B and Mn) in Ganges River Floodplain soils (AEZ 11 and AEZ 12).
II. Evaluation of the effect of Zn and B fertilization on the yield and nutrient uptake of rice, wheat and jute in the Ganges River Floodplain soil.
III. Study on the transformation of applied and native Zn and B in different fractions in soils under crop management practices in Ganges River Floodplain.

CHAPTER II

REVIEW OF LITERATURE

Research works on plant micronutrients have been carried out systematically in the last decades since their low availability in soil has become one of the major limiting factors in crop production. In addition to crop yield, the quality of crop products is impaired due to the deficiency of micronutrients. Except iron (Fe) and manganese (Mn) all the micronutrient elements are found at low concentration in lithosphere and in soils, comprising less than 0.1% (Harmsen and Vlek, 1985). Widespread deficiencies of micronutrients like zinc (Zn), copper (Cu), boron (B) and molybdenum (Mo) have become a major issue in crop production. The present work was done on different aspects of soil Zn and soil B as they relate to plant nutrition. The main topics of the literature review will focus on the following:

- Forms of soil zinc and their distribution in parent rocks, minerals and soils
- Status of Zn in Bangladesh soil
- Soil factors affecting availability of Zn to plants
- Field experiment to study the response of plants to applied Zn
- Fractions of soil Zn, their distribution in soils and influences to plant nutrition
- Methods of extraction and determination of soil Zn and its fractions
- Transformation and redistribution of Zn fractions in soil
- Forms of soil boron and their distributions in soils
- Factors controlling concentration of soil B
- Causes of B deficiency in the soils
- Chemistry of B under different soil conditions
- Fractionations of soil B and their transformation under soil conditions
- Methods of determination of soil B and its fractions

2.1 ZINC IN PARENT ROCKS

In the earth's crust, zinc (Zn) ranks the 24th among the most abundant elements, with an average value of 70 mg/kg (Krauskopf, 1972; Barak and Helmke, 1993). The concentration of Zn in soils varies profusely because of the variation in parent material, mineralogy and organic matter content (Iyengar *et al.*, 1981; Adriano, 1986; Jikun *et al.*, 1987; Liang *et al.*, 1990; Reed and Martens, 1996). Most of the soil Zn is present as a part of the lattice structure of primary and secondary minerals and only a trace of the total soil Zn is available to the plants (Huang, 1989; Mengel *et al.*, 2001). Soils acquire the elements present in the parent material of the earth's crust in varying degrees during their development process.

The type and composition of rocks influence concentration of soil Zn more than that of the pedogenic processes (Aubert and Pinta, 1980). Soils formed from basic igneous rocks contain more Zn than the soils developed from granite and gneisses (Adriano, 1986). According to Aubert and Pinta (1980), the highest Zn contents (70 - 130 mg/kg) are found in basic eruptive rocks (basalt, gabbro) followed by acid eruptive rocks (granite, rhyolite) (50 - 60 mg/kg). Intermediate Zn contents (70 mg/kg) are observed in metamorphic rocks (schists) and some sedimentary rocks (clays). Loessic loams, glacial clays, carbonated rocks and sandstones contain the lowest Zn contents (16 - 40 mg/kg) (Aubert and Pinta, 1980). In common sedimentary rocks, the greatest concentration of Zn occurs in shales and clayey sediments (80-100 mg/kg), much higher than limestone (20 mg/kg) and sandstone (16 mg/kg) (Krauskopf, 1972; Kabata-Pendias and Pendias, 2001). The Zn concentration of the lithosphere is similar to the average concentration of rocks: 70 mg/kg (Krauskopf, 1972; Aubert and Pinta, 1980). In the nature, zinc occurs as sulfides, carbonates, and silicates (Shuman, 2005).

The average concentration of Zn in mafic igneous rocks is greater than that in felsic rocks (Barak and Helmke, 1993). This occurs due to isomorphous substitution of Fe^{2+} and Mg^{2+} by Zn^{2+} in pyroxene. Zinc can replace Fe^{2+} and Mg^{2+} by isomorphous substitution in the mineral structure since the ionic radius of Zn is similar to that of Fe and Mg, particularly in the ferromagnesian minerals, the amphiboles (augite, horneblende) and biotite (Barak and Helmke, 1993; Mengel *et al.*, 2001). Occasionally, very high levels of Zn may occur in soils affected by wastes and sludges (Mengel *et al.*, 2001). The common ranges of Zn concentration in different types of rocks are mentioned in Table 2.1.

Table 2.1 Concentration of Zn in different rocks (Kabata-Pendias and Mukherjee, 2007).

Environmental compartment	Conc. of Zn (mg kg^{-1})
Earth's crust	52-80
Igneous rock	
Mafic	40-120
Acid	40-120
Sedimentary rock	
Argillaceous	80-120
Sandstone	15-30
Calcareous	10-25

2.1.1 The parent materials of Bangladesh soils

Most of the soils of Bangladesh are relatively young and their properties are heavily influenced by the nature of their parent material and drainage conditions (Islam, 2003). Almost the entire parent materials are transported by the rivers flowing through Bangladesh and are deposited in different environment. Sediments belonging to three distinct ages, viz Tertiary, Pleistocene and Holocene, occur in Bangladesh. Unconsolidated floodplain sediments occupy about 80% of Bangladesh and are termed recent alluvium (Holocene sediment). Different rivers bring sediments from areas of different geology. These sediments are far from homogeneous in age, texture and mineralogy. Most floodplain sediments have high silt content (Huq and Shoaib, 2013). Clay deposits occur on the surface over most of the Ganges Floodplain. According to Hassan (1999), the natural fertility of the Floodplain soils is high due to their higher content of mineral nutrients, high CEC, base saturation percentage and dominance of either smectitic or vermiculitic clays in the Gangetic and Non-Gangetic materials, respectively. The Gangetic sediments contain variable quantities of calcite as well. Under wetland agriculture, the floodplain soils may show deficiency symptoms of Zn and S (Hassan, 1999).

2.2 ZINC CONTAINING MINERALS IN SOILS

Most of the Zn in the soils is made up of the minerals. Naturally, Zn is found in numerous minerals that differs widely including sulfides (ZnS, Spharelite and Wurtzite), sulfates ($ZnSO_4$, Zincosite, $ZnSO_4.2H_2O$, Goslarite), oxides (ZnO, Zincite, $ZnFe_2O_4$, Franklinite, $ZnAl_2O_4$, Gahnite), carbonates (Smithsonite, $ZnCO_3$), phosphates [$Zn_3(PO_4)_2.4H_2O$, Hopetite] (Barak and Helmke, 1993). In the lithosphere, the most abundant Zn mineral is sphalerite (ZnS), although it also occurs in silicate minerals such as wilemite (Zn_2SiO_4) and

Hemimorphite ($Zn_4(OH)_2Si_2O_7.H_2O$) (Harmsen and Vlek, 1985; Kabata-Pendias and Pendias, 2001).

In the metamorphic and igneous rocks, Zn is infrequently present as the sulfide (sphalerite), and most of it is distributed as a minor constituent of rock-forming minerals, particularly the iron-enriched magnetite, the pyroxenes, the amphiboles, biotite, spinel, garnet, and staurolite (Adriano, 2001). Zinc substitutes the major constituents of minerals without major distortion or charge imbalance of a large number of minerals (Barak and Helmke, 1993). The consideration that Zn is the 24th most abundant element in the earth's crust, is largely on the basis of its presence as a minor constituent in common rocks, minerals and in soils (Barak and Helmke, 1993). According to Wedepohl (1978), the abundance of Zn in the different minerals is controlled by its concentration in the magma and the ability of the crystal lattice to incorporate it.

2.2.2 Clay minerals and Zinc

Zinc is also a part of alumino-silicate clay minerals. The ranges of Zn in common clay minerals are as follows: muscovite: 2-200 mg/kg, illite: 120 mg/kg, chlorite: 33-1600 mg/kg, montmorillonite: 73-156 mg/kg, and kaolinite: 14-264 mg/kg (Adriano, 2001). Besides, Zn is also associated with oxides, hydroxides and hydrous oxides of Fe, Mn and Al in the soil.

2.2.3 Clay mineralogy of Bangladesh soils

In Bangladesh, the alluvial sediments of different rivers contain different amounts of micas, feldspars, hornblende, etc. (Islam, 2003). Ganges alluvium contains lesser amounts of biotite but significant amounts of lime. The deposits of Surma, Karnafuli and other rivers draining the eastern hills contain little biotite and no lime. Thus there is great diversity in the parent material occurring in Bangladesh, from which soils with different properties were developed.

The dominant clay minerals of Mio-Pliocene Hill soils and Pleistocene Terrace soils are illite and kaolinite (Hassan, 1999). The clay mineralogy of the Ganges sediments is dominated by illite and smectite with traces of kaolinite, vermiculite and chlorite. Non-Gangetic sediments have illite and vermiculite as dominant minerals with traces of Kaolinite and chlorite (Hassan, 1999; Moslehuddin *et al.*, 1999a). Recent studies show that the smectite of Ganges river sediment is disappearing followed by decalcification (Moslehuddin and Egashira, 1997). Thus, the conc. of Zn in the soils of Bangladesh varies substantially due to the variation in their parent rocks and their constituent primary and secondary minerals.

2.3 ZINC CONTENT IN THE SOILS

2.3.1 Total zinc in the world soils

The total Zn content in the world soils varies from 3 to 770 mg/kg with an average of 64 mg/kg (Storey, 2007), while the mean total Zn content of lithosphere is about 80 mg/kg (Lindsay, 1972). Shacklette and Boerngen (1984) reported that the concentration of Zn in 1300 surface soils of the United States ranged from 5 to 2900 mg/kg with a mean of 60 mg/kg. Abundance of quartz in the soil dilutes the concentration of soil Zn because the concentration of zinc in quartz is very low (Barak and Helmke, 1993). In general, high amount of Zn is found in soils derived from shales and mafic crystalline rocks that are rich in ferromagnesian minerals such as augite, hornblende and biotite (Parveen, 1993). Similarly, soils derived from clastic sediments has less total Zn than soils formed on either limestone or sandstone-limestone mixtures (Iyengar *et al.*, 1981).

Soils formed from limestone generally contain more Zn than those formed from gneiss or quartzite (Stevenson, 1986). Highly weathered soils also contain low Zn since the quantity of Zn is higher in soils with higher amount of weatherable minerals. For example, the mean total Zn (34 mg/kg) of Australian soils that include ancient, heavily weathered areas is lower than for world soils (55 mg/kg) (Tiller, 1983; Sadeghzadeh and Rengel, 2011). The total Zn contents in the world soils reported by Alloway (2009) are presented in Table 2.2.

Table 2.2 Representative total Zn concentrations in soils (Alloway, 2009).

Country	**Soil type**	**Total Zn (mg/kg)**
India	Various	2-1205
China	Various	3-790
England & Wales	Various	5-3548
Baltic Region	Various	33 (5-125)
New Zealand	Pasture soils	42-91
USA	Various	43 (3-264)
Germany	Sandy soils	27
	Loam/ silt	59
	Clay soils	76
France	Sandy soils	17
	Silty soils	40
	Loam	64
	Clay soils	98
	Very clayey soils (>50%)	132
World (average)	Various	64

2.3.2 Total Zn content of Bangladesh soils

Total zinc content in the soils of Bangladesh varies substantially with physiography. The mean total Zn contents in Ganges River Floodplain soils are higher compared to terrace or hill soils (Hassan, 1999). Higher contents of trace elements in the floodplain soils may be due to higher silt and clay contents. Also the higher contents of primary minerals present in the silt fractions probably contribute to the high content of trace elements in these soils (Huizing, 1971; Hassan, 1999). The recent formation of floodplain soils may be responsible for the higher amount of weatherable minerals in these soils. The floodplain soils that are youngest contain higher amount of silt and, in turn, higher quantities of trace elements compared to Terrace or Hill soils. Data presented by Hassan (1991) shows that among the Floodplain soils, the highest total Zn content (159 mg/kg) was found in Phagu series in Meghna Floodplain soils followed by Ghior series (141 mg/kg) in Ganges Floodplain soils. All the series studied in Ganges Floodplain (Ishurdi, Ghior, Barisal and Hatiya) contained > 100 mg/kg. The lowest total Zn was observed in Chhiata and Nijhuri series in Terrace soils. The Ganges Tidal Floodplain soils had the highest content of total Zn followed by Old Brahmaputra and Ganges River Floodplain soils (active part). Hassan (1999) reported that the mean total contents of Zn of 30 soils from all over Bangladesh were 63 mg/kg. The element was found to be higher in clay fractions than either in silt or sand fractions.

According to Moslehuddin *et al.* (1999b) total Zn content in 10 paddy soils covering all physiographic units ranged from 19 to 92 mg/kg in top soil and 27 to 91 mg/kg in the subsoil. Domingo and Kyuma (1983) found 10 to 110 mg/kg total Zn with a mean of 68 mg/kg in 53 soils of Bangladesh, while Khan *et al.* (1997) found 97 to 447 mg/kg of total Zn in Floodplain topsoils of Bangladesh. Total Zn content of the soils showed a variation with physiography apparently due to difference in parent material (Moslehuddin *et al.*, 1999b). Zinc content was found to be positively correlated with sand content and montmorillonite and kaolinite type clay in Bangladesh (Domingo and Kyuma, 1983). Variation of soil Zn with clay content in Bangladesh has also been reported elsewhere (Moslehuddin *et al.*, 1997). The problem of Zn deficiency was related to soils derived from tertiary sandstone, marine alluvia and those derived from granite (Domingo and Kyuma, 1983). Jahiruddin *et al.* (2000) showed that the level of total Zn varied considerably between the locations irrespective of land type. Total Zn content of non-calcareous soils ranged from 45 to 94 mg/kg while that of calcareous soils from 51 to 111 mg/kg. The mean concentration of total Zn in Old Brahmaputra Floodplain (AEZ 9) and High Ganges River Floodplain (AEZ 11) were 66 and

79 mg/kg, respectively. They also observed positive relationship between total Zn and other elements with organic matter and clay content of the soils studied.

2.3.3 Available Zn status of Bangladesh soils

In Bangladesh, Zn deficiency is the most widespread micronutrient problem (Islam *et al.*, 1992; Moslehuddin *et al.*, 1997; Jahiruddin and Islam, 2014). About 1.7 million ha of land have been estimated to be deficient in Zn supply (Huq and Shoaib, 2013). Portch and Islam (1984) studied 63 soil samples from different regions of Bangladesh and found that 79% of them were deficient in Zn. Mayer *et al.* (2010) studied Zn status of soils collected from 6 districts of Bangladesh in two seasons and found that 51% of the soil samples had <0.8 mg/kg available Zn, a critical concentration for rice. In general, Ganges Floodplain and coastal saline soils and the area covered by HYV rice are reported to be deficient in Zn (Moslehuddin *et al.*, 1997). Available Zn concentration ranged very narrowly from 0.6 to 1.3 mg/kg in these regions (Moslehuddin *et al.*, 1999). The Ganges River Floodplain soils that are situated in the calcareous Gangetic Alluvium and contain variable quantities of calcite are prone to Zn deficiency as reported by Jahiruddin *et al.* (2000). Khan *et al.* (1997) also reported similar results in the Ganges River Floodplain soils. Considering 0.8 mg/kg DTPA extractable Zn as critical limit, Ganges River Floodplain, Old Brahmaputra Floodplain and Meghna Estuarine Floodplain were found to be deficient in Zn (Moslehuddin *et al.*, 1997). Domingo and Kyuma (1984) reported an average of 2 mg/kg acetic acid extractable and 10 mg/kg HCl extractable Zn in Bangladesh soils. Jahiruddin and Islam (2014) reported that the Zn status of 30% soils in AEZ 1 is very low while that of 40% soils is low; in AEZ 3 the status of 28% soils is very low and 58% is low.

Huq and Shoaib (2013) stated that although Zn deficiency occurs locally, it may be wide encompassing in the calcareous soils with moderate to high organic matter content, peat soils, saline soils, and light-textured piedmont soils of Bangladesh.

2.4 FORMS AND DISTRIBUTION OF SOIL ZINC

Identifying the forms of Zn in soils is becoming more important because the knowledge of the total soil content provides little information about its availability to plants. Research is being continued for better extraction of the plant available forms and to know the behaviour of both native and applied Zn. Zinc is present in soils in a number of theoretical chemical forms based on the methods of their extraction by chemical agents and on their reactivity, solubility and availability to plants (Pickering and Shuman, 1981; Adriano, 1986; Shuman, 1991). The commonly considered conceptual forms of Zn are i) free and complexed ions in soil solution, ii) exchangeable and non-specifically adsorbed Zn, iii) as ions specifically adsorbed and occluded in oxides and hydrous oxides of metals, carbonates and clay minerals, iv) organically bound i.e. bound in biological residues and living organisms and v) in the lattice structure of primary and secondary silicate minerals (Tessier *et al.*, 1979; Iyengar *et al.*, 1981; Adriano, 1986; Mandal and Mandal, 1986; Shuman, 1991; Parveen, 1993; Reed and Martens, 1996; Chowdhury *et al.*, 1997).

According to Viets (1962), there are five distinct pools of soil micronutrients. The pools are defined as i) water soluble, ii) exchangeable, iii) adsorbed and complexed, iv) associated with secondary minerals and metal oxides, and v) associated with primary minerals (Regmi *et al.*, 2010). Many schemes of Zn fractionation have been reported yielding different measurable pools (Shuman, 1979; Iyengar *et al.*, 1981; Neilsen *et al.*, 1986; Rauret *et al.*, 1999). Only a trace of the total soil Zn is available to plants and bulk of the soil Zn is present in the lattice structure of primary and secondary of minerals (Huang, 1989; Mengel *et al.*, 2001). Availability of Zn to plants depends on the dynamic equilibrium that prevails among these fractions. Due to difference in strength, these pools differ in their exposure to plant uptake, leaching, and extractability. Water-soluble, exchangeable, and organically complexed forms are considered as available; amorphous sesquioxide-bound form is potentially available; and crystalline sesquioxide-bound and residual Zn forms are unavailable to plants (Sureshkumar *et al.*, 2004). According to Cakmak and Kutman (2018), the potentially bioavailable Zn in the soil comprises the soluble, exchangeable and organically-bound pools, and plant roots absorb Zn mainly from the soil solution. When soil pH is above 8, Zn is bound to soil components (such as Fe oxides and calcites) strongly, causing decreased availability of Zn to plant roots (Cakmak and Kutman, 2018). Forms of Zn in soluble organic complexes and exchange positions are considered significant in maintaining the Zn level necessary for wetland rice (Murthy, 1982; Sharma and Subehia, 2014). A brief description of the common Zn forms is given in the following sections.

2.4.1 Zinc in Soil Solution

Soil solution form of Zn is the most important among the forms since plants absorb this form as nutrient. The concentration of an element in soil solution is influenced by many factors including moisture content, pH, oxidation/reduction status, temperature, fertilizer addition, and plant uptake (Shuman, 1991). The solution form of Zn exists as free ions, or as soluble complexes with inorganic anions or organic ligands (Fletcher and Beckett, 1987; Shuman, 1991). Usually, the forms of Zn in soil solution include simple cation (Zn^{2+}) or hydroxy metal cation [$Zn(OH)^{+}$] (Brady and Weil, 2014). Under acidic condition, the cation form is dominant while the more complex hydroxy form becomes prominent under alkaline soil conditions (Brady and Weil, 2014). The hydroxy form is relatively insoluble.

The concentration of Zn in soil solution is reported to be very low (Shuman, 1991). Hodgson *et al.* (1966) reported that Zn levels in soil solution averaged from < 2 µg/l to 74 µg/l in Colorado and New York soils. On an average 60% and 55% of the soluble Zn occurred apparently in soluble organic complexes for the Colorado and the New York soils, respectively. McBride and Blasiak (1979) reported that the proportion of Zn complexed in solution increased as soil pH increased and at soil pH above 6.5, much of the Zn in solution was complexed with soluble organic material.

2.4.3 Exchangeable Zn

The plant available forms comprise both soluble and exchangeable Zn. Exchangeable Zn is adsorbed as a cation on negatively charged sites on clays, alumino-silicate minerals, hydrous oxides of Al, Fe and Mn, solid organic matter, or on amorphous materials by electrostatic force in a low soil pH environment (Adriano, 1986; Beckett, 1989; Shuman, 1991). Exchangeable cations are isotopically exchangeable and can be displaced by other basic cations present in soil solution. The adsorption of Zn on the colloidal surfaces is related to their concentration in solution and properties like soil pH, concentration of other metallic cations and presence of organic and inorganic ligands (Shuman, 1991). The amount of Zn in soil solution is also controlled by the sorption and desorption from oxide surfaces (Jenne, 1968). The fixed Zn in the clay lattice can only become available to plants after weathering (Adriano, 2001). In some extraction schemes exchangeable and adsorbed Zn ions are distinguished as weakly adsorbed (non-specific sites) and strongly adsorbed (specific sites) (Brar *et al.*, 1986; Shuman, 1991).

2.4.4 Specifically adsorbed Zn

This form of Zn is usually held relatively strongly on inorganic sites by predominantly covalent or coordinate forces (Miller *et al.*, 1986; Beckett, 1989). Ions held in this form are retained and released more slowly than exchangeable ions, and are more easily replaced by other trace metals than by basic cations (Hodgson, 1963). The specific sites exist on clay minerals or other mineral surfaces in small quantities, but numerous sites occur on the surfaces of amorphous precipitates of aluminosilicates, silica, or the oxides of iron, aluminium, and manganese at neutral or higher pH, as well as on the zone of alteration on the surfaces of crystalline oxides, carbonates, phosphates, etc. (Beckett, 1989). Researchers consider oxides and hydrous oxides of Fe, Mn and Al as the principal factor for fixation of trace metals in soil (Jenne, 1968; Shuman, 1991). Trace metals are associated with these oxides by adsorption, surface complex formation, ion exchange, occlusion on the crystal lattice, and co-precipitation (Sposito, 1983; Shuman, 1991).

The retention of specifically adsorbed cations becomes stronger with time as the cations diffuse into the body of a precipitate (Beckett, 1989). In some cases, crystallization of an amorphous precipitate may expel the occluded foreign cations which then become concentrated in its outer, and still amorphous zone (McLaren and Crawford, 1973; Beckett, 1989; McBride, 1989).

2.4.5 Carbonate bound Zn

Trace element cations may be incorporated in newly precipitated carbonates of calcium, magnesium, iron, or aluminum, or may be adsorbed on the amorphous surfaces of such precipitates, either as exchangeable form, or as specifically adsorbed when the surface layers crystallize (Beckett, 1989). Significant trace metal concentrations can be associated with sediment carbonates and would be susceptible to changes in pH (Tessier *et al.*, 1979). Carbonates present in alkaline soils adsorb and occlude Zn and other metals (Shuman, 1991). The unavailability of Zn in calcareous soils is partly due to the adsorption by carbonates or precipitation of Zn $(OH)_2$ or $ZnCO_3$ (Kalbasi *et al.*, 1978; Singh and Singh, 1980). It was observed that Zn is most strongly adsorbed by magnesite, to an intermediate degree by dolomite and least of all by calcite (Jurinak and Bauer, 1956). The adsorption of Zn by carbonates increases with the increase in the quantity of clay size $CaCO_3$ (Navrot and Ravikovitch, 1969).

2.4.6 Organically bound Zn

The organic matter fraction contains a significant amount of Zn in soils (Lindau and Hossner, 1982; Miller and Mc Fee, 1983). Like other micronutrients, Zn is associated with various forms of soil organic matter including water-soluble and solids (Shuman, 1991). The association of Zn may be in the form of i) incorporation in the structure of less decomposed material, ii) chelation, causing resistance to exchange, and iii) specific and exchangeable adsorption (Lindsay, 1972; Shuman, 1991). Soluble organic matter-Zn complexes brings Zn to plant roots, while solid organic matter help in adsorbing Zn by providing negative adsorption sites and specific adsorption sites and decrease plant availability temporarily (Shuman, 2005). As a result, Zn availability is low in organic soils. However, the bound Zn may be released by microbial activity during the decomposition of organic matter and thus plant uptake is increased (Shuman, 2005). Organic colloids may be intimately linked to other fractions of Zn like the iron or aluminium oxide and sulfide bound forms, making specific fractionation difficult (Warren, 1981; Smith and Mitchell, 1984). The organically bound Zn plays important role in Zn nutrition of lowland rice (Murthy, 1982; Mandal and Mandal, 1986).

2.4.7 Manganese oxide bound Zn

Manganese oxides in soils have a high sorption capacity for trace metals (Jenne, 1968; Tokashiki *et al.*, 1986). According to Jenne (1968) retention and release of Zn from the oxide surfaces is the main contributor of the soil solution Zn. The manganese oxides occur in soils as coatings on other soil particles, as deposits in cracks and mixed with iron oxides and other soil constituents. Manganese oxides are less abundant than Fe oxides, being 1/50 part of Fe oxides, but demonstrate more chemical reactivity and mineral forms than that of Fe oxides (Chao and Theobald, 1976; Scheinost, 2005). Thus, trace element concentrations are often high in the Mn oxides bound form (Taylor and McKenzie, 1966; Shuman, 1991). The amount of MnOx-bound Zn increases with an increase in both soil pH and free manganese (Sims and Patrick, 1978; Iyengar *et al.*, 1981; Chandi and Takkar, 1982). Heavy application of organic manures increases soil organic C levels and develops reducing conditions in top soil (Hinesley, 1972; Mandal and Mandal, 1987), causing increased levels of labile Fe and Mn (Robertson *et al.*, 1982). Thus the elements associated with Mn and Fe become more soluble under reducing conditions (Sims and Patrick, 1978).

2.4.8 Iron oxide bound Zn

The oxides of iron are the most abundant metallic oxides in most soils (Schwertmann and Taylor, 1989). Regarding sorption of cations (e.g., Zn^{2+}, Cd^{2+}), the crystal forms, crystal size and crystallinity of iron oxide species are of great importance (Loeppert and Inskeep, 1996). During decomposition of silicate minerals trace elements like iron and manganese are released and precipitated as hydrous oxides. These oxides may exist as unconfined in soil or as coatings on clay minerals, cutans, concretions and colloidal particles or within the soil capillary networks (Thomas and Swoboda, 1962; Schwertmann, 1988; Wild, 1988). As the oxides form, Zn and Cu can be occluded in the precipitates. After adsorption, Zn^{2+} may enter into the lattice through solid state diffusion. However, it is possible that hydrous oxide can dissolve and precipitate again due to changes in pH or redox potential (Wild, 1988). As long as the host oxides are amorphous, cations like Zn are easily adsorbed on to Fe/Al oxide precipitates. Initially after adsorption, Zn may be held as exchangeable form, but becomes more covalent with time and during the crystallization of the oxides, the adsorbed Zn becomes occluded in crystal structure (Loeppert and Inskeep, 1996). The amorphous iron oxides are often called noncrystalline or poorly crystalline iron oxides and are the most reactive iron oxides in the soil due to their small size and consequently high surface area. This class of oxides includes ferrihydrite and the ferrihydrite-like minerals (Loeppert and Inskeep, 1996).

Enrichment of Zn in Fe and Mn nodules in soils has been observed in several studies (Dawson *et al.*, 1985; Gasparatos, 2013). The general occurrence of these oxides may make them important in retention and release of Zn. For instance, most of the soils of Soth West Australia, where kaolinite is the dominant clay mineral are extremely infertile and inherently deficient in P, Mo, Zn, Cu and other nutrients (Robson and Gilkes, 1981).

2.4.9 Zinc associated with primary and secondary minerals

Trace elements do not form mineral on their own, but become incorporated in silicate minerals during weathering which is largely controlled by their ionic radii (Wild, 1988). Replacement of Mg and Fe by Zn and Cu in basic igneous rocks occurs, as mentioned earlier, and consequently soils formed on basic rocks are enriched with micronutrients. In contrast, acid igneous rocks are deficient in micronutrients (Wild, 1988). Zinc is infrequently present in metamorphic and igneous rocks as the sulfide (spharelite) and most of it exists as a minor constituent of rock-forming minerals, especially those rich in iron including magnetite, the pyroxenes, the amphiboles, biotite, and staurolite (Adriano, 2001). According to Wedepohl (1978), abundance of Zn in different minerals is controlled by its concentration in the magma and pre-metamorphic rock, and the capability of the crystal lattice to incorporate it. Details about Zn associated with primary and silicate clay minerals are presented earlier in Section 2.2 and 2.2.2.

2.5 SELECTIVE CHEMICAL EXTRACTION OF ZINC FROM SOILS

Various chemical extraction procedures are employed to determine the soil Zn fractions selectively. Sequential selective extraction schemes furnish detailed information on the origin, mode of reactivity and transport of trace metals in soil. Also the information about the distribution of the element among solid and liquid phases and relationship of the fractions with factors controlling their distribution are generated by the fractionation schemes (Shuman, 1991).

The objective of selective extraction methods is to determine the amounts of metals associated with various operationally defined phases (e.g., carbonates, organic matter, metal oxides, silicate minerals) in soils. The principal limitations of these selective extraction methods are the lack of selectivity of most extractants for the particular fractions of interest, the potential of re-adsorption of extracted element by other soil components during the extraction procedure, and other related artifacts introduced during extraction procedures (Reed and Martens, 1996). For these reasons, selective extraction methods, as with most analytical methods for soils, are operationally defined and are used to know the distribution of Zn among principal soil components (Campbell and Beckett, 1988; Beckett, 1989; Shuman, 1991).

Generally, from the least to the most aggressive reagents are employed to extract the fractions easily soluble to more resistant (Beckett, 1989). However, the most appropriate sequence to employ is a subject of continued research efforts (Miller *et al.*, 1986; Shuman, 1991).

2.5.1 Extraction procedures for specific soil Zn fractions

2.5.1.1 Water soluble fraction

Several workers have measured a water-soluble fraction of the trace metals by shaking soil with unspecified water or with distilled or deionized water (Viets, 1962; Sims and Patrick, 1978; Iyengar *et al.*, 1981; Miller and Mc Fee, 1983; Sposito, 1983; Miller *et al.*, 1986). In the usual fractionation schemes, the water-soluble fraction is the first to be dissolved and separated (Shuman, 1991). The extractant is usually purified water, and the only difference among procedures is the soil-to-solution ratio, and the shaking method and time. The separation of water soluble fraction usually precedes the measurement of exchangeable or specifically adsorbed forms (Shuman, 1991). Sims and Patrick (1978) divided the water-soluble fraction into free ions and ions complexed by organic matter as extracted with cation- and anion-exchange resins.

The quantity of micronutrients brought into solution by water usually is very low and is often difficult to detect by analytical methods. However, their concentrations may be significant in this fraction where micronutrient fertilizers or sewage sludge have been applied. Thus, the water soluble fraction usually is not separated, unless there is a reason to expect this form to be important because of the treatments imposed (Shuman, 1991).

2.5.1.2 Exchangeable fractions

The amount of exchangeable fraction is usually most significant in relation to biological uptake. This is why many extractants have been tested for their quantification. Among the extractants commonly used to extract the exchangeable Zn are 1 M NH_4OAc at pH 7.0 (Gupta and Chen, 1975; Gibson and Farmer, 1986), 1 M $MgCl_2$ (Stewart and Berger, 1965; Tessier *et al.*, 1979; Iyengar *et al.*, 1981; Ma and Uren, 1997), 0.05 M $CaCl_2$ (Elsokkary, 1979; Mathur and Levesque, 1983; Goldberg and Smith, 1984), 1 M NaOAc (Sims and Patrick, 1978; Tessier *et al.*, 1979), 1 M $Mg(NO_3)_2$ at pH 7.0 (Shuman, 1985; Sims, 1986), $BaCl_2$ (Meguellati *et al.*, 1982), KNO_3 (Sposito, 1983) and $Ca(NO_3)_2$ (Miller *et al.*, 1986).

Since the exchangeable metals are held by electrostatic forces on colloid surfaces and in specific sites with high affinity for the metal, large excesses of cations are necessary to replace them (Shuman, 1991). Common cations used to replace the metals are Ca^{2+}, Mg^{2+}, and NH_4^+, usually at a concentration of one molar (Beckett, 1989; Shuman, 1991). Although the divalent ions have more replacing power than the monovalent, the monovalent ions like K^+ can replace some of the ions entrapped in between the layers of clay minerals (Shuman, 1991). Anions used with the exchangeable salts are Cl^-, NO_3^-, and CH_3COO^-, among which chloride (Cl^-) is sometimes preferred because of its resistance against change of pH (Shuman, 1991). However, since Cl^- is a stronger complexing anion than NO_3^-, the later has been used in the extraction schemes (Stover *et al.*, 1976; Sposito, 1983; Shuman, 1985; Singh *et al.*, 1988). Use of acetate (CH_3COO^-) will lower the pH releasing more metals; however, these may come from other than exchange sites as the clays are hydrolyzed (Shuman, 1991). Acetate has disadvantages of being nonspecific for exchangeable ions and for dissolving carbonates and dissolving or complexing oxide coatings (Gibbs, 1973; Robbins *et al.*, 1984).

2.5.1.3 Organic fraction

Separation of the organic fractions is difficult because of the lack of selective power of the extractants used. The usual approach of extracting organic fraction is the oxidation of the material to release the metals. However, the extractants used to oxidize organic fractions oxidize sulfides also and thus combine the fractions (Shuman, 1991). To extract the metals chelated by the soil humic materials, some chelating agents are also used (Mathur and Levesque, 1983; Goldberg and Smith, 1984). One of the extractants used initially for the separation of organic fraction was pyrophosphate ($K_4P_2O_7$) (Bascomb, 1968; McLaren and Crawford, 1973; Stover *et al.*, 1976; Iyengar *et al.*, 1981; Miller *et al.*, 1986). Pyrophosphate stabilizes the organic matter by complexing the cations, causing it to disperse (Shuman, 1991). Pyrophosphate was originally introduced in soil flocculation studies as an extractant for soil organic matter (Beckett, 1989). Since pyrophosphate does not dissolve sulfides (Chao, 1984), it would be useful if sulfides are to be separated from the organic fraction. McLaren and Crawford (1973) reported that it extracted more colloidal organic matter than EDTA. Likewise, Miller *et al.* (1986) reported that it extracted more organic matter than H_2O_2 or NaOCl, and that its efficiency increased with pH. Miller *et al.* (1986) recognized that pyrophosphate solubilized oxides that hydroxlyamine hydrochloride ($NH_2OH \cdot HCl$) did not and recommended using hydroxylamine before pyrophosphate in the sequence, thus removing the oxides before the organic fraction (Shuman, 1991).

Acid peroxide (H_2O_2) is another extractant used to destroy organic matter from clays prior to mineralogical analysis (Kittrick and Hope, 1963). However, peroxide has some disadvantages including (i) extraction of the Mn oxide fraction (Shuman, 1991); (ii) dissolution of sulfides (Gupta and Chen, 1975; Gatehouse *et al.*, 1977) and (iii) formation of oxalates that attack Fe oxides (Lavkulich and Wiens, 1970). Some of these problems can be avoided by placing the acid peroxide after the extraction of Mn oxide and amorphous Fe oxide fractions (Tessier *et al.*, 1979).

Another oxidizing agent, sodium hypochlorite (NaOCl) at pH 8.0 to 9.5, has been used extensively in sequential procedures (Shuman, 1991). It is more effective than H_2O_2 for extracting organic matter with less destruction of carbonates and oxides (Anderson, 1961; Lavkulich and Wiens, 1970; Omueti, 1981). Shuman (1983) stated that NaOCl seems to be a good compromise for an organic extractant, dissolving the most metals from the desired fraction and the least from others. Use of sodium hydroxide (NaOH) as an extractant of organic Zn fraction has also been reported (Sposito *et al.*, 1982; Beckett, 1989).

2.5.1.4 Manganese oxide Fraction

For the extraction of manganese (Mn) oxides, a reducing agent is required that would reduce Mn, but not iron (Fe) (Shuman, 1991). Hydroxylamine has become a standard extractant for selective extraction of Mn oxides. The method of Chao (1972) is commonly used, who used 0.1 M hydroxylamine in 0.01M HNO_3 at pH 2. This extractant dissolves 85% of the Mn oxide and only 5% of the Fe in various sediments (Chao, 1972). Several studies have verified that hydroxylamine specifically extracts Mn-oxides (Frampton and Reisenauer, 1978; Shuman, 1982). In case of sodium dithionite ($Na_2S_2O_4$), another popular extractant for Mn oxide, pH and reducing conditions controls the amount of Mn extracted (Daniels *et al.*, 1962). However, this reagent also dissolves Fe oxides. Generally, the methods that dissolve Fe oxides will also remove Mn oxides (Shuman, 1991).

2.5.1.5 Amorphous iron oxide fraction

The most commonly used method for obtaining quantitative estimates of amorphous iron oxide fraction is 0.2 M ammonium oxalate adjusted at pH 3.0 (Tamm's reagent) in the dark for either 2 h (Schwertmann, 1964) or 4 h (McKeague and Day, 1966). Samples are shaken in the dark to prevent photolytic reduction (Shuman, 1991; Loeppert and Inskeep, 1996). This extractant has been verified to dissolve the amorphous Fe fraction and not the more crystalline Fe fraction (McKeague, 1967; Dudas and Harward, 1971). Pawluk (1972) reported a double extraction with acid oxalate to solubilize amorphous Fe oxides. However, since the amorphous and crystalline phases are in continuum, exact separation by this method is difficult (Shuman, 1991). In this method, calcareous soils must be pretreated to remove $CaCO_3$, since oxalic acid will react with $CaCO_3$ to change the pH of the oxalate/oxalic acid buffer, precipitating oxalate as Ca salt (Loeppert and Inskeep, 1996). This is accomplished by separating carbonate bound fraction before this step. Chao and Zhou (1983) observed that extraction with a mixed solution of 0.2 M hydroxylamine hydrochloride and 0.2 M HCl at 50°C for 30 minutes extracted amorphous oxide similar to those obtained with the ammonium oxalate extraction in the dark. Alkaline EDTA also has been used to dissolve noncrystalline iron oxides (Borggaard, 1988); however, reaction times of 90 days or more are required for quantitative extraction in this method (Shuman, 1991).

2.5.1.6 Crystalline iron oxide fraction

The best recognized method for the extraction of crystalline Fe oxide fraction is that of Mehra and Jackson (2013) using dithionite ($Na_2S_2O_4$) in a citrate/bicarbonate buffer (CBD), which was developed to remove all the Fe- and Al-oxides from clays before mineralogical examination (Kittrick and Hope, 1963). However, dithionite is several disadvantages including i) contamination with Zn, requiring a purified reagent and ii) precipitation of metal sulfides (Shuman, 1991). Citrate dithionate buffer has been used as a general oxide extractant dissolving the Mn oxide, amorphous and crystalline Fe oxide fractions, or it has been used more selectively after the removal of the first two (Shuman, 1991). Another popular method to extract crystalline Fe oxide is the use of oxalate solutions with UV light (De Endredy, 1963; Schwertmann, 1964). Ascorbic acid has been used by Shuman (1982, 1985) as a reductant with oxalate, to overcome the problems of standardizing UV methods and the problems related to CBD. Kawai (1977) used a fluorescent lamp with 0.1 M oxalic acid to remove Fe oxides. Chester and Hughes (1967) developed 1M hydroxylamine with 25% acetic acid to dissolve all the soil oxides. By varying the hydroxylamine concentration and the acid (HNO_3 vs. acetic), Frampton and Reisenauer (1978) distinguished between Mn oxides and crystalline Fe oxides. Robbins *et al.* (1984) buffered the hydroxylamine with Na citrate at pH 5 to prevent breakdown of silicates, which can caused by the low pH acetic acid.

2.5.1.7 Carbonate bound fraction

The carbonate bound elements are usually extracted by acidified sodium acetate (NaOAc-HOAc) (Tessier *et al.*, 1979; Hickey and Kittrick, 1984; Shuman, 1991; Han *et al.*, 1992) or by using chelating agents, like EDTA (Stover *et al.*, 1976; Emmerich *et al.*, 1982; Miller and Mc Fee, 1983; Sposito, 1983; Chang *et al.*, 1984; Shuman, 1991; McGrath and Cegarra, 1992). However, lack of specificity and selectivity in EDTA has been reported for carbonate phase (Han and Banin, 1995). Gupta and Chen (1975) used 1 M HOAc and Mathur and Levesque (1983) used 0.1 M HCl to extract carbonate bound fraction. Care should be taken that the acids used to dissolve the carbonates must not be so strong as to attack the silicates (Shuman, 1991). Use of 1 M NaOAc adjusted to pH 5.0 with HOAc completely dissolves calcite and dolomite without attacking silicates (Tessier *et al.*, 1979; Robbins *et al.*, 1984). According to Han and Banin (1995), NaOAc-HOAc buffer solution at pH 5.5 with a soil to solution ratio 1:25 can dissolve all the carbonate from calcareous soils with 10 - 20% of $CaCO_3$, and from soils with 30-50% $CaCO_3$ at pH 5.0. Extraction of carbonate fraction before the organic and oxide fractions have been performed to avoid an appreciable dissolution of Zn associated with the latter fractions (Singh *et al.*, 1988; Shuman, 1991).

2.5.1.8 Residual (mineral bound) fraction

The metals in the remaining silicates and other resistant minerals are dissolved by digesting the soil with strong mineral acids (HF, HNO_3, HCl, or $HClO_4$) in heat-resistant plastic containers (Beckett, 1989; Shuman, 1991). Fusion with alkali salts and dissolution in HNO_3 has also been used (Gibbs, 1973). Dissolution of the residual solids with strong mineral acids without completely destroying the matrix assumes that the majority of the metals would be extracted (Shuman, 1991). Digestion with 90% HNO_3/10% HCl adequately extracted total metals in a U.S. Bureau of Standards new industrial river sediment (Sinex *et al.*, 1980). Use of $HClO_4$ along with HNO_3 to dissolve total trace metals has also been reported by many researchers (Schalscha *et al.*, 1982; Parveen, 1993; Lucho-Constantino *et al.*, 2005; Ranjbar and Jalali, 2013). According to Aitang and Häni (1983), 2 M HNO_3 dissolved 59 and 68% of total Cu and Zn, respectively, and 3M HCl solubilized 59 and 85% of the total Cu and Zn, respectively. Thus, the concentrations of total element are not well estimated by the methods that do not destroy the sample completely (Shuman, 1991).

2.6 DISTRIBUTION OF THE ZINC FORMS AND THE EFFECT OF SOIL PROPERTIES

The distribution of soil Zn among fractions has been related to the type and nature of soil constituents (Liang *et al.*, 1990; Adriano, 2001). Shuman (1979) reported that 1-7% of Zn was in exchangeable form and 40% and 20% in the clay and Fe-oxide fractions, respectively, in 10 Georgian soils. He found that fine textured soils contained higher amounts of Zn associated with clay fractions while the coarse textured soils had more in the organic fraction. In another study, Zn associated with oxides and hydrous oxides of Fe and Al ranged from 14 to 38% and with clay minerals it ranged from 24 to 62% (Zyrin *et al.*, 1976; Kabata-Pendias and Pendias, 2001). The soluble Zn fraction and organic complexed Zn constitute only 1 - 2% and 1.5 - 2.3%, respectively. Iyengar *et al.* (1981) reported wide variation in the distribution of Zn fractions in 19 soils of USA with different chemical and physical properties. They observed that on an average, most of the Zn was in the Fe oxide (25%) and residual (70%) fractions, while exchangeable, organically bound and Mn oxide bound Zn fractions comprised 3.7, 2.5 and 2% of total Zn, respectively. These findings depict that most of the Zn in the soils are generally in the oxide bound and residul fractions. The other forms that are potentially available to the plants represent only a negligible fraction of total Zn content.

The soluble, weakly bound and adsorbed Zn has been found to vary with soil pH. Neilsen *et al.* (1986) found that Zn in the exchangeable and organic fractions was negatively correlated to both pH and residual Zn, suggesting a redistribution of soil Zn from the residual fraction into exchangeable and organic fractions with acidification. Recently, Shuman (1988) found that increasing pH decreased exchangeable and increased organic Zn. Obviously, variations in soil properties play a major role in controlling the distribution of Zn among various chemical forms and their supply to plants.

Organic matter also plays an important role in influencing the availability of Zn in soils and its uptake by the plants. It is evident that Zn forms stable complexes with soil organic matter having variable solubility (Stevenson, 1986; Harter, 1991; Adriano, 2001; Kabata-Pendias and Pendias, 2001). The humic and fulvic acid fractions of organic matter are prominent in Zn adsorption. According to Tisdale *et al.* (1993), following three reaction mechanisms have been identified between organic matter and Zn: i) immobilization by high molecular weight organic substances like lignin, ii) solubilization by short chain organic acids and bases, and iii) complexation by initially soluble organic substances, which finally form insoluble salts.

2.7 TRANSFORMATION AND REDISTRIBUTION OF ZINC IN SOILS

Variation of soil environment determines the magnitude of transformation of Zn in soil and its redistribution among different fractions. Zinc in soils is transformed by various mechanisms like sorption by soil components including clays, hydrous oxides, organic matter etc. which affect the availability of Zn in soils. Usually, the percentage of less plant available forms e.g. oxide and residual fractions are higher than more plant-available forms (Kittrick and Hope, 1963; Emmerich *et al.*, 1982; Ma and Uren, 1997). According to LeClaire *et al.* (1984), water-soluble and organic pool of Zn are labile and bioavailable, carbonate pool is potentially bioavailable or quasi-labile, and the mineral form is nonlabile or unavailable to plants. The DTPA extractable Zn and other extractable forms are often highly positively correlated with the more available fractions, like exchangeable and organic fractions, and are considered plant available (LeClaire *et al.*, 1984; Rappaport *et al.*, 1986; Shuman, 1986; Shuman, 1988). Organic Zn was, however, negatively correlated with DTPA Zn, indicating that a portion of this fraction is not plant available (Rappaport *et al.*, 1986; Shuman, 1991). A brief discussion on the transformation of Zn under various soil conditions is presented in the following sections.

2.7.1 Effect of changes in soil pH

Micronutrient metals become less plant available as soil pH increases as indicated by numerous literatures. Zinc distribution in soil is also affected by soil pH changes, usually increasing in more plant-available form as pH decreases (Neilsen *et al.*, 1986; Sims, 1986). Increasing soil pH was found to decrease the water-soluble fraction of Zn (El-Kherbawy and Sanders, 1984) and the exchangeable fraction (Elsokkary and Låg, 1978; Iyengar *et al.*, 1981; Sanders *et al.*, 1986; Sims, 1986). A diagram of Zn redistribution from the exchangeable to the oxide form due to changes in soil pH reported by Shuman (1991) is presented in Fig. 2.1.

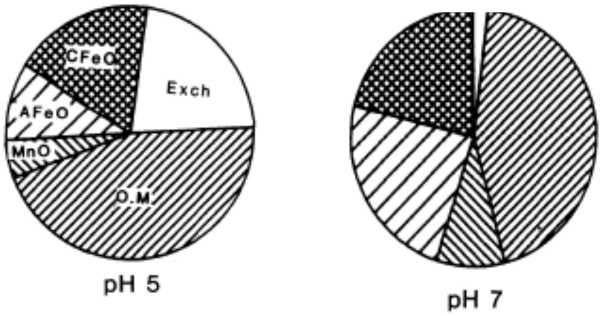


Fig. 2.1 Redistribution of soil Zn fraction due to changes in pH (Source: Shuman, 1991).

Increasing soil pH was also found to increase Zn in the organic fraction (Estepp and Keefer, 1969; Shuman, 1986). On the other hand, Neilsen *et al.* (1986) found that Zn was redistributed from the residual to the exchangeable and organic fractions with acidification, which would increase the plant availability of Zn.

2.7.2 Application of Zn to soils

Application of Zn has been found to increase the exchangeable and amorphous FeO-bound Zn in alkali soils that contributed more to plant available form (Singh and Abrol, 1986). Added Zn was found in both plant-available and non-available forms in a field experiment by Mullins *et al.* (1982). The more reactive forms of the applied Zn is soil have been found to transform to unavailable forms with time (Ma and Uren, 1997). Reports are also found that the more bioavailable Zn forms, e.g., water soluble, exchangeable and organic forms are usually low in sewage sludge amended soils compared to other forms (Sposito, 1983; Adams and Sanders, 1984; Shuman, 1991). However increases of Zn in these forms compared to untreated soils are important for the environment (Schalscha *et al.*, 1980; Knudtsen and O'Connor, 1987).

2.7.3 Addition of organic amendments

The quantity of Zn in the organic fraction is generally higher than that in the exchangeable fraction (Sanders et al., 1986). The organic fraction of Zn is directly related to the quantity of organic matter present in the soil (Elsokkary and Låg, 1978; Iyengar *et al.*, 1981; Mandal and Mandal, 1986; McGrath *et al.*, 1988). Organic matter additions to soil usually causes redistributions of the soil Zn. Mandal *et al.* (1988) reported that added organic matter caused applied Zn to increase in all fractions, except the crystalline Fe oxides and the residual, implying an increase in availability to plants. Likewise, adding organic matter to soil increased organic and exchangeable fractions of Zn, and decreased the oxide fractions due to prevalence of reducing conditions making Zn more bio-available (Mandal and Mandal, 1987). Yoo and James (2003) observed an increase in the non-exchangeable forms of Zn in the flooded soils due to addition of organic matter, whereas it was unaffected in the non-flooded soils. Similarly, manure amendment has been found to increase the water-soluble Zn fraction and its bioavailability by Singhania *et al.* (1983). Shuman (1991) stated that organic matter additions resulted in a redistribution of Zn from the oxide to organic fraction. In contrast, a decrease in the availability of Zn due to the shift of Zn to the Mn and Fe oxide fractions from other fractions has been found by Shuman (1988). Thus, factors other than organic matter additions can affect redistribution of Zn. Soil properties, such as pH and redox status can be affected by the added organic matter which causes variation in redistributions depending on the specific conditions involved (Shuman, 1991).

2.7.4 Changes in oxidation and reduction status

Submerging a soil causes a decrease in the Eh and an increase in soil pH (Lindsay, 1979). This situation makes the oxides more soluble to release adsorbed and occluded metals. Thus, oxidation/reduction changes bring about redistributions of Zn and other metals among their fractions (Shuman, 1991). The inorganic (oxide) fractions was found to increase when the soil was kept constantly wet, but alternate wetting and drying caused increases in the organic fraction (Estepp and Keefer, 1969). According to Yoo and James (2003), reduced soil conditions lowers exchangeable Zn and increases non-exchangeable Zn in the ponded soils, apparently due to the enhancement of surface-induced hydrolysis of Zn caused by rise in soil pH after flooding. Mandal and Mandal (1987) reported that both the submergence of soil and alternate wet and dry conditions caused decreases in the exchangeable, organic, and amorphous Fe oxide fractions of Zn. However, earlier, they found an increase in organic and amorphous Fe oxide Zn due to submergence (Mandal and Mandal, 1986). Hazra *et al.* (1987)

reported that reducing conditions increased amorphous and crystalline Fe oxide fractions and decreased exchangeable and organic fractions of Zn. In contrast, Sims and Patrick (1978) and Ghanem and Mikkelsen (1987) found that reducing conditions caused increase in the exchangeable and organic fractions and decrease in the oxide fractions of Zn. Thus, even though there are contradictions, usually reducing conditions increase Zn availability in soil (Shuman, 1991).

2.7.5 Effect of time

The changes in the forms of metals added to soil with time have been assessed by the selective sequential extraction (Shuman, 1991). Initially, added metals exist in soluble fractions, but transform to the less soluble oxide and residual fractions with time (Silviera and Sommers, 1977; Emmerich *et al.*, 1982; Sarkar and Deb, 1985; Ma and Uren, 1997). However, metals may become more available to plants with time. Chang *et al.* (1984) observed that in sewage sludge amended soil, the highest Zn content was in the carbonate and organic (labile) fractions compared to untreated soil where the highest Zn was in residual-sulfide (non-labile) fraction. However, after 4-week interval from planting to harvest, there was no redistribution of Zn. Brar *et al.* (1986) reported that over a 13-year period, soil Zn decreased in all fractions, the maximum depletion being in the acid-soluble and weakly adsorbed fractions, which are highly plant available. Thus, plant available Zn decreased with time.

Intensive cropping for more than three decades decreased the concentrations of Zn in the organic and carbonate fractions in an Inceptisol (Behera *et al.*, 2008). Soon (1994) reported the decrease of exchangeable and sorbed Zn in soil as a result of 23 years of cropping probably due to sorption and fixation by oxides in soil. Sposito (1983) found that Zn from sewage sludge increased in the carbonte fraction with time. Thus, in these studies Zn became less plant available with time. In contrast, Keefer and Estepp (1971) found that added Zn initially existed in the acid-soluble (clay) fraction but decreased with time, whereas the organic Zn increased, indicating a shift to more available forms.

2.7.6 Other factors related to Zn redistribution

Besides the factors discussed in the previous sections, transformation of Zn is affected by other factors like texture and depth of soil, temperature and solar radiation (Moraghan and Mascagni Jr, 1991). Kuo *et al.* (1983) observed that Zn in contaminated soil decreased sharply in all fractions with soil depth and existed largely in the crystalline Fe oxides, with small amounts in the amorphous Fe oxides. Similarly, Chandi and Takkar (1982) found that added Zn was restricted in the 0 to 30-cm depth. Study on the influence of cropping systems on Zn fractions revealed that a cereal-cereal system caused low exchangeable Zn^{2+}, a legume-millet system caused low adsorbed Zn, and a cereal-legume system caused low organic fraction Zn (Shuman, 1991). Tillage treatments were found to have little effects on Zn fractions (Shuman and Hargrove, 1985). Shuman (1988) reported that added P redistributed Zn from the Mn-oxide and crystalline Fe-oxide forms to the exchangeable form for eight soils, making it more plant available. In another study, however, the P level did not influence the Zn distribution (El-Kherbawy and Sanders, 1984). Zinc adsorption was found to decrease after the removal of Fe oxides (Cavallaro and McBride, 1984) and Mn oxides (Shuman, 1988). Zinc adsorption was also decreased by organic matter removal. Iyengar and Deb (1977) showed that 4 to 6% of added $ZnCl_2$ is taken up by plant and the rest is converted to unavailable forms. Ma and Uren (1997) reported that most of the endogenous Zn in field soils was found to exist in the residual fraction, while the Zn added as fertilizer in soils was found mainly in the EDTA-extractable and iron (aluminum) [Fe(Al)] and Mn oxides fractions. They observed that recently added Zn was more in the reactive forms in the soil (water-soluble plus exchangeable and EDTA-extractable Zn) than the Zn that was added for long-term. With time, the EDTA-extractable Zn transformed into the unreactive forms e.g., Fe (Al) and Mn oxide bound Zn.

2.8 PLANT UPTAKE OF SOIL ZINC FRACTIONS

Fractionation study depicts the scenario of different Zn forms absorbed by the plants. Mandal and Mandal (1986) reported that Zn bound to hydrous oxides contributed as much to plant uptake as exchangeable Zn, whereas Murthy (1982) reported a smaller contribution of hydrous oxide-bound Zn. However, Iyengar *et al.* (1981) reported negative partial correlations between Zn associated with oxides and Zn uptake. Behera *et al.* (2008) reported that DTPA extractable Zn was prominently influenced by easily reducible manganese, carbonate, and sesquioxide bound Zn-fractions both in pre-maize and post-wheat soils. Ahmed (1993) studied relative contribution of different fractions to Zn uptake by rice and reported the highest values for the complexed Zn, followed by residual Zn. In the same way, Behera *et al.* (2008) found that sorbed and organic matter bound zinc contributed directly and positively to Zn uptake by wheat and maize.

2.9 ZINC IN PLANTS

2.9.1 Role of Zinc in plant nutrition

In higher plants, Zn is involved in the activity of a large number of various types of enzymes, (Römheld and Marschner, 1991; Kabata-Pendias and Pendias, 2001; Barker and Pilbeam, 2007; Alloway, 2009; Marschner, 2012; Brady and Weil, 2014). It has been reported that Zn deficiency reduces root system development in crop plants (Fageria, 2014). This may disrupt absorption of water and nutrients and, consequently, growth and yield. Under severe Zn deficiency, flowering and fruiting in plants are significantly reduced (Epstein and Bloom, 2005). Brady and Weil (2014) reported that Zn promotes seed maturation and production in higher plants.

2.9.2 Critical limit in plants

In general, Zn deficiency in plants is observed when the plant contains less than 20 mg Zn kg^{-1} and toxic effects are expected when Zn concentration exceeds 300–400 mg kg^{-1} (Kabata-Pendias and Mukherjee, 2007). According to Riley *et al.* (1992), the critical limit of Zn in wheat plant is 10 mg/kg as mentioned by Brennan *et al.* (1993). Yoshida (1981) reported critical limit for Zn deficiency in rice plant to be 15 mg/kg. These values may, however, vary significantly because of the variation in the requirements of each crop species, genotype and the interactions of Zn with other elements within the plant tissues (Kabata-Pendias and Pendias, 2001).

2.9.3 Extraction of plant available Zinc

Development of soil tests to estimate the availability of Zn to plants requires the selection of extractant before their evaluation and calibration in greenhouse and in the field (Reed and Martens, 1996). The extractant should be effective in dissolving Zn in amounts that are proportional to that absorbed by plants during a single growing season, over a wide range of soil types. The DTPA method of extraction of soil micronutrients was developed by Lindsay and Norvell (1978). The pH of the extractant was adopted to be 7.3 to prevent the dissolution of $CaCO_3$ in calcareous soils and of occluded Fe in soil with low pH (Loeppert and Inskeep, 1996). Although developed for calcareous soils, the method was found to be useful for almost all soil pH ranges. The DTPA molecules form water-soluble Zn complex and decrease the activities of Zn^{2+} in soil solution resulting in desorption of Zn from soil surfaces to replenish the soil solution Zn^{2+} (Lindsay and Norvell, 1978; Reed and Martens, 1996).

Critical limit of Zn in soils

A level lower than 0.8 mg DTPA extractable Zn/kg in near-neutral and calcareous soils indicated inadequate Zn for field crops (Reed and Martens, 1996; Doberman and Fairhurst, 2000). However, the level of bioavailability of Zn varies among plant species as well as genotypes within a species (Brennan *et al.*, 1993; Alloway, 2009; Marschner, 2012). Sims and Johnson (1991) mentioned 0.20 – 2.0 mg Zn/kg soil extracted by DTPA as critical range for plants depending upon soil factors including pH, $CaCO_3$, P, organic matter and cation exchange capacity that influence the extractability and availability.

2.10 CAUSES OF ZINC DEFICIENCY IN SOILS

Several reasons have been reported to be responsible for Zn deficiency in soils. Effect of soil pH, redox potential, soil texture, type of clay and oxide minerals, soil depth, climatic conditions (temperature and rainfall), moisture status, organic matter content, and soil nutrient interactions on Zn availability have been extensively discussed in the literature (Domingo and Kyuma, 1984; Jahiruddin, 1986; Moraghan and Mascagni Jr, 1991; Ahmed, 1993; Brennan *et al.*, 1993; Shuman, 2005). Some of the major reasons for deficiency of Zn in soils as described by Doberman and Fairhurst (2000) and Alloway (2009) are as follows:

- Low total soil Zn (e.g., sandy soil).
- Small amount of available Zn in the soil.
- High soil pH ($\geq$7 under anaerobic conditions; calcareous soils).
- High HCO_3^- concentration in calcareous soils because of reducing conditions with high organic matter or because of large concentrations of HCO_3^- in irrigation water.
- Immobilization of Zn following large applications of P fertilizer (P-induced Zn deficiency).
- High P content in irrigation water (only in areas with polluted water).
- Large applications of organic manures and crop residues.
- Excessive liming.
- Depressed Zn uptake by crops because of an increase in the availability of Fe, Ca, Mg, Cu, Mn, and P after flooding.

Soils that are particularly prone to Zn deficiency include leached, old acid-sulfate, sodic, saline-neutral, calcareous, peat, sandy, highly weathered, acid, and coarse-textured soils (Doberman and Fairhurst, 2000). The low availability of Zn in calcareous soils is not mainly due to the adsorption of Zn to clay or $CaCO_3$, rather than due to the formation of sparingly soluble $Zn(OH)_2$ or $ZnCO_3$ (Trehan and Sekhon, 1977; Marschner, 2012). This type of deficiency in calcareous soils can be corrected by applying inorganic Zn salts readily (Cakmak *et al.*, 1996; Marschner, 2012). Soils with high available P and Si status are also prone to Zn deficiency. Deficiency of Zn also occurs in intensively cropped soils with large application of N, P, and K fertilizers (which do not contain Zn), and soils where triple-rice crop systems is practiced. Islam *et al.* (1992) reported that the reasons behind Zn deficiency in the soils of Bangladesh may be high soil pH, presence of lime, soil submergence, and interaction with phosphate ion.

2.10.1 Reduced availability of Zinc in flooded soils

Flooding causes many changes in the soil chemistry that affect the availability of Zn (Ponnamperuma, 1972; Bunquin *et al.*, 2017). In submerged soils, primary redox induced changes involving sulfide, amorphous Fe and Mn-(hydr)oxides, organic matter, pH and solution bicarbonate strongly control the availability of Zn (Neue and Mamaril, 1984; Du Laing *et al.*, 2009; Bunquin *et al.*, 2017). For instance, sulfides decrease the mobility of trace metals like Zn, Fe, Cd and Cu by forming insoluble sulfide precipitates upon flooding (Du Laing *et al.*, 2009; Bunquin *et al.*, 2017). Similarly, Fe and Mn-(hydr)oxides provide adsorption sites for trace metals and can reduce their availability. Formation of insoluble Zn-compounds, e.g., franklinite ($ZnFe_2O_4$), sphalerite (ZnS), $ZnCO_3$ (due to high partial pressure of CO_2 from the decomposing organic matter), Zn-phosphate, $Zn(OH)_2$, adsorption of soluble Zn^{2+} by oxides, hydrous oxides, organic matter, carbonates, sulphates, clay minerals may decrease the availability of Zn in the submerged soils (Sajwan and Lindsay, 1988; Mandal *et al.*, 1997; Wissuwa *et al.*, 2008; Alloway, 2009).

On the other hand, soil organic matter safeguards Zn and trace metals from adsorption by complexing them with soluble humic and fulvic acids, thus increasing their mobility in soil (Bunquin *et al.*, 2017). However, Bunquin *et al.* (2017) reported that Zn solubility was maintained in the flooded soils during the reduced phase which could be due to competition between Fe and Zn for precipitation with sulfide.

Zinc acts as a co-factor of alcohol dehydrogenase (ADH), an enzyme that is responsible for anaerobic metabolic activity in flooded rice plants (Moore Jr and Patrick Jr, 1988; Fageria, 2009). The activity of ADH in the roots of rice seedling increases markedly after flooding compared with rice seedlings that are not flooded. According to Moore Jr and Patrick Jr (1988), addition of Zn substantially increases ADH activities in the roots of rice plants. They observed that, when Zn is deficient, metabolic activities of rice roots decrease due to decreased activity of ADH and, in turn, the ability of the rice seedling to tolerate anaerobic conditions declines (Moore Jr and Patrick Jr, 1988; Fageria, 2009). This is why the deficiency symptoms of Zn in rice plants appears after flooding and the removal of flood water allows rice seedlings to resume aerobic respiration (Moore Jr and Patrick Jr, 1988; Wilson Jr *et al.*, 2001).

Another factor for lower Zn availability in flooded soils is the changes in pH. Under flooded conditions, Zn activity decreases with the increase in soil pH (Fairhurst *et al.*, 2007). Zinc deficiency in rice was formerly recognized as ‘‘alkali disease’’ since it occurred more in sodic soils (Alloway, 2009). Johnson-Beebout *et al.* (2009) reported that flooding of soil brings about a decline in availability of Zn due to changes in soil pH and the formation of insoluble Zn compounds.

Apparently half of the total paddy rice land may have Zn deficiency to some extent (Scharpenseel *et al.*, 1983). Usually, lowland rice cultivation takes place on Gleysols and soils that have been converted to gleys by the construction of paddy fields with ponded water (Alloway, 2009). Some of the soils are both gleyed and calcareous thus the availability of Zn is affected by a combination of factors like soil pH, redox conditions, release of P from the oxides and sorption of Zn on calcite (Sims and Patrick Jr, 1978; Sims, 1986; Sajwan and Lindsay, 1988; Alloway, 2009).

Zinc deficiency in flooded soils is also attributed to a high concentration of bicarbonate, since it inhibits the uptake and transport of Zn in the plants from roots to shoots in Zn-efficient varieties (Marschner, 1993; Marschner, 2012). High concentrations of bicarbonate results in accumulation of organic acids in root cells which inhibit root growth in lowland rice (Doberman and Fairhurst, 2000). Yang *et al.* (1994) reported that Zn deficiency symptoms occurring in rice in early growth stage are linked to high bicarbonate concentrations in soil when reducing conditions are at their peak. Hajiboland *et al.* (2005) showed that high bicarbonate concentrations in the soil solution increased the growth of fine roots in Zn-efficient rice genotypes, but inhibited root growth in Zn-inefficient genotypes.

2.11 FERTILIZER TRIAL AND RESPONSE STUDY INVOLVING ZINC

Essentiality of Zn in plant nutrient can be tested by the field studies showing significant positive response of the tested crops to Zn application. The response of crops to micronutrient fertilization has been reviewed by Takkar and Randhawa (1978). According to Marschner (1993), plant species differ in their sensitivity to Zn deficiency, with maize and rice being more sensitive than rye, oats, or pea. A brief review of crop response to added Zn is given in the following sections.

2.11.1 Response of rice to zinc application

Çakmak *et al.* (1999a) stated that cereal crops are generally more prone to Zn deficiency than legumes causing substantial reduction in yield and nutrition. The occurrence of Zn deficiency is greater in rice than other crops, with more than half of the crops worldwide being prone to Zn stresses (Doberman and Fairhurst, 2000; Fageria *et al.*, 2002; Quijano-Guerta *et al.*, 2002). Thus, In Asia, Zn deficiency is considered as one of the major nutritional constraints limiting irrigated rice production (Quijano-Guerta *et al.*, 2002; Alloway, 2009). Zinc deficiency and significant response of rice to Zn under flooded condition have been reported earlier (Naik and Das, 2007; Fageria *et al.*, 2011). In Bangladesh, significant response of rice to Zn application has also been reported (Bhuiya *et al.*, 1981; Moslehuddin *et al.*, 1997; Hossain *et al.*, 2008). Saha *et al.* (2013) found higher response of local rice varieties followed by hybrid, aromatic and HYV rice to Zn at different levels of application. Concentration of grain Zn was also higher in aromatic rice. In calcareous soils of Ganges River Floodplain, rice responded to Zn application when the soils contain less than 0.83 mg/kg DTPA extractable Zn (Rahman *et al.*, 2007). Deb (1986) recommended application of 5 kg Zn/ha for rice in Zn deficient soils of Bangladesh. According to Slaton *et al.* (2005), application of Zn significantly increased rice grain yield in four field trials with different Zn sources and application time. On the contrary, there are reports of no response of rice to Zn application (Fageria, 2001).

2.11.2 Zinc deficiency in wheat

Similar to rice, significant response of wheat to Zn application has been reported in numerous reports. Kalayci *et al.* (1999) reported significant yield increase due to Zn fertilization in 40 wheat cultivars in Turkey. They reported that the yield response varied significantly between the cultivars with some being more efficient under low Zn conditions. Zou *et al.* (2012) conducted a response study in 23 locations of seven countries of the world over three years and observed that significant increase in grain yield in response to Zn fertilization occurred only at locations in Pakistan. However, like rice plant, there is report of no response of wheat to Zn application (Curtin *et al.*, 2008).

2.11.3. Effect of zinc on jute

There are reports of both positive response and non-response of jute to Zn addition. Maitra *et al.* (2000) reported that the effect of Zn interaction on jute fiber and wood did not show any significant results. According to Ahmed and Majlis (1983) there was 6.4% to 11% increase in plant height and 18% to 21% increase in fiber yield in Zn added plot over no Zn addition. On the contrary, jute leaf concentrations of N, P, K and S were not noticeably changed due to various treatments including Zn (Ali and Razzaque, 1986). The effect of additions of K, S and Zn fertilizers was not significant in any of the experimental sites of Ali and Razzaque (1986).

2.12 RESIDUAL EFFECT OF APPLIED ZINC

Most of the applied Zn in one crop cannot be fully utilized by the stranding crop and remains in the soil. Deb *et al.* (1986) found that 1 - 2% of the applied Zn was utilized by the current rice crop while 0.5 - 1.5% residual Zn remained for the succeeding crop. According to Brennan (2005), only 7% of the applied Zn had been removed by the harvested grains over the subsequent 14 years. However, in intensive cropping systems such as rice-wheat rotations, application of Zn at higher rates or more frequent applications is necessary to maintain adequate supply, since the rate of removal by the crops per year may be higher (Brennan, 2005; Bell and Dell, 2008).

2.13 BORON IN SOIL-PLANT SYSTEM

2.13.1 Boron in parent rocks

Boron (B) was first recognized essential element for plants in the early twentieth century (Gupta, 1980). The work of Warington (1923) in England confirmed the B requirement for a variety of crops (Gupta, 1980). Later the works of Sommer and Lipman (1926) established the essentiality of B in plants.

Boron ranks 37th in abundance of the elements in the earth's crust (Adriano, 2001). The average concentration of B in earth crust is 50 mg/kg and its concentration ranges from 5-10 mg/kg in rocks (Shorrocks, 1997; Shuman, 2005). The distribution of B among the common rock types is presented in Table 2.3.

Table. 2.3 Distribution of B in common rocks (Krauskopf, 1972; Keren, 1996).

Rock class and type		Content (mg/kg)
Igneous	Granite	15
	Basalt	5
Sedimentary	Limestone	20
	Sandstone	35
	Shale	100
Soils		7-80

Soils developed from marine clays and shales generally have abundant B since its compounds are dissolved in sea water (Adriano, 2001). Aubert and Pinta (1980) stated that as high as 500 mg B/kg or more can be found in sedimentary rocks of marine origin. Marine clays contain more B than lacustrine or floodplain clays.

2.13.2 Boron in minerals

In nature, B is found as a constituent of borax ($Na_2B_4O_7.10H_2O$), kernite ($Na_2B_4O_7. 4H_2O$), colemanite ($Ca_2B_6O_{11}.5H_20$), ulexite ($NaCaB_5O_9.8H_2O$), tourmaline, and axinite (Adriano, 2001). Krauskopf (1972) divided soil B minerals as hydrous, anhydrous and complex borosilicates as shown in Table 2.4.

Table 2.4 Common boron containing minerals in soil (Krauskopf, 1972).

Mineral class	**Subclass**	**Chemical formula**
Hydrous borates	Borax	$Na_2B_4O_7.10H_2O$
	Kernite	$Na_2B_4O_7.4H_2O$
	Colemanite	$Ca_2B_6O_{11}.5H_2O$
	Ulexite	$NaCaB_5O_9.8H_2O$
Anhydrous borates	Ludwigite	Mg_2FeBO_5
	Kotoite	$Mg_3(BO_3)_2$
Complex borosilicates	Tourmaline	$Na(Mg,Fe, Mn)_3Al_6Si_6O_{18}(BO_3)(OH,F)_4$
	Axinite	$(Ca,Mn,Fe)_3Al_2BO_3Si_4O_{12}(OH)$

Tourmaline is the most prominent B containing mineral in most of the well-drained soils developed acid rocks and metamorphic sediments (FAO, 1983; Gupta, 2007). It is a complex flourine containing borosilicate, as Ca and Mg borates, as complexes with Fe and Al, and in association with organic matter (Stevenson, 1986; Keren, 1996). Tourmaline is very insoluble and resistant to weathering. It contains about 3-4% B and is not considered as a good source of plant B (Adriano, 2001; Gupta, 2007). Boron may be entrapped in the clay lattice by substituting for Al^{3+} and/or Si^{4+} ions. According to Goldberg (1993), phyllosilicate clay minerals contain substantially higher B than other minerals. Among them, illite can have 100 to 2000 mg B/kg followed by muscovite, montmorillonite, kaolinite, chlorite and biotite in decreasing order (Goldberg, 1993).

2.13.3 Total boron in soils

Most of the total B in soils is found within the crystal structures of minerals (such as tourmaline) ranging from 7 to 80 mg B/kg soil (Krauskopf, 1972; Keren, 1996). The ranges of total B in the world soils are wide. Ranges from 1 to 467 mg B/kg have been reported, although 2 to 100 mg B/kg is considered as common range with the mean value being 30 mg/kg (Kabata-Pendias and Pendias, 2001; Gupta, 2007). Borkakati and Takkar (1996) reported 8 to 18 mg of total B/kg in Indian Inceptisols and Alfisols. Such variation was attributed to the types of parent rock and the soil under diverse geographical and climatic zones. Soils generated from marine sediments are usually high in B (Gupta, 2007). In the soils derived from igneous and sedimentary rocks in the USA, values between 14 and 40 mg of total B/kg were observed with the highest values occurred in arid saline soils (Adriano, 2001). Fine textured humid soils had 30 to 60 mg total B/kg whereas the range for sandy soils was as low as 2-6 mg/kg B (Adriano, 2001). According to Kot (2015), B concentration in normal soils varied approximately in the range of 10 to 100 mg/kg.

The soils of China contain higher total B (average 68 mg/kg) than that of other countries (Adriano, 2001). Low total B content is observed in soils originated from acid igneous rocks, freshwater sedimentary deposits, and in coarse-textured soils low in organic matter. Domingo and Kyuma (1983) studied the micronutrient content of 482 Asian paddy soils and reported that the highest content of total B was found in the Himalayan region where soils were of marine sediment origin. The mean total B content of tropical Asian paddy soils was 96 mg/kg. Their study showed that the Bangladesh soils contained 25 to 104 mg/kg total B, with a mean of 68 mg/kg. Hassan (1999) found that the mean total B content of 30 soils from all over Bangladesh was 24 mg/kg. Similar to Zn, soil total B was also found to be higher in clay fractions than either in silt or sand fractions in Bangladesh (Hassan, 1999).

2.13.4 Plant available boron in soil

The plant available form of B comprises only a trace of the total soil B, usually less than 5% (Keren, 1996). In agricultural soils, available B varies from 0.5 to 5 mg/kg as measured by various extraction methods (Gupta, 2007). Arid soils generally show higher available B levels compared to temperate or humid regions (Aubert and Pinta, 1980).

Domingo and Kyuma (1984) observed up to 4 mg/kg of available B in a study consisting of 482 Asian paddy soils with a mean of 0.37 mg B/kg. Although they obtained as much as 4 mg/kg B, the maximum occurrence (40%) of B was in the range of 0.16 to 0.32 mg/kg.

The available B content of the major soil types in Bangladesh ranged from 0.1 to 1.9 mg/kg soil (Ahmed and Hossain, 1997). Ahmed and Hossain (1997) reported that non-calcareous grey floodplain soil (Typic Fluvaquent), Terrace soil (Typic Haplaquept) and Hill soil (Lithic Udorthent), which are the principal light textured acid soils generally contained low levels of available B (0.1-0.3 mg/kg) in Bangladesh. Domingo and Kyuma (1984) observed that the average concentration of soluble B in Bangladesh soils was less than 1 mg/kg.

2.14 METHODS OF EXTRACTION OF AVAILABLE BORON FROM SOIL

The hot-water-extraction (HWE) method developed by Berger and Truog (1939) was the first widely accepted method for extracting plant-available B and is still the most popular (Gupta, 2007). However, there are some disadvantages of the method such as difficulty in standardization, time consumption and tedious for routine usage (Sah and Brown, 1997). Several modifications have been made in the procedure to improve precision and efficiency in analysis (Cartwright *et al.*, 1983; Kaplan *et al.*, 1990; Gupta, 1993; Keren, 1996). Parker and Gardner (1981) modified the HWE method by replacing hot water with dilute $CaCl_2$, to lessen the turbidity in filtrates without any significant variation in extractable B (Jeffrey and McCallum, 1988; Sonon *et al.*, 2014). Other major modifications in HWE method include variation in the extraction and cooling times. For example, Odom (1980) extended the boiling time from 5 to 10 minutes to allow the extractable B to reach a steady state. Likewise, Gupta (1967) suggested not to extend the cooling period over 10 minutes to avoid possible re-fixation of B. Hot water soluble B is usually considered as the best index of plant availability of B since its adoption by Berger and Troug in 1939 (Sims and Johnson, 1991; Adriano, 2001). This procedure has been found to be a useful index of plant responses to B fertilization in deficient soils (Singh and Sinha, 1976; Cartwright *et al.*, 1983).

2.14.1 Determination of available Boron

Once extracted from the soil, B can be determined by several methods using reagents such as carmine (Hatcher and Wilcox, 1950), curcumin (Dible *et al.*, 1954; Johnson and Ulrich, 1959), azomethine-H (Wolf, 1971), and most recently by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Keren, 1996). The use of azomethine-H is an preferred to the use of carmine, quinalizarin, and curcumin, since the procedure does not require the use of a concentrated acid (Gupta, 1993). In a comparative evaluation of azomethin H, curcumin and carminic acid methods, the azomethine H method underwent the least interferences and was the most sensitive (Sah and Brown, 1997). Azomethine H method is also used for plant and fertilizer B determination.

To achieve a clear solution for colorimetric B detection by the azomethine-H method, Gupta (1979) suggested using activated charcoal to eliminate the turbidity or yellowish color usually found in soil extracts containing high organic matter. Using excess charcoal, however, can lead to a loss of B from solution and a low value for extractable B (Gupta, 1979). Gross *et al.* (2008) suggested a modification of the standard azomethine-H method, in which the solution is pre-digested with potassium persulfate to overcome the color interference in wastewater treated soils.

2.15 FRACTIONS OF SOIL BORON

Boron can exist in a number of chemical fractions differing in their solubility and reactivity in soil. The forms include readily soluble, non-specifically adsorbed (exchangeable), specifically adsorbed, amorphous and crystalline oxide bound, organically bound and residual or mineral lattice bound fractions (Jin *et al.*, 1987; Hou *et al.*, 1994; Hou *et al.*, 1996; Padbhushan and Kumar, 2017). These fractions differ remarkably in solubility and chemical behaviour and can be transformed to other B forms as influenced by several soil factors such as soil pH, OM, types of clay minerals, oxides and carbonates and soil management practices. (Goldberg and Glaubig, 1985; Jin *et al.*, 1987; Gu and Lowe, 1990; Goldberg and Forster, 1991; Goldberg, 1993; Hou *et al.*, 1994; Keren, 1996; Goldberg, 1997; Su and Suarez, 1997; Padbhushan and Kumar, 2017). According to Jin *et al.* (1987), water soluble and non-specifically (exchangeable) B are readily available to plants and act as ‘intensity factor’, while specifically adsorbed, oxide bound, organically and residual forms are called ‘capacity factor’ that determine the B supplying power of the soil.

Several sequential extraction schemes were applied to separate B fractions (Jin *et al.*, 1987; Hou *et al.*, 1996; Gupta, 2007; Ren *et al.*, 2009; Ranjbar and Jalali, 2013). A short description of the various soil B fractions is presented in the following sections.

2.15.1 Water soluble boron

This form of B consists of the free ions in soil solution regarded as a plant-response indicator in soil and is necessary to be maintained for plant nutrition (Keren and Bingham, 1985; Hou *et al.*, 1996). Solution B is maintained by the equilibrium among different soil B fractions (Ren *et al.*, 2014). The readily soluble B comprises only a trace (1- 2%) of the total B (Jin *et al.*, 1987). However, soils in arid and semiarid regions may contain 5 to 16% of total B as water-soluble form (Aubert and Pinta, 1980).

2.15.2 Non-specifically adsorbed boron (Exchangeable B)

Adsorbed B represents the fraction that is weakly bound to the surfaces of variable charged soil components and is in equilibrium with the solution B (Hou *et al.*, 1996). Under normal conditions, field soils contain only a small amount of soluble and adsorbed B. Exchangeable and non-specifically adsorbed ions are commonly grouped as one pool to be extracted together (Shuman, 1991).

2.15.3 Specifically adsorbed B

This form of B is strongly adsorbed on the specific sites in surfaces of clays, the oxides and (oxy)hydroxides of Fe, Mn or Al, organic complexes and carbonate minerals by covalent bonds (Jin *et al.*, 1987; McBride, 1989; Hou *et al.*, 1996; Goldberg, 1997). Specifically adsorbed B comprises 0·01 - 0·61% of total soil B (Xu *et al.*, 2001; Padbhushan and Kumar, 2015).

2.15.4 Oxide (Fe/Al/Mn) bound B

This form of B is a part of the structure of Fe, Al and Mn oxides and oxyhydroxides through isomorphous substitution (Hou *et al.*, 1996; Padbhushan and Kumar, 2015). Jenne (1968) asserted that sorption and desorption from oxide surfaces controlled the amounts of metals in solution. This pool constitutes less than 3% of total boron (Hou *et al.*, 1994).

2.15.5 Organically bound B

This form of B is complexed or chelated by several forms of organic materials, such as humic substances, organic coatings on mineral particles (Hou *et al.*, 1996). Organic matter adsorbs B and acts as a reservoir to replenish solution B (Goldberg, 1997). Boron in organic matter is primarily released through the actions of microbes (Kot, 2015). Hou et al. (1994) reported that B in organic fraction ranged from 0 to 22.97 mg B/kg soil, while Lambert *et al.* (1997) found 15.0 to 60.8 mg/kg organic B in soil.

2.15.6 Residual B

This form of B is associated with the structures of primary (e.g., colemanite) and secondary silicate minerals (e.g. tourmaline) (Jin *et al.*, 1987; Hou *et al.*, 1996). The major portion of soil B exists in the residual form as reported earlier by many researchers (Jin *et al.*, 1987; Hou *et al.*, 1994; Olykan *et al.*, 1995; Xu *et al.*, 2001; Raza *et al.*, 2002).

2.16 EXTRACTION SCHEME FOR VARIOUS SOIL BORON FRACTOINS

Most of the extraction schemes for trace elements in soil are modified from the scheme of Tessier *et al.* (1979). The widely cited fractionation schemes of soil B are those proposed by Jin *et al*. (1987) and Hou *et al.* (1996) that attempted to differentiate soil B into various fractions. The method of Hou *et al*. (1996) fractionated B into readily soluble (0.01 M $CaCl_2$ extractable), specifically adsorbed (0.05 M KH_2PO_4 extractable), oxide bound (0.2 M acidic NH_4-oxalate extractable), organically bound (0.02 M HNO_3-30% H_2O_2 extractable) and residual forms (HNO_3-HF-HCl extractable). Earlier Jin *et al*. (1987) separated soil B into soil solution B (water extractable), non-specifically adsorbed ($CaCl_2$ extractable), leachable B (mannitol extractable), specifically adsorbed B (Mn-oxide) (Acidified NH_2OH-HCl extractable), non-crystalline and crystalline Fe and Al oxide B (extracted by NH_4-oxalate) and residual B. Modifications to the extraction schemes have been applied by several workers to adjust with the soil conditions and ease of determination (Datta *et al.*, 2002; Gross *et al.*, 2008; Ranjbar and Jalali, 2013; Ren *et al.*, 2014). A brief review of the extraction methods for various B fractions follows:

2.16.1 Fraction 1: Readily soluble B

The widely used extractant to dissolve soluble trace elements is $CaCl_2$. Extraction of soil with a 0.01 M $CaCl_2$ solution removes solution B and non-specifically adsorbed B on clay surfaces by anion exchange or mass reaction mechanism (Parker and Gardner, 1981; Jin *et al.*, 1987; Hou *et al.*, 1994).

2.16.2 Fraction 2: Specifically adsorbed B

This fraction is extracted by 0.05 M potassium phosphate (KH_2PO_4) solution. According to Barrow (1989), since phosphate reduces adsorption of B over a large pH range in soils, it could be effective in desorbing B from hydrous oxides through ligand exchange reactions. The KH_2PO_4 solution was thus preferred for the extraction of specifically adsorbed B (Raza *et al.*, 2002). Potassium phosphate was first introduced by Chao and Sanzolone (1989) as an extractant for selenium. Some researchers used mannitol to extract leachable B that includes B in soil solution, nonspecifically and specifically adsorbed forms (Rhoades *et al.*, 1970; Keren, 1996).

2.16.3 Fraction 3: Oxide bound B

The oxide bound B is extracted by 0.2 M acidic NH_4-oxalate adjusted to pH 3.0. Acidic NH_4-oxalate can solubilize non-crystalline, and some crystalline, oxyhydroxides of Fe and Al from soils (Loeppert and Inskeep, 1996). This extractant removes tightly bound B at the mineral surface, and B that has isomorphously replaced Al^{3+} or Fe^{3+} in clay lattice (Hou *et al.*, 1994; Jin *et al.*, 1987).

2.16.4 Fraction 4: Organically bound B

This fraction is extracted by 0.02 M HNO_3 and 30% H_2O_2 as used by Tessier *et al.* (1979) to degrade organically bound forms (Hou *et al.*, 1994). After extraction, organic B is usually determined in Inductively Coupled Plasma spectroscopy. However, modified methods were applied by Datta *et al.* (2002) to determine the extracted organic B by colorimetry.

2.16.5 Fraction 5: Residual B fraction

After the removal of first four fractions, B exists in the primary and secondary mineral structures (Hou *et al.*, 1996; Jin *et al.*, 1987). A mixed acid solution including HNO_3, HCl and HF is used to extract the residual B. Hydrofluoric acid is used to dissolve silicate structures (Hou *et al.*, 1994). Deduction of the sum of all the extracted fractions from the total B is also performed for estimation of the residual B. Total B concentration in soil is usually determined by sodium carbonate fusion method (Keren, 1996).

2.17 DISTRIBUTION OF SOIL BORON FRACTIONS

Boron fractionation was studied in relation to its availability to corn using 14 soils by Jin *et al.* (1987). They observed that up to 0.34% of the total B existed in the water-soluble form, 0.0 to 0.23% was nonspecifically adsorbed (exchangeable), 0.05 to 0.30% was specifically adsorbed, 0.23 to 1.52% was in the Mn oxide form, 2.8 to 34.4% was in the amorphous Fe-oxide form, 17.5 to 73.9% was in the crystalline Fe oxide form, and 2.4 to 79.2% was in the residual fraction. Jin *et al.* (1987) found that the water-soluble, nonspecifically adsorbed (exchangeable), specifically adsorbed, and Mn-oxide fractions were available to corn, whereas unavailable B resided in the amorphous and crystalline Fe oxide forms. Likewise, Raza *et al.* (2002) found that the mean percentages of total B in various fractions were 1.02% as the readily soluble, 0.69% as specifically adsorbed, 0.40% as oxide bound and 0.86% in the organically bound form.

2.18 ADSORPTION OF BORON TO DIFFERENT SOIL COMPONENTS

Adsorption of solution B to various soil components is one of the major factors controlling B availability in soil. The principal B adsorbing surfaces in soils are oxides, clay minerals, calcite, and organic matter (Goldberg, 1997). The adsorbed B may buffer fluctuations in solution B concentration (Keren, 1996). Illite is the most reactive clay mineral in adsorbing B whereas, kaolinite is the least reactive (Keren, 1996). Soil properties that affect B adsorption include soil pH, surface area and contents of clay, organic matter, and oxyhydroxides (Gupta, 1979; Keren and Bingham, 1985; Jin *et al.*, 1988). Boron forms strong inner-sphere complexes on amorphous iron oxide and allophane (Goldberg *et al.*, 1993). Since B is largely adsorbed by the clay minerals, fine textured soil contain more B than the coarse textured soils (Kot, 2015). Yermiyahu *et al.* (1988) reported higher sorption of B on soil organic matter than on clay. Hence, B deficiency has been observed in soils with high organic matter contents.

2.19 SOIL FACTORS CONTROLLING BORON AVAILABILITY

2.19.1 Soil pH

Increases in soil pH, make B less available to plants. Therefore, application of lime to acid soils can result in B deficiency in plants due to increased B adsorption (Sherrell, 1983; Goldberg, 1997; Gupta, 2007; Kot, 2015). Soluble B content in soils was found to highly significantly correlate with solution pH (Berger and Truog, 1945; Elrashidi and O'connor, 1982). Thus, uptake of B by the plants at identical water soluble B was found to be higher at low soil solution pH (Wear and Patterson, 1962).

2.19.2 Soil texture

Boron concentration was reported to be higher in clay and loam soils than in sandy soils (Gupta, 1993). Hence, coarse textured soils of humid regions may have B deficiency due to loss of B through leaching (Shuman, 2005). Atique-ur-Rehman *et al.* (2018) stated that rice cultivated in coarse-textured soils faces B deficiency due to high leaching losses. On the other hand, the uptake of B by plants was found to be higher in soils with less clay than in soils with higher clay content (Keren, 1996). Fine-textured soils retain B for longer periods than do coarse-textured soils due to the higher adsorption affinity of the former (Gupta, 1968; Goldberg and Glaubig, 1986; Nicholaichuk *et al.*, 1988).

2.19.3 Soil organic matter

Organic matter is an important soil constituent affecting the availability of B (Goldberg, 1997; Kabata-Pendias and Pendias, 2001). There are reports that native soil B and hot water soluble B were highly significantly correlated with organic carbon content (Berger and Truog, 1945; Elrashidi and O'connor, 1982). Soil organic matter adsorbs more B than mineral soil constituents (Yermiyahu *et al.*, 1988; Gu and Lowe, 1990). The adsorption of B in mineral soil increased with increasing additions of composted organic matter (Yermiyahu *et al.*, 1995).

2.19.3 Soil moisture

Lack of soil moisture has been reported to reduce the mobility of B and restricts its uptake by plant roots (Goldberg, 1997; Kot, 2015). The effect of drying was found to become more pronounced with increasing additions of B (Goldberg, 1997).

2.19.4 Submerged soil and B

The concentration of B in the soil solution is believed to remain constant following soil submergence (Ponnamperuma, 1975). Adsorption of B by the oxides of Fe and Al is an important mechanism in controlling B solubility in flooded soils (Sims and Bingham, 1968; Fageria, 2014).

2.20 TRANSFORMATION AND RE-DISTRIBUTION OF BORON IN SOIL

Transformation occurs among different B fractions when B is added to the soil. Boron distribution and its transformations vary due to difference in soil types, use of soil amendments, and management practices, which affect the availability of B to plants (Xu *et al.*, 2001). Ren *et al.* (2014) reported transformation of Fe-oxide bound B to exchangeable B due to addition of B containing Goethite in soil. Similarly, they observed an increase in easily soluble B due to addition of oxide B.

2.21 CROP RESPONSE TO BORON APPLICATION

Boron deficiency in plants is more widespread than that of other micronutrients (Keren, 1996). Boron deficiency has been documented in at least 80 countries on 132 plant species over a period of 70 years (Shorrocks, 1997; Atique-ur-Rehman *et al.*, 2018). The requirement of boron is generally larger in dicot plants than in monocot plants (Srivastava and Gupta, 1996). Yield responses in wheat to B applications have been reported in many countries including Bangladesh, Brazil, China, India, Pakistan, USA, and Russia (Shorrocks, 1997; Rerkasem and Jamjod, 2004; Jahiruddin, 2015). The cereal growing areas of India, Nepal and Bangladesh is the world’s largest known area of B-deficiency in wheat (Rerkasem and Jamjod, 2004). Forage legumes are more prone to B deficiency than grasses and cereals which are the least responsive to B (Gupta, 2007).

In rice-growing soils, B deficiency has been reported to cause substantial yield loss (Rashid *et al.*, 2004; Atique-ur-Rehman *et al.*, 2018). About 35% of the 2.6 million ha rice area in Pakistan is under B deficiency (Atique-ur-Rehman *et al.*, 2018). The reproductive phase in wheat is the most sensitive to B deficiency resulting in male sterility (Rerkasem and Jamjod, 2004). This causes a substantial reduction in the numbers of grain set and, thus, in grain yield.

Under low rainfall conditions, B cannot be leached sufficiently and may accumulate to a toxic level for the plants (Keren, 1996; Reid, 2007). This is very often found in arid and semiarid regions with high groundwater B, where toxic B levels reduce crop yields (Keren, 1996; Kot, 2015).

2.22 CRITICAL LIMIT OF BORON IN SOIL AND PLANT

The critical limit of B depends on the crop species and its growing environment. In Bangladesh soils, 0.2 mg/kg B is considered as critical limit for agricultural crops (BARC, 2012). According to Adriano (1986), B deficiency occurs in plants when the concentration in leaves is <15 mg/kg while the sufficiency range is between 20 and 100 mg/kg. The critical level of B deficiency in rice flag leaf is 6 mg/kg and that of wheat shoot is 4 to 6 mg/kg (Atique-ur-Rehman *et al.*, 2018). Optimum leaf tissue B of rice has been reported to be 6-15 mg/kg while critical level for B deficiency is <3 mg/kg (Doberman and Fairhurst, 2000). The toxic level of rice tissue B is 100 mg/kg at maturity. Gupta (2007) mentioned the toxicity level of bean at B conc. > 160 mg/kg of 43 days old plant. The range between deficiency and toxicity of B in plants is quite narrow, being in the range of 0.028 to 0.093 mmol/l solution B for susceptible crops and 0.37 to 1.39 mmol/l for tolerant crops (Goldberg, 1997; Zhu *et al.*, 2007).

2.23 BORON IN IRRIGATION WATER

Kot (2015) stated that the threshold B concentration for irrigation water which is the maximum permissible concentration for a crop that does not reduce yield or lead to injury ranged from 0.3 mg B/l for sensitive crops to as high as 2.0 mg B/l for tolerant crops.

2.24 TOXICITY OF BORON IN PLANTS

Boron toxicity occurs most frequently in soils of arid and semiarid regions (Keren, 1996). The reasons for B toxicity in these areas are high levels of B in soils and in irrigation water. When irrigation with water high in B is planned, special attention should be paid to avoid toxicity in plants. In arid and semiarid areas, B toxicity results from high levels of B in soils and a high evaporation rate together with additions of B from irrigation water (Kot, 2015).

2.25 INTERACTION BETWEEN BORON AND ZINC

Significant interaction between B and Zn has been reported in the literature. Boron uptake to toxic levels in plants may be expected in soils with a low level of available Zn and a high level of B in combination with a high P fertilization rate (Graham *et al.*, 1987). Singh *et al.* (1990) reported that Zn application appears to have created a protective mechanism in the root cell environment against excessive uptake of B, as evidenced by the reduction of B uptake in Zn treated plants. Zinc treatments partially depressed the inhibitory effect of boron on tomato growth (Gupta, 2007).Recent studies showed that applied Zn plays role in partially alleviating B toxicity by decreasing the plant B accumulation (Gupta, 2007).

2.26 RESIDUAL EFFECT OF APPLIED BORON

There are reports of residual effect of applied B on the yield of crops. Yang *et al.* (2000) reported that the application of B fertilizer at different rates in the first year showed a different residual effect on oilseed rape yield in successive years. The residual effect remained fully effective in correcting B deficiency in oilseed rape for 2 years in Inceptisols, and at least 3 years in both the Inceptisols and the Ultisol at a higher rate.

From the literature so far reviewed it is revealed that extensive studies were carried out throughout the world on the chemistry of soil Zn and B, factors affecting their availability, their fractionation and transformation into various chemical forms, and crop response to Zn and B fertilization. However, in the context of Bangladesh, the information available is still limited.

Generation of information on the transformation of Zn and B particularly in the floodplain soils, which is the major part of agricultural land of the country, will be useful in assessing the changes in the fertility status of Zn and B in these soils due to various factors. Thus, the present investigation can help improving the fertilizer recommendation as well as management of Zn and B in the soils of Bangladesh.

CHAPTER III

MATERIALS AND METHODS

Experiments was carried out in the Ganges River Floodplain soils representing Agroecological zones (AEZ) 11 and 12 having calcareousness as a general diagnostic feature. To study the distribution of zinc (Zn), boron (B) and other micronutrients namely, iron (Fe), manganese (Mn) and copper (Cu), soil samples were collected from 25 locations of each of the High (AEZ 11) and Low Ganges River Floodplain (AEZ 12). Basic information about the soil samples is presented in Appendix 1. The results of micronutrient analysis of these soils are presented in Table 4.1 of Section 4.1. In addition, soil samples were collected from other parts of the country representing three major AEZ with contrasting soil types and physiography, for comparisons of the micronutrient status as well as the fractions of Zn and B with the Ganges River Floodplain soils. These were i) Old Himalayan Piedmont Plain (AEZ 1, 0.398 mha), ii) Old Brahmaputra Floodplain (AEZ 9, 0.723 mha), and iii) Madhupur Tract (AEZ 28, 0.424 mha). Five locations from each of five AEZs were sampled to study the distributions of micronutrients. The description of the soils is discussed in section 3.10 of this chapter and the basic information is presented in Appendix 2. Based on the analystical data, field experiments were conducted in a farmer's field of Rajbari sadar upazila (AEZ 12) having low level status of soil Zn and B. Besides, laboratory incubation study and experiment on transformation of Zn and B were conducted with soils under field experiment. The objectives of the experiments were to i) study the response of wheat, jute and rice crops to applied Zn and B, ii) to study the transformation of native and applied Zn and B in the soils of field experiment, and iii) to study the transformation of Zn and B in the test soil under laboratory condition. A brief outline of the materials and methods applied during the present investigation is described in the following sections.

3.1 FIELD EXPERIMENTS

Designed field experiments were done to study the effect of Zn and B on the yield and nutrient uptake of field crops in Low Ganges River Floodplain (AEZ 12) soils during 2013 to 2015. Two separate experiments were conducted in the study with different crops. In one experiment, Wheat, Jute and Transplanted Aman (T. Aman) rice crops were tested; while in another experiment, the crops were Boro and T. Aman rice.

3.1.1 Location of the fields

The research fields were situated in Char Bagmara and Ramkantapur areas under Sadar upazila of Rajbari district under Dhaka division of Bangladesh (Fig. 3.1). The Char

Bagmara site, where Wheat-Jute-T.Aman rice (WJR) experiment was set up, lies between 23°45'18" N latitude and 89°37'21" E longitude, while the Boro-Fallow-T. Aman rice (RFR) experiment was conducted in Ramkantapur which lies between 23°45'23" N latitude and 89°37'6" E longitude. The soil series was identified by the technical personnel of Soil Resource Development Institute (SRDI), Faridpur.

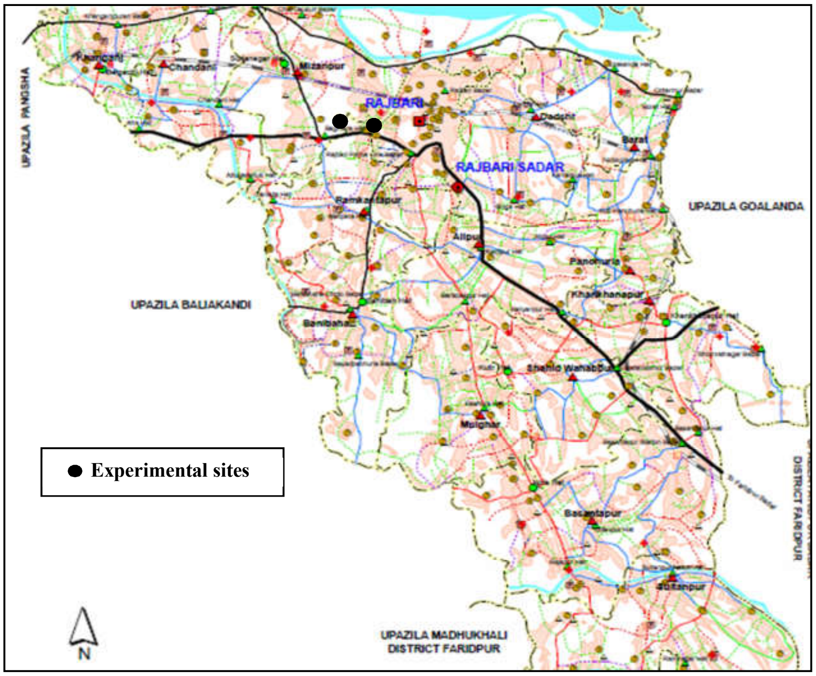


Fig 3.1 Location of the experimental site at Rajbari sadar upazila.

3.1.2 Landscape, physiography and drainage of the field

The land type of both experimental sites was medium highland. The site is situated in a region in which the landscape is characterized by broad, smooth ridges and basins with areas of irregular relief being a typical meander floodplain under Low Ganges River Floodplain physiography. The General Soil Type (GST) was Calcareous Dark Grey Floodplain soils. Tropical monsoon rains drench the landscape. The topography of the Rajbari sadar upazila can be divided into highland, medium highland and medium lowland (FAO-UNDP, 1988). The Low Ganges River Floodplain (AEZ 12) is lower-lying than High Ganges River Floodplain (AEZ 11) (FAO-UNDP, 1988). Seasonal flooding is mainly ponded rainwater or the raised water table during periods of heavy rainfall (FAO-UNDP, 1988). Ganges alluvium is calcareous when deposited, but most basin clays and some older ridge soils have been decalcified and acidified in their upper layers; lime is found only in the subsoil or substratum of such soils (Islam, 2003). Soils of the region are silt loams and silty clay loams on the ridges and silty clay loams to heavy clays on lower sites. Clay soils predominate in basins and on the middle parts of most ridges, with loamy soils (and occasionally sands) occurring mainly on ridge crests (Islam, 2003).

3.1.2.2 Agroecological Region and Subregion

The study area (Rajbari Sadar upazila) lies in the agroecological 'Subregion' 12a (Central part)' under AEZ 12, that includes a higher proportion of highland and medium highland than the other Subregion (12b-Eastern Subregion). General soil types in the Subregion 12a predominantly include Calcareous Dark Grey Floodplain soils (61%) and Calcareous Brown Floodplain soils (19%). The organic matter content is higher (2-5%) in the former GST than the latter (<1.5%) (FAO-UNDP, 1988). Calcareous Dark Grey Floodplain soils are calcareous within 125 cm from surface. Dark grey ridge soils are generally calcareous and moderately alkaline throughout the profile. Decalcification occurs in the cultivated basin soils having a neutral to strongly acid topsoil and a near-neutral subsoil over calcareous substratum at 40 - 60 cm (FAO-UNDP, 1988).

3.1.2.3 Soil Series

The soils of the experimental site belong to Ishurdi series (Typic Haplaquepts) under the order Inceptisols in the USDA Soil Taxonomy (Hussain, 1992; SRDI, 2001). The soils of Ishurdi series in the Ganges River Floodplain (AEZ 12) is poorly drained in the highland and medium highland (SRDI, 2001). The topsoil is grey clay loam while the subsoil is calcareous, brown clayey textured. There is usually a gradual decrease in clay content with depth in the Calcareous Dark Grey Floodplain soil type (Hussain, 1992). Soil reaction of the region is slightly alkaline to moderately alkaline.

3.1.2.4 Characteristics of the experimental field soil

Some basic soil properties of the experiment field are presented in Table 3.1. Based on the soil nutrient level guideline presented by (SRDI, 2001), both the field soils were slightly alkaline (pH 7.7 - 8.2), with medium level of organic matter content (Table 3.1). The concentration of available P and S of WJR soil were optimum and low, while that of RFR were very high and high, respectively. The status of exchangeable K was high (0.34 me/100 g) in the WJR soil and very high (0.47 me/100 g) in the RFR soil. Available Zn concentration was very low and available B was low in the W-J-R soil, while in the R-F-R soil the concentration of Zn was optimum and B concentration was medium.

Table 3.1 Basic properties of the soils under the two experiments, at Rajbari.

Soil parameters	Char Bagmara, Sadar, Rajbari Wheat-Jute-T. Aman rice	Ramkantapur, Sadar, Rajbari Boro-Fallow-T. Aman rice
soil pH	8.22	7.68
Organic C (%)	1.20	1.51
Total N (%)	0.13	0.16
Available P (mg/kg)	21	43
Available K (mg/kg)	0.34	0.47
Available S (mg/kg)	16	41
Available Fe (mg/kg)	15	48
Available Mn (mg/kg)	12	15
Available Zn (mg/kg)	0.44	1.52
Available Cu (mg/kg)	2.6	4.0
Available B (mg/kg)	0.26	0.41
Texture	Clay loam	Clay loam

Thus, the Char Bagmara soil was comparatively poor with regard to soil fertility as well as Zn and B status compared to Ramkantapur soil, with higher soil pH. Hence, it is expected that field crops in the W-J-R soil would show response to the application of Zn and B. However, wetland rice grown in both soils could show response to Zn application.

3.1.2.5 Cropping practice and related information of the study location

Irrigated boro rice, wheat, onion and other rabi crops e.g. pulse, mustard, linseed etc. are cultivated during Rabi season in the area, while, jute, B. Aman and transplanted Aman rice are the major crops in the Kharif seasons (FAO-UNDP, 1988). Sugarcane is also cultivated in some areas. Most of the cultivable land of Rajbari sadar upazila is double cropped area (Mostafizur *et al.*, 2017). The major cropping pattern of the upazila is Boro-Fallow-Fallow (15% of net cropped area, NCA). The other popular cropping patterns of Rajbari sadar upazila include wheat-jute-T.Aman rice (9.3% of NCA) and Boro-Fallow-T.Aman rice (7.5% of NCA) (Mostafizur *et al.*, 2017). Based on the existing cropping patterns of the upazila, wheat-jute-T.Aman and Boro-fallow-T.Aman rice patterns were selected for this study.

3.1.2.6 Cropping history of the experiment field

Before setting of the experiment, the field in Char Bagmara site was cultivated to wheat, jute and T. Aman rice crops, while that of Ramkantapur site was cropped to Boro and T. Aman rice, respectively for several years. Farmers used to apply major nutrients (N, P and K) and organic manures to the crops at rates estimated by their own experience about soil fertility and crop yield.

3.1.3 EXPERIMENTAL DETAILS

3.1.3.1 Crops and variety

As mentioned earlier, two cropping patterns were followed in the present study. The crops, their seasons and varieties were as follows:

Expt.	Site location	Rabi	Kharif-1	Kharif-2
1	Char Bagmara	Wheat (BARI Gom 26)	Jute: Tossa (JRO-524)	Transplanted Aman rice (BRRI dhan49)
2	Ramkantapur	Boro rice (BRRI dhan29)	Fallow	Transplanted Aman rice (BRRI dhan49)

3.1.3.2 Land preparation

Land was prepared well ahead of seed sowing in respective site with proper management implements. Ploughing, leveling, bund construction and other operations were done for the fruitful accomplishment of the experiment. Layout of the experiment layout was done according to the statistical design of the experiment. The size of the individual plots (sub plot) was 3m x 5m. The plots were separated by 30 cm bunds. Drains were constructed in between the blocks to facilitate irrigation and drainage of water.

3.1.3.3 Treatment details and layout

Experiment was set up following randomized complete block design (RCBD) with three replications. The effects of Zn and B application were tested either i) on the 1st crop of the pattern, or ii) two subsequent or alternate crops (1st and 2nd or 1st and 3rd) and iii) all the three crops. The field was sub-divided into three blocks (as three replications) having ten sub-plots in each block. The layout was kept undisturbed until completion of 2-crop cycle. Details of the treatments are shown in Tables 3.2 and 3.3. The objective of such treatment design was to evaluate whether 1-crop or 2-crop or 3-crop application of Zn and B is required to correct their deficiency and achieve satisfactory crop yield. Four Zn doses (0, 2.0, 4.0, and 6.0 kg ha ^{1}) and three B doses (0, 1.5, and 3.0 kg ha ^{1}) were applied to the first crop of the cropping pattern, making up four selected treatment combinations: T1 (Zn_0B_0), T2 ($Zn_2B_{1.5}$), T3 ($Zn_4B_{1.5}$), and T4 (Zn_6B_3). To accommodate additional treatments for the second and third crops, T2 was split again to six sub-plots, while T3 in two sub-plots in each replication. In the second crop, two additional treatments receiving 2.0 kg Zn ha ^{1}, and 2.0 kg Zn + 1.5 kg B ha ^{1} were added under T2, while in the third crop, other four treatments were added with further application of 2.0 kg Zn ha ^{1}. Hence, the number of treatments for the first, second and third crops were 4, 6 and 10, respectively (Table 3.2). The introduction of the two new treatments of T2 in the second crop and four in the third crop were to justify the impact of direct, residual as well as the cumulative application of Zn and B on the tested crops under a particular cropping pattern.

In the second experiment involving Boro and T. Aman rice, the treatment plan was similar to the first one, except that the treatments of the second crop was omitted since the field was fallow in that season (Table 3.3).

Table 3.2 Treatment distribution in the Wheat-Jute-T.Aman rice experiment.

Wheat	Jute	T.Aman rice
T1=Zn_0B_0*	T1= Zn_0B_0	T1= Zn_0B_0
T2=$Zn_2B_{1.5}$	T2.1= Zn_0B_0	T2.1.1= Zn_0B_0
		T2.1.2= Zn_2B_0
	T2.2= Zn_2B_0	T2.2.1= Zn_0B_0
		T2.2.2= Zn_2B_0
	T2.3=$Zn_2B_{1.5}$	T2.3.1= Zn_0B_0
		T2.3.2= Zn_2B_0
T3=$Zn_4B_{1.5}$	T3=Zn_0B_0	T3.1= Zn_0B_0
		T3.2= Zn_2B_0
T4=Zn_6B_3	T4= Zn_0B_0	T4= Zn_0B_0

* subscripts denote Zn and B rate @ kg/ha.

Table 3.3 Treatment distribution in the Boro-Fallow-T.Aman rice experiment.

Boro rice	T. Aman rice
T1: Zn_0B_0	T1: Zn_0B_0
T2: $Zn_2B_{1.5}$	T2.1: Zn_0B_0
	T2.2: Zn_2B_0
T3: $Zn_4B_{1.5}$	T3.1: Zn_0B_0
	T3.2: Zn_2B_0
T4: Zn_6B_3	T4: Zn_0B_0

3.1.3.4 Fertilizer sources and application rates

Zinc and boron were added as zinc sulfate ($ZnSO_4.7H_2O$) and boric acid (H_3BO_3), respectively. The major nutrients namely, nitrogen (N), phosphorus (P), potassium (K) and sulfur (S) were applied to all the plots equally on soil test basis (STB) as recommended in Fertilizer Recommendation Guide (FRG-2012) of Bangladesh Agricultural Research Council (BARC, 2012). The sources of N, P, K and S were urea, triple super phosphate (TSP), muriate of potash (MoP) and gypsum, respectively. The rates of N, P, K and S for wheat crop were 134, 37, 20 and 20 kg/ha, respectively. For jute crop, the rates were 123, 25, 54 and 25 kg/ha for N, P, K and S, respectively. In T. Aman rice, the mentioned nutrients were applied at 100, 19, 17 and 16 kg/ha, respectively.

In the Boro rice-Fallow-T.Aman rice experiment, the rate of nutrients for Boro rice was 187, 37, 33 and 24 kg/ha of N, P, K and S, respectively, and in T. Aman rice, the rates were 100, 37, 33 and 24 kg/ha, respectively. Application of the nutrients was rationalized as per recommendation of FRG-2012 considering the application in the preceding crop(s). The sowing, transplanting at specified distance and the necessary intercultural operations of the tested crops were performed following the recommendations of Bangladesh Agricultural Research Institute (BARI, 2011) for wheat, Bangladesh Jute Research Institute for jute (BJRI, 2002) and Bangladesh Rice Research Institute (BRRI, 2013) for Boro and T. Aman rice, respectively.

The seed rate of the crops, spacing, dates of seeding and transplanting and crop cut are presented in Table 3.4. The dates of seeding and transplanting were maintained for each of the crops every year.

Table 3.4 Crop establishment information of the tested crops.

Crop	Seed rate	Date of seeding	Date of transplanting	Spacing	Date of harvest
Wheat (BARI Gom 26)	120 kg/ha	Last week of November	Broadcasted		110 DAS*
Jute (JRO-524)	8 kg/ha	1st week of April	Broadcasted		120 DAS
T. Aman rice (BRRI dhan49)	80-100 g/m^2	1st week of July	25 DAS	20 X 20 cm	137 DAS
Boro rice (BRRI dhan29)	80-100 g/m^2	1st week of December	35 DAS	20 X 20 cm	158 DAS

* DAS = days after seeding. Rice planted at 2-3 seedlings/hill

3.1.3.5 Crop management

The crops were irrigated and management practice was performed as per the institutional recommendations (BJRI, 2002; BARI, 2011; BRRI, 2013). Insect and disease management, weeding and other necessary intercultural operations e.g., thinning of jute, top dress of urea and MoP fertilizers and mulching in rice and wheat, etc. were carried out as per requirement of the crop situation.

3.1.3.6 Harvesting and plant sample collection

The crops were harvested plot-wise at full maturity. For rice and wheat, crops were cut from $5m^2$ (2.5 m X 2 m) area, avoiding at least two border rows of each plot, cut at ground level, the whole plant was threshed, sun-dried and the grain weight recorded. The grain yield was adjusted at 14% moisture content and converted to t/ha. Straw yield of the sampled area was recorded after sun-dry of threshed straws for 3 days. A sub-sample was oven dried at 70°C for 48 hours for chemical analysis.

The jute plants were harvested at the early pod stage. The plants were cut at ground level, bundled and kept standing on ground to shed the leaves. After shedding of leaves, the bundles were steeped in pond water for retting. The retting process completed in 21 days after steeping. Then the fibers were extracted by stripping and washed thoroughly in water. The extracted fibers were sun-dried and weighed for fiber yield. Likewise, after stripping, the jute sticks were sun-dried and weighed to record the stick yield. Plant samples of rice and wheat (grain and straw) and stick of jute were collected at the time of harvesting for tissue analysis. Straw and stick samples were air-dried and chopped off into smaller pieces before oven drying at 70°C for 48 hours. The samples were finely ground by grinding-mill for homogenization. The processed plant samples were chemically analyzed for Zn and B concentrations following the methods described in section 3.2.

3.1.3.7 Agronomic data collection

The following agronomic data of the tested crops were recorded:

Rice and wheat: Grains (spikelet) count per spike, 1000-grain weight (g), plant height (during crop cut) (cm), grain yield (t/ha) and straw yield (t/ha).

Jute: Plant height (cm), stick yield (t/ha) and fiber yield (t/ha).

3.1.3.8 Calculation of Zn and B uptake by crops

Nutrient (Zn and B) uptake by the plants was calculated from the yield and nutrient concentration data as follows: Nutrient uptake (g/ha) for Zn and B = Zn or B concentration in plant sample (grain or straw or stick) (mg/kg) X Yield (kg/ha)/1000

3.2 SOIL AND PLANT ANALYSIS

3.2.1 Soil sampling and processing procedure

Before setting the experiments the initial soil sample was collected from W-J-R and R-F-R experimental fields. After completion of the two cropping cycle, the final crop (T. Aman rice) was harvested during 2015 and soil samples were collected from the W-J-R field, from each unit plot to a depth of 0-15 cm to study the transformation of Zn and B in the soils. Three sub-samples collected from each unit plot were composited, bagged, tagged and transported to the laboratory. Prior to laboratory analysis, the soil samples were air-dried, ground with wooden hammer and screened to pass through a 2-mm sieve. The sieved samples were preserved in plastic containers and labeled properly for laboratory analysis. In addition to soil samples, the irrigation water samples from the source were collected and preserved for B analysis. The measured concentration of B in the irrigation water sample was 0.08 mg/l.

Relevant chemical and physical properties were measured by following the procedures as described in section 3.2.2. The chemical and physical analyses were carried out in the laboratories of Department of Soil, Water and Environment, University of Dhaka. All determinations were performed in triplicate.

3.2.2 METHODS OF SOIL ANALYSIS

3.2.2 1 Moisture content

The moisture content of air-dry sample was determined gravimetrically by heating pre-weighed known amount of sample in an oven at 105^0C for 48 hours until constant weight was obtained and the moisture percentage (%) was calculated from the loss of the moisture.

3.2.2.2 Particle size analysis

The particle size analysis of the soils was determined using mechanical analysis by Bouyoucos hydrometer method (Piper, 1966).

3.2.2.3 Soil pH

Soil pH was measured electrochemically in distilled water by using a glass electrode pH meter (Jenway 3305). The soil samples were mixed with water at a ratio of 1:2.5 and the mixture stirred with glass rod for 30 minutes. The electrode was inserted in the suspension and soil pH recorded as outlined by Thomas (1996).

3.2.2.4 Soil organic carbon

Organic carbon content of the soil was determined by wet oxidation with potassium dichromate in concentrated sulfuric acid and rapid titration of the residual dichromate with iron (II) sulfate solution following Walkley and Black (1934) method as described by Nelson and Sommers (1996).

3.2.2.5 Total nitrogen (N)

For the determination of total N content the soil sample was digested by Kjeldahl's method as described by Jackson (1958). The digestion was accomplished by heating the soil with digestion mixture ($CuSO_4$+K_2SO_4+Se) and conc. H_2SO_4 in Kjeldahl flask at 350-410°C until clear green solution was formed. The NH_4^+-N content of each digest was determined by steam distillation using 2% boric acid solution plus mixed indicator and by titration with 0.01 M H_2SO_4 (Bremner, 1996).

3.2.2.6 Carbonate content of soil

Soil carbonate content was determined by titrimetric method (Bundy and Bremner, 1972). This procedure is based on the dissolution of soil carbonate by HCl evolving CO_2 and the subsequent absorption of CO_2 with aqueous NaOH (Loeppert and Suarez, 1996). An aliquot of the aqueous NaOH absorbent is first titrated with standard HCl to the phenolphthalein endpoint, and then to the bromocresol green endpoint. The inorganic carbonate content is proportional the HCl consumed. Total carbonate content was expressed as percent of $CaCO_3$.

3.2.2.7 Available phosphorus (P)

Available P was extracted by 1M $NaHCO_3$ at pH 8.5 following Olsen's method (Olsen *et al.*, 1954) and the extracted P in the solution was colorimetrically determined at 880 nm wavelength by ascorbic acid blue colour method of Murphy and Riley (1962) as described by Kuo (1996) using spectrophotometer (HACH DR5000).

3.2.2.8 Available sulfur (S)

Available S was extracted with 500 µg P/ml solution prepared from $Ca(H_2PO_4)_2.2H_2O$ (Fox *et al.*, 1964). The extracted S was determined turbidimetrically (Hunt, 1980). The turbidity of the sample was determined by using Spectrophotometer (HACH DR5000) at 420 nm wavelength.

3.2.2.9 Exchangeable potassium (K)

Exchangeable K was extracted by 1M ammonium acetate, pH 7.0 following the method of Schollenberger and Simon (1945) and analyzed in a Flame Analyzer (Jenway PFT7) (Helmke and Sparks, 1996).

3.2.2.10 DTPA extractable micronutrients (iron, manganese, zinc and copper)

Available iron (Fe), manganese (Mn), zinc (Zn) and copper (Cu) were extracted by DTPA-TEA (diethylenetriaminepentaacetic acid and tri-ethanol amine) method of Lindsay and Norvell (1978) as described by Reed and Martens (1996). The extracting solution consisted of 0.005M DTPA, 0.01M $CaCl_2$, and 0.1M TEA adjusted to pH 7.3 with dilute HCl. The extracted elements were directly determined in Atomic Absorption Spectrophotometer (Varian AA240).

3.2.2.11 Available Boron

The available B was extracted by hot calcium chloride ($CaCl_2$) method (Gupta and Stewart, 1975; Parker and Gardner, 1981) based on the classical hot-water extraction (HWE) method of Berger and Truog (1939) and modified by Gupta (1967). Advantages of using $CaCl_2$ is that it extracts very low color from the soil, and predicted error due to this color is low and that the filtered extracts are also free of colloidal matter (Parker and Gardner, 1981; Hettiarachchi and Gupta, 2008). This method involved adding 40 ml of 0.02 M $CaCl_2$ to a 250 ml flat bottom flask containing 20 g of soil. The solution was then heated until boiling. At the point of boiling, a glass funnel was inserted into each flask to reflux the soil solution. The solution was allowed to boil under this reflux condition for 5 minutes. The flasks were promptly removed from the heat at the end of the boiling period and allowed to cool, and filtered through Whatman No. 44 filter paper. All glassware used in soil B analyses was washed in 1:1 mixture of HCl and distilled water (Hettiarachchi and Gupta, 2008). The extracted solution was analyzed by Azomethine H method (Wolf, 1971; Keren, 1996).

Before performing B analysis by Azomethine H method, activated charcoal (0.2 g) was added to the extracts to remove color that developed due to the presence of oxides and humic substances as suggested by Gupta (1979). The solution was clarified using activated charcoal that had been thoroughly washed with respective extracting solutions prior to clarifying each sample solution. Tests conducted prior to actual analysis showed that adding 0.2 g of charcoal did not alter B concentrations in known solutions. After shaking with the charcoal, the suspension was filtered with Whatman no. 44 and the clear solution was collected.

3.2.2.11.1 Azomethine H method of B determination

The extracted solution was analyzed by Azomethine H method (Wolf, 1971; Keren, 1996). Color was developed by adding EDTA (0.005M) solution, ammonium acetate buffer solution and Azomethine-H solution to a known volume of extract and then the content was mixed well. The mixture was allowed to stand for 2 h to develop yellow colour. The absorbance of the colour was read on spectrophotometer at a wavelength of 420 nm (HACH DR5000).

3.2.2.11.2 Curcumin method

Boron fractions (e.g., oxide bound B) extracted in the fractionation study as well as total B of the soil was determined by the Curcumin method (Naftel, 1939; Dible *et al.*, 1954; Keren, 1996). This was done since the interferences in the extracts could not be offset by the Azomethine H method. In the Curcumin method, a known volume of sample was taken into a porcelain evaporating dish where curcumin-oxalic acid solution was added and mixed. The dish is then placed on a water bath maintained at 55 ± 3°C, and the content is taken to dryness. After cooling, alcohol is added to completely extract the colored compound. The absorbance of the reddish-brown (rosocyanin) colored solutions was read at a wavelength of 540 nm in spectrophotometer (HACH DR5000).

3.2.2.12 Total Zn and B in soil

Total Zn and B were dissolved by digesting the soil with HNO_3 and $HClO_4$ (Jackson, 1958; Piper, 1966; Schalscha *et al.*, 1982; Ranjbar and Jalali, 2013). Briefly, 10 ml of concentrated nitric acid (HNO_3) was added to 0.5 g of duplicate soil samples in pyrex beakers and heated at 80-90°C on a hotplate till the evolution of reddish fume of N oxides subsided. Then the beakers were removed from the hotplate, cooled and 5 ml of concentrated perchloric acid ($HClO_4$) was added. The contents then were heated at 180-200°C for several hours until the denseness of the white fumes dissipated and heating was continued to a clear solution. The beakers were removed, cooled and diluted with distilled water to the volume required for the B analysis. Duplicate reagent blanks were run for every set of samples digested. The extracted B was determined by the curcumin method as described in previous section.

3.3 METHODS FOR PLANT ANALYSIS

Plant samples collected from plots of different experiments were analyzed to determine the Zn and B concentration of the tested crops. The procedures used for the determination are as follows.

3.3.1 Digestion of plant samples

The plant samples (0.2 – 0.5 g) were digested, at first, with concentrated acids (HNO_3 and $HClO_4$) to bring the nutrients in solution (Jones Jr, 2001). The procedure was similar to that done for total Zn and B of the soil samples (section 3.2.2.12). Duplicate reagent blanks were run for every set of samples digested. The digests were analyzed for tissue Zn and B.

3.3.2 Determination of plant tissue Zn and B

The Zn contents in the HNO_3-$HClO_4$ digest were determined after necessary dilution by Atomic Absorption Spectrophotometer (Varian AA240). Plant B was determined by Azomethine H method (section 3.2.2.11.2) in spectrophotometer after proper dilution of the digest.

3.4 INCUBATION STUDY

To study the transformation of Zn and B in the soil under controlled (laboratory) condition, an incubation study was conducted with the soil from Wheat-Jute-T. Aman rice experiment. Two sets of experiments were conducted for each of Zn and B. Two Zn treatments: 0 and 5 mg/kg were tested at two moisture regimes: field capacity (0.33 bar) and submerged condition of soil. In case of B, two treatments: 0 and 3 mg/kg were added under the above mentioned moisture regimes. In brief, 1-g ground soil sample (oven dry basis) was taken into a 10 ml test tube and moistened or submerged with distilled water and mixed with Zn (as $ZnSO_4$) in one set, and B (as H_3BO_3) in another set. The tubes were covered and incubated at room temperature (28-30°C) for 28 days. Each treatment was replicated thrice. In the submerged soil, 4 cm standing water level was maintained throughout the experiment. The tubes were aerated time to time to circulate the air in the headspace and moisture content was maintained. After completion of the incubation period, the samples were extracted sequentially with the respective extractants to get the different fractions of Zn and B, as described in section 3.7 for Zn and section 3.8 for B.

3.5 TRANSFORMATION OF ZINC AND BORON IN SOIL

The soils of the W-J-R field experiment were also subjected to sequential fractionation of Zn and B in the laboratory with a view to observe the transformation of Zn and B under applied and native Zn and B as affected by soil and crop management practices.

The post-harvest soils from the four main treatments of Wheat-Jute-T. Aman rice experiment were collected. The treatment plots from which the soil samples were taken were: i) Zn_0B_0, ii) $Zn_2B_{1.5}$, iii) $Zn_4B_{1.5}$ and iv) Zn_6B_3. To avoid the complexity that may arise from recurrence effect Zn and B, the samples of the repeated application plots in the second or third crops (e.g. T2.2 or T2.2.1 etc. see Table 3.2) were not considered in the scheme. The post-harvest soil was tested so that it may reflect the transformation status of Zn and B after two years of cropping with Zn and B application. The fractionation procedures are described in sections 3.7 and 3.8 for Zn and B, respectively.

3.6 FRACTIONATION OF ZINC AND BORON IN SOILS WITH VARIABLE PHYSIOGRAPHY

In another program, the selected soils from AEZs 1, 9, 11, 12 and 28 (as described in section 3.3) were also subjected to fractionation study to observe the effect of physiographic variability of soil on the fractions of Zn and B in the soil. The procedure of Zn fractionation is described briefly in the following section.

3.7 SOIL ZINC FRACTIONATION SCHEME

The selective extraction methods presented here are based on methods developed by Tessier *et al.* (1979) and others (Chao, 1972; Shuman, 1985; Miller *et al.*, 1986) with minor modifications. Carbonate bound Zn was also separated in the soils from Ganges River Floodplain soils. Extraction of carbonate fraction was performed before the organic and oxide fractions to avoid appreciably dissolution of Zn associated with the latter fractions (Singh *et al.*, 1988; Shuman, 1991). Duplicate sub-samples of each soil were analysed. The steps of the fractionation scheme are as follows:

3.7.1 Exchangeable Zn

An amount of 2.5 g air dry (sieved <2 mm) soil sample was shaken in reciprocating shaker with 10 ml of 1 M $Mg(NO_3)_2$ solution in a 50-mL graduated plastic centrifuge tube for 2 hours at 180 cycles/min. Then the suspension was centrifuged for 10 min at 1500 rpm. The supernatant was decanted, filtered through Whatman No.42 paper to remove floating organic matter, and the residue retained for analysis. The residue was washed with 10 ml of distilled water, centrifuged for 5 min at 1500 rpm to separate the residual salts, and the supernatant was discarded.

3.7.2 Carbonate bound Zn

To the residue from the previous step 10 ml of 1 M NaOAc (pH 5.0) was added, mixed thoroughly and shaken for 5 hours at 180 cycles/min and centrifuged for 10 min at 1500 rpm. The supernatant was decanted, filtered if necessary, and retained for analysis. The residue was washed with 5 mL of ethanol, and evaporated to dryness.

3.7.3 Organically bound Zn

To the residue from the previous step, 10 ml of 0.7 M NaOCl (pH 8.5, adjusted just prior to analysis to avoid instability) was added. Then it was mixed thoroughly, and heated in a boiling water bath for 30 min. Thereafter, the content was centrifuged for 10 min at 1500 rpm and the supernatant was decanted and filtered using Whatman No. 42 paper. To destroy the organic matter completely, this step (boiling with 10 ml NaOCl) was repeated with no water wash in between, and the filtrates combined. Since the extracts may cause bubble formation in the atomic absorption spectrophotometer (AAS) aspiration capillary tube, an aliquot was evaporated on hot plate, and the residue was taken up in 0.1 M HNO_3 and made up to previous volume.

3.7.4 Manganese oxide bound Zn

The residue from the previous step was mixed with 25 ml of 0.1 M $NH_2OH.HCl$ (hydroxyamine hydrochloride) (pH 2.0) and shaken for 30 min at 180 cycles/min. Then the content was centrifuged, the supernatant decanted and filtered and retained for analysis, as described earlier. The residue was washed with distilled water, centrifuged and the resultant supernatant was discarded.

3.7.5 Amorphous Fe oxide bound Zn

This procedure was based on oxalate (Tamm's reagent) extraction method (Schwertmann, 1964; McKeague and Day, 1966; Loeppert and Inskeep, 1996). To the residue from previous step, a solution of 25 ml of 0.2 M ammonium oxalate + 0.2 M oxalic acid, adjusted at pH 3.0, was added and the mixture was shaken for 4 hours in the dark. The suspension was centrifuged, filtered and washed as in the previous step.

3.7.6 Crystalline iron oxide bound Zn

The residue was mixed with 25 ml of pH 3, 0.2 M ammonium oxalate + 0.2 M oxalic acid + 0.1 M ascorbic acid. Then the mixture was heated in a boiling water bath for 30 min with occasional stirring. The content was centrifuged, filtered and washed with distilled water as in previous step. High concentrations of oxalate can result in clogging of the burner head during the nebulization process as well as interference with AAS analysis; therefore, the oxalate extracts were decomposed prior to analysis (Loeppert and Inskeep, 1996). This step was accomplished by digesting 1 mL of the ammonium oxalate extract with 10 ml of concentrated HNO_3 to dryness and dissolving the sediment in 10 ml 1 M HCI.

3.7.7 Residual Zn

The residual fraction was determined by deducting the sum of all the fractions determined from the total Zn concentration of the soil. The method of total Zn determination is described in section 3.2.2.12.

3.8 FRACTIONATION SCHEME FOR SOIL BORON

The fractionation scheme for soil boron was based on the sequential B extraction method of Hou *et al.* (1994) who modified the previous extraction schemes for trace elements (Tessier *et al.*, 1979; Shuman, 1985; Jin *et al.*, 1987). The oxide bound B was determined by the curcumin method (Ren *et al.*, 2014), instead of ICP, mentioned in the original method. Determination of the organically bound B which was extracted by 0.02 M HNO_3 + 30% H_2O_2, could not be done due to strong interference of other ions/compounds encountered during the colorimetric determination using either azomethine H, curcumin or carmine method. Modified method of Datta *et al.* (2002) using perchloric acid was also applied to eliminate the interfering colour. However, no reproducible result was obtained. Therefore, the concentration of organic B fraction was included in that of the residual B. The detailed description of the fractionation scheme is presented in the following sections.

3.8.1 Fraction 1. Readily soluble and non-specifically adsorbed B

Duplicate 1g homogenized sub-sample soil was taken into a 50 ml polypropylene centrifuge tube. To the tube, 20 ml of 0.01 M $CaCl_2$ was added and shaken in reciprocating shaker for 16 hours, centrifuged at 15,000 rpm for 30 minutes. The supernatant was collected, filtered with Whatman paper no.44 and analysed for B by Azomethine H method.

3.8.2 Fraction 2. Specifically adsorbed and carbonate bound B

To the residue from the first step, 10 ml of 0.05 M KH_2PO_4 was added and the resulting suspension was shaken for 1 hour in the shaker. Then centrifuged for 30 minutes and the supernatant was collected and filtered for B analysis as described previously.

3.8.3 Fraction 3. Oxide bound B

The residue in the tube was again suspended with 20 ml of 0.2 M acidic NH_4-oxalate (pH 3.25) and shaken for 4 hours in the shaker followed by separation of the solid and suspension phase. The supernatant was filtered. To remove the interfering color, 10 ml of the extract was digested in 2 ml conc. $HClO_4$ acid, evaporated to almost dryness and the digest was made up to 10 ml with distilled water before analysis for B by curcumin method.

3.8.4 Fraction 4. Residual B

The residual B was determined by subtracting all of the above fractions from the total B. The method of total B determination is described in section 3.2.2.12.

3.9 STATISTICAL ANALYSIS

The recorded data on different parameters and various characteristics of crops and soil were subjected to statistical analysis. Descriptive statistics of soil micronutrients and various graphs were performed by Microsoft Excel 2007 and Minitab statistical software version 17.1.0 (Minitab, 2014). Means of micronutrient concentration of the two soil groups (AEZ 11 and 12) were compared by Student's t test. Skewness and kurtosis analyses were performed to assess the normality of micronutrient data distribution. The significance of normality was tested by applying z-test using skewness and kurtosis. Calculation of t-test, skewness, kurtosis and z-test were performed in Minitab software. The analysis of variance (ANOVA) for crop yield, yield contributing parameters, nutrients concentration and uptake was performed by statistical package STAR (IRRI, 2013). Mean comparison of yield data was done by post-hoc tests e.g., least significant difference (LSD) test, Duncan's multiple range test (DMRT) or Tukey's honestly significant difference (HSD) test depending on the number of treatments (Gomez and Gomez, 1984). Regression analysis and linear regression models of i) plant uptake vs. soil nutrient fractions and ii) nutrient availability vs. soil properties was developed in IBM SPSS Statistics, Version 22.0 (IBM, 2013).

3.10 DESCRIPTION OF THE SOILS FROM DIFFERENT AEZs

The soil samples collected from the aforementioned five major Agro ecological zones (AEZ 1, 9, 11, 12 and 28) differed in soil properties, land type, physiography, parent material and the crop growth. The objective of these sampling was to study the comparison between micronutrient content of these AEZs and those of Ganges River Floodplain soils. Also, the variability of Zn and B fractions in soils due to the changes in the mentioned soil parameters was studied. Five samples from each of AEZ 1, 9 and 28 were sampled to study the distribution of soil micronutrients. Out of five samples, two were selected for the fractionation study. Some basic information about the collected soil samples are presented in Appendix 2.

CHAPTER IV

RESULTS AND DISCUSSION

The results of the different field and laboratory experiments conducted in this investigation along with relevant discussions on the results obtained are described in the following individual sections.

4.1 Status of micronutrients and related properties in Ganges River Floodplain Soils

Soil samples from High and Low Ganges River Floodplain soils (AEZs 11 and 12) were analyzed for five micronutrients, namely, iron, manganese, zinc, copper and boron. Besides, soil pH, soil organic carbon and total nitrogen were also determined. Detailed results are presented in the following sections.

4.1.1 Soil pH

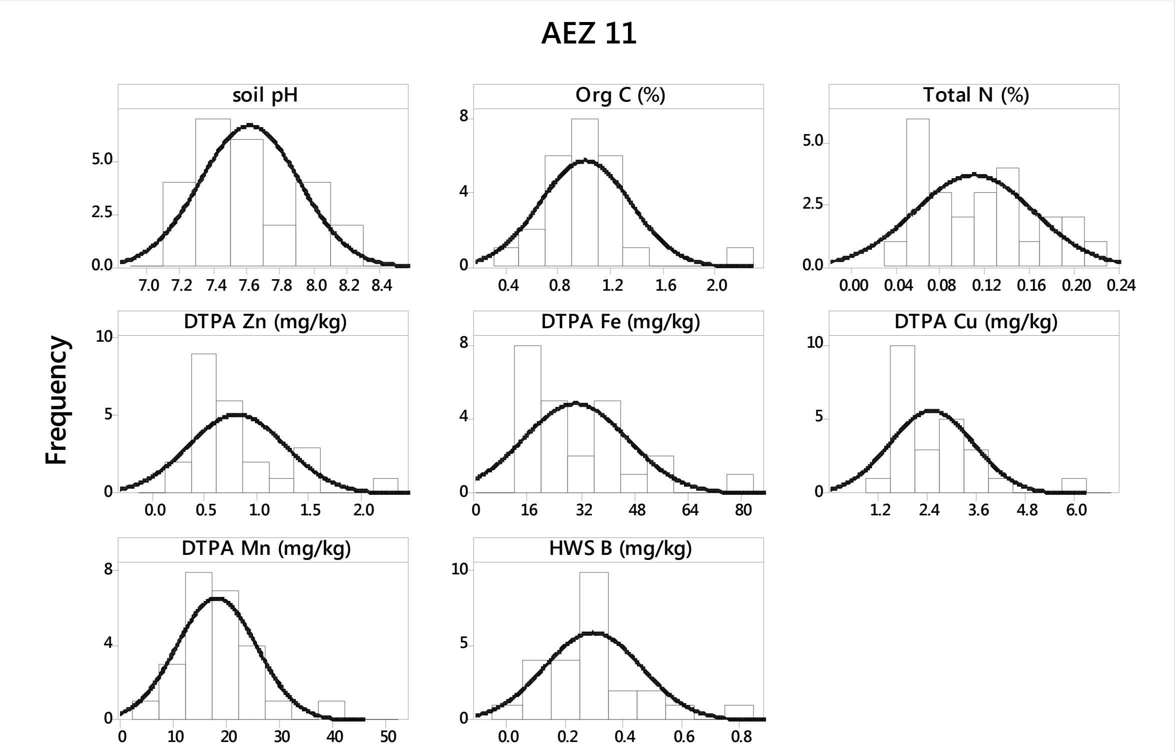
Soil pH of the samples collected from AEZ 11 ranged from 7.17 to 8.22 with a mean of 7.62 (Table 4.1). The majority of the studied soils in this AEZ are in the range of 7.2 - 7.8 (neutral to slightly alkaline) as reflected by the non-normal distribution (Fig. 4.1). Some samples, however, showed pH more than 8.0. In AEZ 12, soil pH varied from 6.98 to as high as 8.46 with a mean of 7.88 (Table 4.1). Thus, most of the soils of this AEZ were slightly to strongly alkaline in nature. The reason of the higher pH values might be due to the presence of calcium carbonate in these soils (Hassan, 1999). The land type of AEZ 12 is the lower part of the Ganges River Floodplain where the cation accumulation is expected to be high which is, probably, reflected in high soil pH. The range of soil pH in AEZ 11 was narrower than that of AEZ 12, which indicates that soil properties of the latter are more diverse than the former.

Table 4.1 Concentration of available micro-nutrients, pH, organic C and total N of the soils from AEZ 11 and AEZ 12.

Soil parameter^a	AEZ 11 (n=25)				AEZ 12 (n=25)				t value
	Mean	SD^b	Min.	Max.	Mean	SD	Min.	Max.	
soil pH	7.62	0.30	7.17	8.22	7.88	0.44	6.98	8.46	-2.50*
Organic C (%)	1.01	0.35	0.41	2.27	1.04	0.39	0.14	1.67	-0.27
Total N (%)	0.11	0.05	0.04	0.23	0.13	0.04	0.05	0.21	-1.21
Avail. Zn (mg/kg)	0.82	0.47	0.19	2.18	0.47	0.36	0.06	1.56	3.00**
Avail. Fe (mg/kg)	30.4	15.8	12.8	76.5	18.6	15.1	2.00	67.6	2.71**
Avail. Cu (mg/kg)	2.52	1.03	1.20	5.70	2.97	1.67	1.20	6.40	-1.12
Avail. Mn (mg/kg)	18.27	7.55	7.40	41.0	14.11	9.75	2.60	50.40	1.70
HWS-B (mg/kg)	0.30	0.17	0.01	0.80	0.21	0.16	0.05	0.68	1.92

$^{*, **}$ Difference between AEZ 11 and 12 significant at 5% and 1% level of significance, respectively.

^{a} Zn, Fe, Cu & Mn DTPA extractable and B hot water extractable; ^{b}SD = Standard deviation



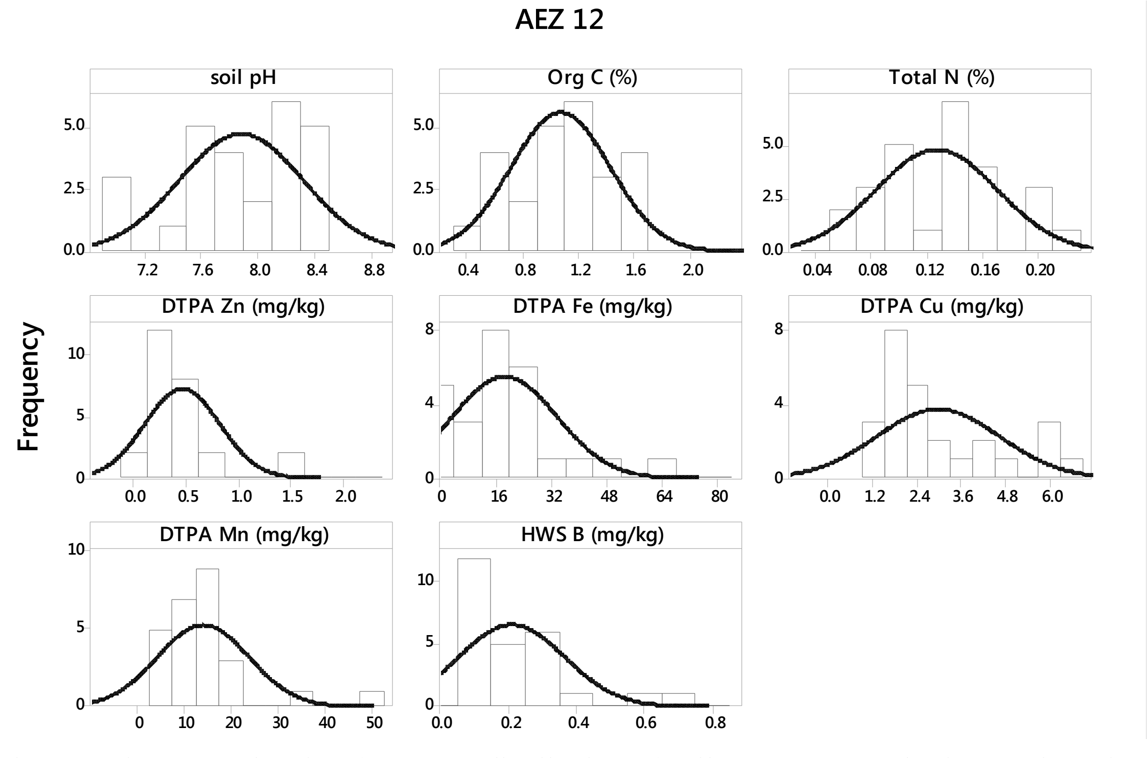


Fig. 4.1 Histogram showing frequency distribution of soil parameters and micronutrients in AEZ 11 and 12

The high pH of soils of both the AEZs implies a deficiency of available micronutrients since their availability to plants is affected at high pH (Brady and Weil, 2014).

The absolute values of skewness and kurtosis of the parameters are presented in Table 4.2. The data presented in Table 4.2 as well as in Fig. 4.1, imply that the distributions of the five micronutrients are not normal and skewed significantly positively in both AEZs. This means that a large number of the surveyed samples possess lower than average concentration of the micronutrients in both the AEZs.

Table 4.2 Values of skewness and kurtosis of soil micronutrient distribution.

Soil parameters	Skewness		Kurtosis	
	AEZ 11	AEZ 12	AEZ 11	AEZ 12
soil pH	0.46	-0.59	-0.87	-0.42
Organic C	1.86*	-0.55	6.64	-0.29
Total N	0.53	0.14	-0.66	-0.66
Available Zn	1.32*	2.20*	1.81	5.15
Available Fe	1.23*	1.62*	1.7	3.6
Available Cu	1.40*	1.09*	2.69	-0.16
Available Mn	1.18*	2.32*	2.4	7.36
Available B	1.08*	1.90*	2.32	3.65

* Distributions are highly skewed (non-normal) based on z-test (α=0.05).

4.1.2 Organic carbon

Organic carbon in AEZ 11 ranged from 0.41 to 2.27% with a mean of 1.01% (Table 4.1). If extreme values are disregarded, the majority of the samples remained between 0.5 to 1.5%. Thus, the org. C content of these soils and, in turn, the soil fertility is quite low (BARC, 2012). In AEZ 12, org. C ranged from 0.14 to 1.67% with a mean of 1.04%. The data depict that both AEZ soils are similar in organic C content and the difference between the values is statistically insignificant (value of t is insignificant) (Table 4.1). Islam *et al.* (1992) found that organic matter ranged from 0.6 to 1.7% in 29 soil series from different regions of the country. Islam (1990) observed that 90% soils of Bangladesh contained 0.5 - 1.0% organic matter where the minimum requirement of organic matter for successful crop production is at least 2% (Moslehuddin *et al.*, 1997).

4.1.3 Total Nitrogen

The analysed values of total N were slightly higher in AEZ 12 soils than those of AEZ 11 (Table 4.1). The range in AEZ 11 was 0.04 to 0.23% while that of AEZ 12 was 0.05 to

0.21%. The samples from AEZ 12 showed more uniform normal distribution compared to AEZ 11, implying that the variability of the extreme values is lower (Table 4.2; Fig 4.1). Considering 0.10 to 0.12% total N as critical limit (based on FRG-2012), more than 50% of collected samples of AEZ 11 and 12 contained percent nitrogen above critical limit for crops (BARC, 2012). The values of total N found was comparable to those reported earlier. Hossain *et al.* (2009) reported 0.06 to 0.17% of total nitrogen in some benchmark soils of Ganges River Floodplain soils. The soils of low-lying areas of most floodplains have a good amount of N because of a good reserve of organic matter (Moslehuddin *et al.*, 1997).

4.1.4 Iron

The range of DTPA extractable Fe concentration in soil was 12.8 - 76.5 mg/kg with a mean of 30.4 mg/kg in AEZ 11 (Table 4.1). Except for a few extreme values, most of the soils had <10 to 55 mg Fe/kg. The mode was around 20 mg/kg. In contrast, the mean Fe concentration of AEZ 12 soils was 18.6 mg/kg. The minimum and maximum were 2.0 and 67.6 mg Fe/kg soil, respectively. In this AEZ, most of the samples contained < 20 mg/kg Fe. Thus, the soils of AEZ 11 contained significantly higher DTPA extractable Fe than AEZ 12 (t value significant at $p > 0.01$). According to Moslehuddin and Egashira (1997), smectite is a characteristic clay mineral of Ganges River Floodplain soils (AEZ 11 and AEZ 12) where it is mainly composed of a high level of Fe-rich biedellite. This might be the reason for higher concentration of DTPA extractable Fe in these soils. The findings of the present investigation were within the range reported by other researchers. Hossain *et al.* (2011) reported 35 to 255 mg/kg Fe in the topsoil of five Ganges River Floodplain soils. Moslehuddin *et al.* (1999) reported 8 to 53 mg/kg Fe in Ganges Floodplain soils. Singh and Sekhon (1991) found 7 to 200 mg/kg DTPA Fe in 20 soils of Indo-Gangetic Plain. However, Khan *et al.* (1997) found higher concentrations of DTPA Fe ranging from 104 to 300 mg/kg in the topsoil and 14 to 44 mg/kg Fe in the subsoil in the floodplains of Bangladesh. The variation in the reported Fe concentration of the different studies may be due to the variation in the location, sample size and time of sampling. From the plant nutrition view point, most of the soils in the two AEZ contained very high levels of plant available Fe (Tables 4.1 and 4.2; Fig. 4.1) against its critical limit of 4.5 mg/kg according to Lindsay and Norvell (1978) and 20 mg/kg based on Agro Services International (Portch and Islam, 1984). Too much solution Fe may inhibit the uptake and utilization of other nutrients by the plants, particularly rice, thus causing reduced yield (Fageria, 2014). However, there is no report of Fe toxicity in the crops in this area. It is possible that although the concentration of soil Fe is excessive, plants only take up the quantity they require by their internal mechanism.

4.1.5 Zinc

In AEZ 11, DTPA extractable Zn ranged from 0.20 to 2.20 mg/kg with a mean of 0.82 mg/kg (Table 4.1). On the other hand, in AEZ 12, it ranged from 0.10 to 1.6 mg/kg with a mean of 0.45 mg/kg. Except extreme values, most of the data remained within <0.20 to 0.80 mg/kg in AEZ 12. Thus, considering 0.8 mg/kg as critical level (Lindsay and Norvell, 1978; Rahman *et al.*, 2007), most top soils of AEZ 12 were found to be deficient in Zn. Similar pattern was also visible in AEZ 11 although Zn level of the soils was slightly higher (Table 4.1; Fig. 4.1). The range of the values found in this study was in agreement with the reports of previous studies done in Bangladesh. Moslehuddin *et al.* (1999b) found 0.6 to 1.3 mg Zn/kg in the Ganges River Floodplain soils. Similarly, Hossain *et al.* (2009) obtained 0.6 to 6.0 mg/kg Zn while Khan *et al.* (1997) reported 0.38 to 1.16 mg Zn/kg in the Ganges River Floodplain soils.

4.1.6 Copper

The concentration of DTPA Cu of the soils in AEZ 11 was normally distributed with a mean of 2.52 mg/kg (Fig. 4.1). The range was 1.16 mg/kg to 5.72 mg/kg Cu (Table 4.1). The mean level of Cu in the soils of AEZ 12 (2.92 mg/kg) was almost similar to that of AEZ 11. However, the distribution was not normal as in the case of AEZ 11.

The mean concentration of Cu in the studied region was much higher than the optimum concentration for plant growth. However, there is no report of Cu-toxicity in this region. Khan *et al.* (1997) noted that the floodplain soils contained higher quantities of Cu as a whole. Moslehuddin *et al.* (1999b) reported 1.7 mg/kg DTPA Cu in Ganges River Floodplain soils and Khan *et al.* (1997) found that none of the soil samples of the same region were deficient in Cu.

4.1.7 Manganese

Most soils of AEZ 12 contained 5 - 25 mg/kg Mn, except the extreme values (Table 4.1; Fig 4.1). Considering 1.0 mg/kg as critical limit for field crops (BARC, 2012), all the samples of topsoil from AEZ 11 and AEZ 12 contained sufficient plant available Mn. The concentration of Mn was not found to be toxic for the crops. The values of Mn observed in the study are consistent with the values reported by others in Bangladesh soils (Hassan, 1999; Moslehuddin *et al.*, 1999; Begum *et al.*, 2016).

4.1.8 Boron

Plant available B (hot water soluble B) concentration ranged from 0.01 to 0.8 mg/kg in AEZ 11 with a mean of 0.30 mg/kg (Table 4.1). Most of the samples contained less than 0.5 mg/kg B as evidenced by significantly positively skewed distribution (Table 4.1, Fig. 4.1). In AEZ 12, the concentration of B ranged from 0.05 to 0.68 mg/kg, the mean being 0.21 mg/kg. If 0.2 mg/kg soil B is considered as critical limit for crops (BARC, 2012), about 66% of the samples of AEZ 12 were B deficient, while in AEZ 11, the percentage was 24. Thus, the soils of AEZ 12 were more deficient in B than those of AEZ 11. According to Ahmed and Hossain (1997), the available B content of the major soil types in Bangladesh ranged between 0.1 and 1.9 mg/kg soil. Islam and Miah (1992) reported that the sandy loam soils of Bangladesh mostly contain 0.1 to 0.3 mg/kg available B. They identified the probable B deficient areas represented by the following soil types: Non-calcareous Grey Floodplain soils, Piedmont soils, Terrace soils and Hill soils, mostly acid soils having medium to light texture.

4.1.9 Relationship between soil properties and micronutrients

The correlation between soil pH, organic C and the micronutrient concentration in AEZ 11 and 12 is shown in Table 4.3. In general the relationship of the micronutrients with soil pH was negative; however, it was significant only in case of Zn, Mn and B (Table 4.3). A negative relationship between soil pH and Fe, Zn, Mn and Cu concentration is well documented (Marschner, 2012; Brady and Weil, 2014). It was previously reported that soluble B content in soils correlate highly significantly with solution pH (Berger and Truog, 1945; Elrashidi and O'connor, 1982). According to Keren (1996), increasing soil pH enhances B adsorption on clay minerals and oxides. Increases in B adsorption were found to increase with solution pH in the range of 3 to 9 (Goldberg, 1997). Thus, at lower soil solution pH, uptake of B by the plants was greater (Wear and Patterson, 1962). A significant and strong correlation was observed between DTPA Zn and Fe concentration. This suggests that Zn might be closely associated with iron rich compounds like oxides and hydroxides. On the other hand, a significant correlation was found between DTPA Cu and organic C in these soils (Table 4.3). Positive significant relationship of organic C with Cu and B implies that these micronutrients may have been released from soil organic matter. Strong correlation of Zn with Mn and B reflects that the same factors are likely to affect these three micronutrients.

Table 4.3 Correlation matrix showing relationship between soil micronutrients and soil pH and organic C in Ganges River Floodplain soils (AEZs 11 and 12) (n=52).

	soil pH	Org. C	Zn	Fe	Cu	Mn
soil pH	1.00					
Org. C	0.03	1.00				
Zn	-0.15	0.14	1.00			
Fe	-0.28*	0.10	0.42**	1.00		
Cu	-0.15	0.29*	0.07	0.20	1.00	
Mn	-0.42**	0.01	0.38**	0.45**	0.15	1.00
B	-0.34*	0.39**	0.44**	0.32*	0.10	0.17

* significant at 5%, ** significant at 1% level.

4.1.10 Relationship between land type, soil series and micronutrients

The variation of the concentration of micronutrients based on land type and soil series is presented in Fig. 4.2. This study was conducted in the soils of four series, namely, Sara, Gopalpur, Ishurdi and Ghior, located in three land types: highland (HL), medium highland (MHL) and medium lowland (MLL). It is noted here that, all the soil series was not available in all the land types. Accordingly, Ishurdi and Ghior series were absent in the HL, while Sara and Gopalpur series were not present in the MLL. Only the MHL contained all the four soil series. It is clear from Fig. 4.2 that the nutrient concentration varied considerably among the four soil series and land type.

There was no consistent trend in the distribution of Zn concentration in different land type and soil series. The range (~0.15 to 1.5 mg/kg) was almost identical in all the three land types (Fig. 4.2a). In the highland, Gopalpur series contained considerably higher Zn than Sara series. In contrast, in the MHL, the range of Zn concentration in Sara series was the widest stretching from <0.1 to 1.5 mg/kg and its mean were higher than that of Gopalpur series, although average Zn concentration of Ishurdi series was slightly higher. The range and mean Zn concentration was the lowest in Ghior series in MHL. In the MLL, both the range and average Zn concentration was higher in Ishurdi sereies compared to Ghior series. Thus, it is evident that the properties of soil series changes with the land type.

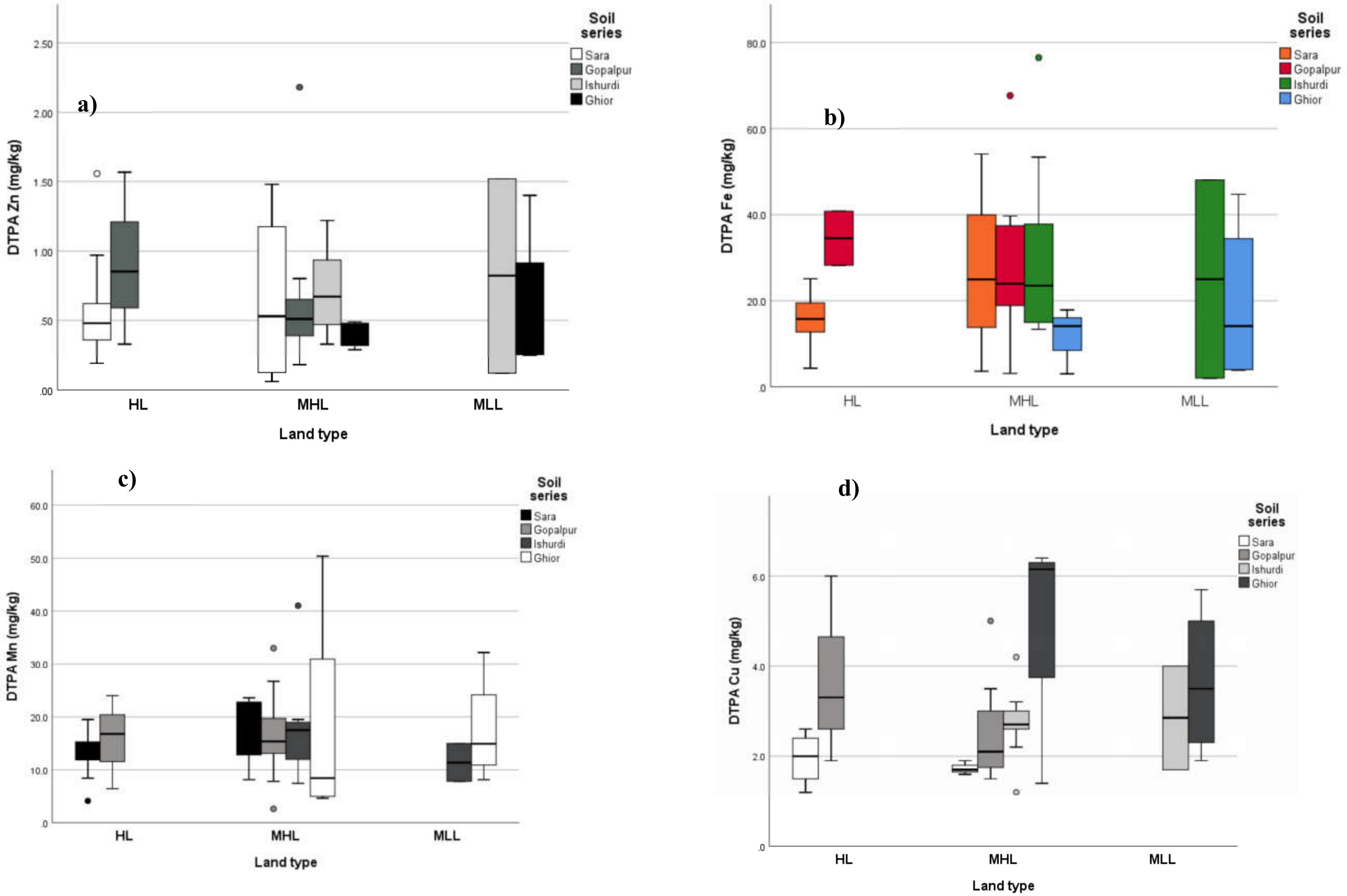


Fig. 4.2 Distribution of DTPA extractable Fe, Mn, Zn and Cu) in surface (0-15 cm) soils of Ganges River Floodplain (AEZs 11 and 12) representing various land types and soil series (n=52)

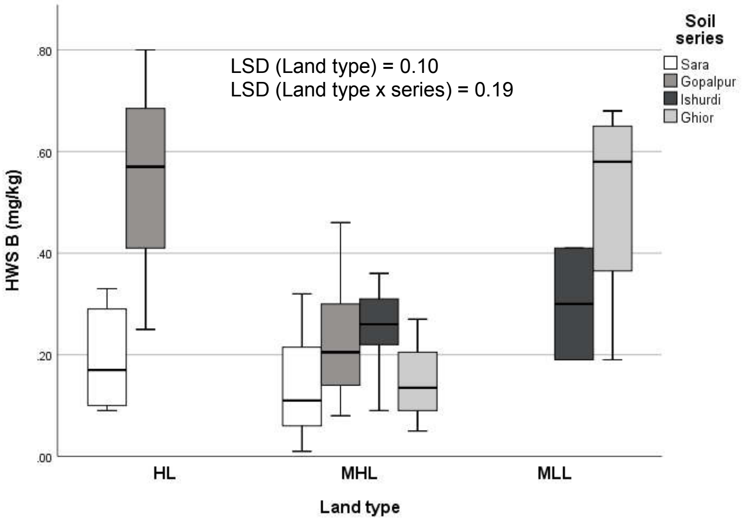


Fig. 4.3 Distribution of available boron (B) in surface (0-15 cm) soils of Ganges River Floodplain (AEZs 11 and 12) representing various land types and soil series (n=52)

The range of available Fe concentration was much wide (5 to > 45 mg/kg) in both MHL and MLL (Fig. 4.2b). Samples from Ghior series of MHL and Sara series of HL had the lowest range (4 - 20 mg/kg) of available Fe.

The distribution of available Mn shows that with few exceptions most of the samples from all land types exhibited values near 20 mg/kg (Fig. 4.2c). Only the samples of Ghior series from MHL and MLL showed wider range from <5.0 to >30.0 mg Mn/kg soil.

There was significant interaction between the Cu concentration of the land types and different soil series (Fig. 4.2d). For example, the range of Cu in Gopalpur series is very narrow (1.7 to 2.7 mg/kg) in MHL while it is quite wider (2.0 to 6.0 mg/kg) in MLL.

The concentration of B was lower in the medium highland (MHL) soils than those of highland (HL) or medium lowland (MLL). The highest B concentration was observed in Gopalpur series, followed by Ghior series (Fig. 4.3).

The overall finding is that from plant nutritional point of view, Gopalpur and Ghior series are rich in available B while Sara, Gopalpur and Ishurdi series have higher available Zn concentration (Figs. 4.2a and 4.3). Soils of Sara and Ghior series in HL and MHL have lower

Fe content and hence there is less risk of Fe toxicity in these soils (Fig. 4.2b). The soils of Gopalpur and Ghior series may provide optimum Cu for the crops (Fig. 4.2d).

4.1.11 Description of the chemical properties of the soils collected from different AEZs

Some important chemical and physical properties of the soils collected from five major AEZ as determined in the laboratory are shown in Table 4.4. The values of AEZ 1, 2 and 28 are average of five samples, while those of AEZ 11 and 12 are average of 25 samples. A brief discussion follows.

Soil pH was the lowest in AEZ 1 and the highest in AEZ 11 and 12 (Table 4.4). Low pH in AEZ 1 implies their genesis from acidic parent materials, light textured soils and rapid leaching of cations while that of AEZs 11 and 12 (Ganges River Floodplain) was due to calcareous parent material (FAO-UNDP, 1988). Among the samples, the lowest organic C was found in AEZ 11 and 12 which necessitates addition of more organic amendments than those of other AEZs. Similarly, the lower available P in the soils of AEZ 9 and 28 implies more P fixation by the soil components and general requirement of more P fertilization than other AEZs. With regard to available K, the Ganges River Floodplain soils showed higher concentrations (0.32 to 0.64 me/100g) compared to other AEZs (Table 4.4), implying the presence of more K-bearing weatherable minerals in those soils. Considering 0.12 me K/100g as critical limit for the plants (BARC, 2012), the samples of AEZs 1 and 9, having 0.07 to 0.10 me K/100g, were deficient in K. Therefore, K application should be emphasized more than the required rates for K build up in those soils. All the AEZ samples showed sufficient available S content, except that of AEZ 9, which indicates the requirement of application of S fertilizer substantially (Table 4.4).

The much higher contents of DTPA-Fe and almost similar DTPA-Mn content of the samples of AEZ 1, 9 and 28 indicates the presence of more Fe and Mn in their parent materials than that of Ganges River Alluvium (FAO-UNDP, 1988). All of the samples except those of AEZ 28 demonstrated deficient or near deficient Zn level, particularly in AEZ 12 (Table 4.4). Thus, Zn is proved to be a critical micronutrient for crop production in Bangladesh. It is notable, that the concentration of available Zn was not related to that of total Zn in the studied soils (Table 4.4).

Table 4.4 Chemical properties of the soils from different AEZs.*

AEZ no.	Name of AEZ	Soil pH	Organic C (%)	Total N (%)	Available			DTPA extr. micronutrients				HWS B	Total Zn	Total B	$CaCO_3$ (%)	Clay (%)
					K	P	S	Fe	Mn	Zn	Cu					
					me/100g	mg/kg										
1	Old Himalayan Piedmont Plain	4.94	1.29	0.12	0.10	23	35	202	15	1.93	1.5	0.38	86	69	ND[a]	24
9	Old Brahmaputra Floodplain	6.59	1.21	0.11	0.07	4.8	13.4	206	33	1.12	3.3	0.32	103	43	ND	37
11	High Ganges River Floodplain	7.62	1.01	0.11	0.32	26	24.7	30	18	0.82	2.5	0.30	120	24	0.08	32
12	Low Ganges River Floodplain	7.89	1.04	0.13	0.64	32	28.2	18	14	0.45	2.9	0.21	122	21	0.17	28
28	Madhupur Tract	5.96	1.52	0.14	0.23	3.2	19.8	187	52	2.49	2.7	0.42	102	29	ND	24

* n=5 for AEZs 1, 9 and 28; and n= 25 for AEZs 11 and 12. [a] ND = not determined.

The concentration of Cu was sufficient in all the samples. In general, the available B content was low in all the samples; being the lowest in Low Ganges River Floodplain soils (AEZ 12) implying the requirement of continued B application in these soils. Here again, available B was not related to total B concentration (Table 4.4).

The percent carbonate contents of the Ganges River Floodplain soil samples were too low (Table 4.4) compared to those mentioned in the literature. This might be due to the decalcification process active in the region (Moslehuddin *et al.*, 1999a). According to Moslehuddin *et al.* (1999a), the soils on the ridges and basins of Ganges River Floodplain had lower smectite and carbonate contents in the upper horizons than in the C horizon due to decalcification. In the present study, higher carbonate content (3.5%) was found in a sub-surface (15-30 cm) soil sample of Rajbari compared to that in the surface (0- 15 cm) soil (0.2%).

Total Zn content was the highest in the Ganges River Floodplain soil and the lowest in the AEZ 1 (Table 4.4). The variation in total Zn content was apparently due to difference in parent material (Moslehuddin *et al.*, 1997). Zinc content was found to be positively correlated with sand content and montmorillonite and kaolinite type clay in Bangladesh (Domingo and Kyuma, 1983). As shown earlier, the Ganges River Floodplain soil possessed more smectite minerals than other regions (Table 3.6). Jahiruddin *et al.* (2000) showed that the level of total Zn content of non-calcareous soils was 45 - 94 mg/kg while that of calcareous soils was 51 - 111 mg/kg.

In contrast to total Zn, the concentration of total B was found to be higher in AEZ 1 and 9 compared to other three AEZs. Higher contents of mica, organic matter and clay have been ascribed to higher total B in soil (Domingo and Kyuma, 1983; Hassan, 1999).

4.2 FIELD EXPERIMENT - 1

Effects of Zn and B on Rice, Wheat and Jute crops

The experiment was set up in farmer's field in Char Bagmara of Rajbari sadar, with Wheat-Jute-T.Aman rice cropping pattern, to study the effect of Zn and B application on yield and nutrient uptake of wheat, jute and T. Aman rice for two years. The soil of the experimental site was deficient in Zn (0.44 mg/kg) while the level of available B (0.26 mg/kg) was low to medium according to the Fertilizer Recommendation Guide (BARC, 2012). The results of Zn and B application on the yield, yield contributing characters and the concentration and uptake of Zn and B of the crops are discussed in the following sections.

4.2.1 Effects of Zn and B on wheat (BARI Gom 26)

4.2.1.1 Yield contributing parameters

Results of the effect of zinc and boron on the yield contributing parameters of wheat crop are presented in Table 4.5. It was observed that the number of grains per spike of BARI Gom 26 increased due to the application of Zn and B in the first year of the experiment, although the variation was not significant (Table 4.5). Both the treatments T3 and T4 having Zn@4 and 6 kg/ha and B@1.5 and 3 kg/ha, respectively, exhibited increased number of grains.

Table 4.5 Effect of Zn and B on the yield and yield parameters of wheat (BARI Gom 26) in wheat-jute-T. Aman rice cropping pattern.

Treatments	Grains/spike		Plant height (cm)		1000-Grain weight (g)		Grain yield (t/ha)		Straw yield (t/ha)	
	Year1	Year2	Year1	Year2	Year1	Year2	Year1	Year2	Year1[a]	Year2
T1=Zn_0B_0[+]	53	40	97	90	45	46	2.60b	2.08d	4.32	4.49
T2=Zn_2B_0	53	44	96	96	44	50	3.02a	2.80b	4.85	4.61
T3=$Zn_4B_{1.5}$	59	40	95	90	46	53	3.08a	3.14a	4.04	4.83
T4=Zn_4B_3	59	43	95	88	44	47	2.91a	2.47c	4.07	4.09
LSD $_{(0.05)}$	NS	NS	NS	NS	NS	NS	0.30	0.30	NS	NS
Mean	56	42	96	92	45	49	2.9	2.90	4.60	4.51
CV%	7.5	25	2.6	4.6	6.1	12.4	6.6	14.6	4.3	11.8

[a]Means followed by same letter are not significantly different.
[+] Subscripts of Zn and B denote rate of application (kg/ha).

In the second year, only the treatment Zn@2 kg/ha increased the number of wheat grains compared to control. Higher rates of Zn (4 and 6 kg/ha) could not increase the grain numbers. Increase in wheat grains per spike due to Zn or B addition is reported by others (Yilmaz *et al.*, 1997; Shivay *et al.*, 2008; Biswas *et al.*, 2015). However, the reverse, i.e., no response of wheat to Zn application, has also been reported by Curtin *et al.* (2008).

Like the case of grains/spike, plant height of BARI Gom 26 was unaffected by the application of Zn and B (Table 4.5). Plant height ranged from 95 to 97 cm in the 1st year and 88 to 96 cm in the following year.

Similar to grains/spike and plant height, thousand grain weight of BARI Gom 26 did not show any response to Zn and B application, in either of the years (Table 4.5). The weight varied between 44 and 46 g in the 1st year and 47 and 53 g in the 2nd year. The weight of 1000 grains was comparatively higher in the 2nd year than that of 1st year, and consequently the mean grain yield was similar in both the years.

4.2.1.2 Crop yield

It is observed from Table 4.5 that the grain yield of wheat (BARI Gom 26) responded significantly to the Zn-B applications, showing a 11.9 - 18.5% yield increase over control in the first year and 18.8 - 51.0% yield increase in the second year. The grain yield in the first year ranged from 2.60-3.08 t /ha and the yield in the second year varied from 2.08-3.14 t/ha. If the two years' yield is pooled, the yield recorded by the four treatments was chronologically 2.34, 2.94, 3.08 and 2.69 t/ha. The treatment $Zn_4B_{1.5}$ (T3) demonstrated the highest grain yield, followed by the Zn_2B_0 (T2). This result clearly indicates that Zn application at 2 t/ha had significant positive effect, but the B effect was additive. Although the grains/spike and 1000-grain weight were not significantly influenced by Zn and B application, their combined effect had produced marked effect on the grain yield.

Significant increase in wheat increase due to Zn (and B) application is well documented. Cakmak *et al.* (1996) reported significant (~ 100%) increases in grain yield in Zn deficient soils of Turkey. Likewise, Kalayci *et al.* (1999) found significant yield increase due to Zn fertilization in 40 wheat cultivars in Turkey. They reported that the yield response varied significantly between the cultivars with some being more efficient under low Zn conditions. Similarly, Khan *et al.* (2007) observed significant increases in wheat grain yield due to Zn application in Pakistan. In West Bengal, India, Biswas *et al.* (2015) found the highest grain yield of wheat after the combined application of Zn and B.

There was no significant variation in straw yield of wheat over the treatments (Table 4.5). This might be due to the fact that plant height and tillers/plant (not reported) was unaffected by the treatments. In value, the T_2 (Zn_2B_0) treatment in the first year and T_3 ($Zn_4B_{1.5}$) treatment in the second year gave the highest straw yield, with a record of 4.85 and 4.83 t/ha, respectively. The control (Zn_0B_0) treatment produced the lowest straw yield.

In this study, a response of wheat to Zn and B application was expected since the soil was deficient in Zn. However, high application rate of Zn and B may reduce crop yield. Lombin and Bates (1982) found that excessive B uptake by crops like mustard, alfalfa and soybean was associated with considerable yield reduction. Gupta *et al.* (1985) found reduced yield of beans due to increase in B application rate.

The requirement of Zn and B by the crops may vary yearly depending on variation in the soil level caused by climatic and other factors. Studying the fractionation of soil Zn and B may answer the question to some extent. The results of fractionation study of the experimental soil are presented in section 4.4.1. In addition to this, the interaction between Zn and B could be a factor that influences the metabolic processes of the plant leading to variation in crop yield (Araújo *et al.*, 2018).

4.2.1.3 Plant Zn concentration

The effect of Zn and B application on Zn concentration of wheat grain and straw is shown in Table 4.6. Application of Zn and B significantly affected grain Zn content of BARI Gom 26 during the 1st year. All the treated plots showed significantly higher grain Zn than the control.

Table 4.6 Effect of Zn and B application on Zn concentration of wheat (BARI Gom 26) in the wheat-jute-T.Aman rice cropping pattern.

Treatment	Grain Zn conc. (mg/kg)[a]		Straw Zn conc. (mg/kg)[a]	
	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[*]	28.1c	36.4b	25.1b	26.3
T2=Zn_2B_0	34.9a	37.3b	30.3ab	27.7
T3=$Zn_4B_{1.5}$	30.3b	36.7b	24.7b	35.3
T4=Zn_6B_3	34.4a	45.3a	33.4a	29.3
$LSD_{(0.05)}$	2.2	5.0	5.4	NS
Mean	31.9	38.9	28.2	29.6
CV%	3.4	6.4	9.6	15.5

[a]Means followed by same letter are not significantly different. [*] Subscripts denote rate of Zn and B (kg/ha).

The highest grain Zn concentration was observed in T2 (34.9 mg/kg) and T4 (34.4 mg/kg) (Table 4.6). Likewise, during the second year, significantly higher grain Zn concentration was obtained by T4 (45.3 mg/kg). Positive response of Zn and B application on the grain Zn concentration of wheat was reported by many researchers earlier (Kalayci *et al.*, 1999; Rengel *et al.*, 1999; Cakmak *et al.*, 2010; Talukder *et al.*, 2011; Prasad *et al.*, 2014; Cakmak and Kutman, 2018). The mean grain Zn concentration of the second year (38.9 mg/kg) was higher than that of the 1st year (31.9 mg/kg). This might be due to variation in climatic condition with time, leading to the increase in the availability and uptake of the nutrients in second year. Variation in air temperature has been shown to affect the availability of soil Zn to the crops (Moraghan and Mascagni Jr, 1991).

It is noteworthy that, wheat grain Zn concentration of the Zn-untreated plot (T1) was >20 mg/kg, although the concentration of plant available Zn in the test soil (0.44 mg Zn/kg) was below critical limit (BARC, 2012). Usually, Zn concentration in the grain and straw of wheat crop grown in Zn deficient field soils are found to be around 10 mg/kg (Cakmak *et al.*, 1996b; Frossard *et al.*, 2000; Cakmak, 2008; Cakmak *et al.*, 2010; Kutman *et al.*, 2010). There may be several reasons behind higher shoot Zn in the test condition including: a) supply of Zn from fertilizers applied for major nutrients, particularly, triple super phosphate (McBride and Spiers, 2001), b) contribution from the residue of the previous crops (Norouzi *et al.*, 2014), and c) genetic efficiency of the wheat variety (BARI Gom 26) to translocate root Zn to the shoot of the plant as well as its tolerance to Zn deficiency. Genetic capacity to tolerate Zn deficiency has been reported earlier in many wheat genotypes by others (Cakmak *et al.*, 1999b; Cakmak *et al.*, 2001).

The highest wheat straw Zn was exhibited by T4 (33.4 mg/kg) in the first year, which was significantly higher than the control plot (Table 4.6). Increase in wheat straw Zn due to Zn application agrees with the findings observed by others (Cakmak *et al.*, 1996a,b; Kutman *et al.*, 2010). However, in the 2nd year, the effect of Zn and B application on straw Zn was not significant, although considerably higher concentration (35.3 mg/kg) was observed in T3. The mean straw Zn concentration of the 1st year (28.2 mg/kg) was almost similar to that of the 2nd year (29.6 mg/kg). The range of grain and straw Zn concentration of wheat found in the present study agreed well with those reported in the literature (Talukder *et al.*, 2011; Prasad *et al.*, 2014; Biswas *et al.*, 2015).

4.2.1.4 Plant Zn uptake

As with Zn concentration, the uptake of Zn by wheat grain increased significantly due to the application of Zn and B during the 1st year (Table 4.7). All the treated plots showed significantly higher grain uptake than that of the untreated plot. The highest uptake was observed in T2 (105 g/ha). Likewise, there was slight increase of grain Zn uptake in the treated plots (T2 and T4) during the second year, although the response was not significant.

The mean grain Zn uptake by BARI Gom 26 was higher in the second year (102 g/ha) than that of the first year (93 g/ha). This might be due to the increase in the availability of the nutrients due to changes in climatic conditions as mentioned earlier.

Table 4.7 Effect of Zn and B application on Zn uptake of wheat (BARI Gom 26) in the wheat-jute-T.Aman rice cropping pattern.

Treatment	Year-1			Year-2		
	Grain[a]	Staw[a]	Total	Grain[a]	Staw[a]	Total
T1=Zn_0B_0[*]	73c	108b	181	76b	118b	194
T2=Zn_2B_0	105a	147a	252	104a	128b	232
T3=$Zn_4B_{1.5}$	93b	100b	193	115a	170a	285
T4=Zn_6B_3	100ab	136a	236	112a	120b	232
$LSD_{(0.05)}$	11	22	-	12	24	-
Mean	93	121	216	102	144	236
CV%	6.2	12.0	-	9.2	10.5	-

[a] Means followed by same letter are not significantly different.

[*] Subscripts denote rate of Zn and B (kg/ha).

As with uptake in wheat grain, the uptake of Zn in wheat straw was also significantly affected by Zn and B application in the 1st year (Table 4.7). The highest uptake (147 g/ha) was exhibited by T2 followed by T4 (136 g/ha). In the 2nd year, however, the effect of Zn and B on Zn uptake was not significant. The highest straw uptake (170 g/ha) was observed in T3. The mean straw uptake was higher in the second year than that of the 1st year (Table 4.7). Total Zn uptake (grain + straw) varied from 181 g/ha recorded in T1 to 252 g/ha in T2 in the 1st year and in the 2nd year it ranged from 194 g/ha in T1 to 285 g/ha in T3. Increases in wheat straw Zn uptake due to Zn addition has been reported by many authors (Cakmak *et al.*, 1996a; Kalayci *et al.*, 1999; Rengel *et al.*, 1999; Behera *et al.*, 2008) while Curtin *et al.* (2008) reported a lack of response by wheat to Zn application.

It was noted from Table 4.7 that 43-46% of the total Zn was accumulated in wheat grain. In this respect, Maqsood *et al.* (2009) reported that 48 to 62% of absorbed Zn was stored in the wheat grain. In contrast, Dang *et al.* (2010) reported that 58% of the absorbed Zn in wheat plant accumulated in the grain. The variation of accumulation in different plant parts might be due to varietal differences.

4.2.1.5 Plant B concentration

The grain B concentration of wheat (BARI Gom 26) increased significantly from that of the control due to the application of Zn and B application in the first year of experiment (Table 4.8).

Table 4.8 Effect of Zn and B application on B concentration of wheat in wheat-jute-T.Aman rice cropping pattern.

Treatment[*]	Grain B conc. (mg/kg)[a]		Straw B conc. (mg/kg)[a]	
	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0	4.2d	6.1a	13.3b	44.3b
T2=Zn_2B_0	6.5c	5.7ab	10.9c	39.3b
T3=$Zn_4B_{1.5}$	10.4a	2.9c	19.2a	53.7a
T4=Zn_6B_3	9.4b	4.6b	18.0a	45.3b
$LSD_{0.05}$	0.61	1.2	1.99	6.7
Mean	7.6	4.8	15.4	45.7
CV(%)	4.0	12.9	6.5	7.3

[a] Means followed by same letter are not significantly different.
[*] Subscripts express rate of Zn and B (kg/ha).

The highest grain B (10.4 mg/kg) was observed in treatment T3 with Zn@4 kg/ha and B@1.5 kg/ha followed by T4 with Zn@6 kg and B@3 kg/ha (9.4 mg/kg). Conversely, in the 2nd year, grain B in the treated plots (2.9 - 5.7 mg/kg) was not higher than the control treatment (6.1 mg/kg). Moreover, the mean grain B was quite lower in the 2nd year (4.8 mg/kg) than that of the 1st year (7.6 mg/kg). Thus, the effect of Zn and B application on grain B concentration was not consistent all the time in the field under study.

Increase in grain B concentration of wheat due to B addition was also observed by others (Johnson *et al.*, 2005; Debnath *et al.*, 2011; Nadeem *et al.*, 2019). However, there are variation in the response to Zn and B depending on soil properties, crop species and variety.

The concentration of wheat straw B increased significantly due to Zn and B application both the years (Table 4.8). The treatment with higher B rates (T3 and T4) showed higher straw B concentration (18.0 - 19.2 mg B/kg) than that of the control or lower B treatment (T2). It is noteworthy that straw B concentration of wheat was unusually higher (39 to 54 mg/kg) in the second year causing higher B uptake in straw. High B level may cause toxicity to plants and, in turn, to the animals. However, visual symptoms of B toxicity did not appear despite the high B content of wheat straw. Also, it can happen that the straw B was not translocated to the edible part (grain) proportionately; and there was no injury symptom or reduction in grain yield (section 4.2.1.2). Rather, the range of grain B agrees well with that stated by Gupta (2007). The reason for higher B accumulation in the vegetative part of wheat is not known. However, soil and climatic factors might have been responsible for making soil B highly available for plant uptake. Sudden increase in the irrigation water B concentration is also possible due to anthropogenic reasons causing increased uptake of B by the standing crop. In general, the measured B concentration of irrigation water of the experiment field was 0.08 mg/l which was below the toxicity or injury level for wheat as reported by Gupta *et al.* (1985). Lower grain B in the plants with high straw B may be due to immobility of the accumulated B in the plant. According to Gupta (2007), B translocates readily in the xylem, but once in the leaves, it becomes one of the least mobile micronutrients. Wheat crop may sometimes exhibit tolerance to excess B. Tolerance of wheat to B toxicity was reported earlier by other researchers (Gupta *et al.*, 1985; Paull *et al.*, 1988).

4.2.1.6 Plant B uptake

Significant effect of Zn and B application on grain B uptake was observed in the first year of the experiment (Table 4.9). The highest uptake was observed in T3 (32.1 g/ha) followed by T4 (27.3 g/ha).

The highest grain B uptake was observed in T3 (32.0 g/ha) followed by T4 (27.4 g/ha). In the 2nd year, Zn and B treatments also increased grain B uptake significantly. The T2 treatment recorded the highest B uptake (16.0 g/ha). However, the B uptake was higher in the B control plot compared to T3 and T4 treatments. This might be due to the contribution of the major nutrients (N, P, and K) applied to the crop. Das *et al.* (2019) reported as much as 15% increase in B availability due to NPK+ farmyard manure fertilization in a long-term experiment with nine crops. Thus, the effect of B on wheat crop nutrition under field condition is not always visible in comparison to that of the major nutrients.

During the first year of experiment, straw B uptake was significantly higher in T3 and T4 (Table 4.9). In the 2nd year, boron uptake in wheat straw was unusually higher (> 150 mg/kg), as mentioned earlier. Interestingly, although the concentration and uptake of B in straw was higher, it was not translocated to grain to that extent (Table 4.9).

Table 4.9 Effects of Zn and B application on B uptake of wheat in the wheat-jute-T. Aman rice cropping pattern.

Treatment[*]	Year-1[a]			Year-2[a]		
	Grain	Straw	Total	Grain	Straw	Total
			B uptake (g/ha)			
T1=Zn_0B_0	10.9d	57.5b	68.4	12.7ab	199b	211.7
T2=Zn_2B_0	19.6c	52.9b	72.5	16.0a	181b	197.0
T3=$Zn_4B_{1.5}$	32.0a	77.6a	109.6	9.1b	259a	268.1
T4=Zn_6B_3	27.4b	73.3a	100.7	11.4b	185b	196.4
$LSD_{(0.05)}$	1.9	13.6	-	6.2	46	-
Mean	22.5	65.3	87.8	12.3	206	218.3
CV%	4.2	9.5	-	22.0	11.2	-

[a] Means followed by same letter are not significantly different.
[*] Subscripts express rate of Zn and B (kg/ha).

The total B uptake (grain + straw) in the 1st year ranged from 68.5 g/ha noted in T1 to 109.6 g/ha in T3 and that uptake value in the 2nd year was 196.4 g/ha in T4 to 268.1 in T3. The percent of mean B uptake by wheat grain in total aboveground B uptake (grain+sraw) was 33% in the first year and 10% in the 2nd year. The values are consistent with the findings of Boparai and Manchanda (2018). It is observed that the majority of the B absorbed by wheat crop remains in the leaf and straw. This is in agreement with the results of Gupta (2007).

4.2.2 Effects of Zn and B on jute

4.2.2.1 Yield components

Jute (cv. JRO 524) was the second crop of the pattern Wheat-Jute-T. Aman rice. The current and residual effect of Zn and B application on jute was evaluated and presented in Table 4.10. There was no effect of Zn and B application on the height of jute plant (Table 4.10). The mean plant height was slightly higher in the 2nd year (259 cm) than 1st year (250 cm). This may be due to the variation in climatic factors as mentioned earlier.

The effect of Zn and B application on the yield of jute stick was significant in the first year (Table 4.10). The highest stick yield was observed in T3 (4.41 t/ha) followed by T4 (4.33 t/ha). In the second year, the yield difference among the treatments was not significant. The highest stick yield (4.83 t/ha) was observed in T2.2. However, the yield increase was not consistent with the rate of Zn application. Increase in jute fiber yield and plant height due to Zn addition was reported by Ahmed and Majlis (1983).

Table 4.10 Effects of Zn and B application on the yield and yield parameters of jute (cv. JRO 524) under Wheat-Jute-T.Aman rice cropping pattern.

Treatment		Plant height (cm)		Stick yield (t/ha)[b]		Fiber yield (t/ha)[b]	
Wheat*	Jute	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0	T1=Zn_0B_0	258	262	3.23bc	4.49ab	1.80bc	2.49
T2=Zn_2B_0	T2.1=Zn_0B_0	246	256	2.73c	4.01b	1.39c	2.42
	T2.2=Zn_2B_0	243	254	3.55b	4.83a	1.94abc	2.69
	T2.3=$Zn_2B_{1.5}$	257	253	2.93bc	4.52ab	1.60c	2.46
T3=$Zn_4B_{1.5}$	T3=Zn_0B_0	238	262	4.41a	4.32ab	2.31ab	2.56
T4=Zn_6B_3	T4=Zn_0B_0	255	265	4.33a	4.30ab	2.64a	2.65
LSD $_{(0.05)}$		NS	NS	1.05	0.59	0.40	NS
Mean		250	259	3.55	4.41	1.95	2.54
CV%		5.2	7.2	10.27	4.7	12.9	6.6

[b] Means followed by same letter are not significantly different.

*Subscripts of Zn and B denote rate of application (kg/ha).

The average yield in the 2nd year (4.41 t/ha) was higher than that of the 1st year (3.55 t/ha). This might be due to variation in factors other than Zn and B like rainfall and temperature in the two years.

4.2.2.2 Crop yield

The highest fiber yield of jute was observed in T4 (2.64 t/ha) which was significantly higher than control, in the first year (Table 4.10). Fiber yields of T2.2 and T3 were statistically similar to T4. Like stick yield, the trend of fiber yield increase was not consistent with the Zn and B application rate. Unlike the results of the first year, fiber yield was not affected by Zn and B application in the second year (Table 4.10). The yield of the treated plots was very close to each other and ranged between 2.42 and 2.69 t/ha.

Residual effect of applied Zn and B in wheat at higher rates (T3 and T4) was observed in stick and fiber yield of jute in the 1st year, with no added Zn and B in jute (current crop) (Table 4.6). Likewise, in the second year, the application of Zn/B at higher rates (T3 and T4) in wheat exhibited statistically similar yield of jute stick and fiber to that of the plots with repeated application of the nutrients to both crops (wheat and jute). However, a fresh addition of Zn and B resulted in better yield than the residual effect. Moreover, frequent application helps build up soil Zn. This is in accordance with the findings of Singh and Abrol (1986) who reported that frequent application of low doses resulted in a higher build-up of available Zn and proved more beneficial than a single application of equivalent amount. However, in general, application of Zn @ 4 - 6 kg/ha in wheat is sufficient for both the crops in the cropping pattern. Similar findings with residual effects of Zn and B were reported in Cumilla district with the same treatment packages with different crops (Sarker *et al.*, 2019). The soils of the two regions, however, differed in characteristics.

4.2.2.3 Plant Zn concentration

The concentration and uptake of Zn in jute plant due to the direct and residual effect of Zn and B application is shown in Table 4.11. No significant changes were observed in plant Zn concentration in the first year, although T4 (Zn@ 6 kg/ha in wheat) showed slightly higher Zn than the other treatments.

Table 4.11 Effect of Zn and B application on the concentration and uptake of Zn in Jute (JRO-524) in wheat-jute-T.Aman rice cropping pattern.

Treatment		Plant Zn conc. (mg/kg)[a]		Plant Zn uptake (g/ha)[a]	
Wheat	Jute	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[b]	T1=Zn_0B_0	34	19c	108ab	86d
T2=Zn_2B_0	T2.1=Zn_0B_0	28	24bc	77b	101d
	T2.2=Zn_2B_0	28	25bc	100b	123bc
	T2.3=$Zn_2B_{1.5}$	32	31b	93b	141b
T3=$Zn_4B_{1.5}$	T3=Zn_0B_0	30	29b	130ab	125bc
T4=Zn_6B_3	T4=Zn_0B_0	36	45a	156a	193a
$HSD_{(0.05)}$		NS	7.6	54.9	33
Mean		31.3	29.0	111	128
CV%		13	9.2	17	9.1

[a] Means followed by same letter are not significantly different.

[b] Subscripts express rate of Zn and B (kg/ha)

However, in the following year, Zn and B addition gradually and significantly increased jute tissue Zn concentration with T4 exhibiting significantly higher Zn (45 mg/kg) than Zn-control (19 mg/kg) or other Zn-treated plots (24 - 31 mg/kg). Ahmed and Majlis (1983) reported positive response of jute to applied Zn. Similarly, Maitra et al. (2000) observed significant response of jute to Zn addition along with K. On the other hand, Ali and Razzaque (1986) did not find any effect of Zn on jute. Residual effect of Zn is well documented in the literature. Bell and Dell (2008) reported in their review that the amount of Zn and other micronutrient fertilizers may remain effective in the soil for many years of crop production. For example, according to Brennan (2005), a single Zn application of 0.75 kg Zn/ha, in low-Zn soils in south-west Australia, would support from six and to an infinite number of wheat crops depending on grain yield, Zn sorption capacity of soil, and the Zn impurities in P fertilizers.

4.2.2.4 Plant Zn uptake

Significant effect of Zn and B on Zn uptake by jute was observed in both the years (Table 4.11). The highest uptake was observed with T4 in both the years (156 and 193 mg/kg), followed by T3 (130 mg/kg) in the 1st year and T2.3 (2 kg Zn/ha in both the crops plus 1.5 kg B/ha in jute) (141 mg/kg) in the 2nd year. In the 2nd year, Zn uptake gradually increased (97 to 142 mg/kg) with repeated application of Zn and B. The average uptake was slightly higher in the 2nd year than that of the 1st year, which might be due to variation in climatic or other environmental factor.

The residual effect of higher Zn application rate (4 - 6 kg/ha) applied in wheat was clearly reflected in plant Zn concentration and uptake (Table 4.11). The highest Zn uptake was observed in both the years with T4 treatment, in which Zn was applied in wheat @ 6 kg/ha. However, the effect of T3 (4 kg Zn/ha in wheat) was statistically similar to T2.2 and T2.3, indicating that similar output can be achieved by applying Zn @ 4 to 6 kg/ha in wheat crop or repeated application of Zn @ 2 kg/ha in every crop.

Increased tissue Zn in jute crop may play role in improving human Zn-nutrition since jute leaf is consumed as a popular vegetable in Bangladesh.

4.2.2.5 Plant B concentration

The effect of Zn and B application in wheat and jute on the concentration and uptake of B in jute stick is presented in Table 4.12. It is observed that in the first year of experiment, stick B conc. (19.7 mg/kg) and uptake (87 g/ha) was significantly higher in T3 treatment ($Zn_4B_{1.5}$) (Table 4.12). In the 2nd year, the effect of Zn and B application was not significant.

4.2.2.6. Plant B uptake

It is seen from Table 4.12 that in the first year of experiment, stick B uptake (87 g/ha) was significantly higher in T3 ($Zn_4B_{1.5}$). In the 2nd year, the effect of Zn and B application was not significant although higher stick B uptake (88 g/ha) was observed in T2.2. The mean stick B uptake was greater in the second year than that of the previous year due to higher stick yield.

The residual effect of the Zn and B applied at higher rates (4-6 kg/ha) in wheat increased jute stick B uptake significantly in the 1st year (Table 4.12). On the other hand, repeated application of Zn@ 2 kg/ha both in wheat and jute exhibited increased stick B uptake in the 2nd year.

Table 4.12 Effect of Zn and B application on B concentration and uptake in Jute (JRO-524).

Treatment		Stick B conc. (mg/kg)[a]		Stick B uptake (g/ha)[a]	
Wheat	Jute	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[+]	T1=Zn_0B_0	14.3b	13.7	43c	62
T2=Zn_2B_0	T2.1=Zn_0B_0	13.0b	16.7	34c	67
	T2.2=Zn_2B_0	11.7b	18.0	43c	88
	T2.3=$Zn_2B_{1.5}$	11.0b	14.3	31c	65
T3=$Zn_4B_{1.5}$	T3=Zn_0B_0	19.7a	14.0	87a	61
T4=Zn_6B_3	T4=Zn_0B_0	15.0b	14.1	68b	60
$HSD_{(0.05)}$		4.5	NS	17.6	NS
Mean		14.1	15.1	51.1	67.3
CV%		11.2	17.5	12.2	16.4

[a]Means followed by same letter are not significantly different. [+] Subscripts express rate of Zn and B (kg/ha).

4.2.3 Effects of Zn and B on T. Aman rice

4.2.3.1 Yield components

The effect of Zn and B application on the yield parameters of T. Aman rice (BRRI dhan49) is presented in Table 4.13. The residual effect of Zn and B applied in wheat and jute on T. Aman rice was also evaluated. Following is a brief discussion on the individual parameters.

In the first year, the number of grains per spike of BRRI dhan49 varied insignificantly from 91 to 121, (Table 4.13). In the second year, the effect of Zn and B was significant, the highest number of grains (126) being observed in T2.3.1. The number of grains in T3 was the lowest among all the treatments. Thus, the variation of grains/spike of T. Aman rice was not consistent with the variation of Zn and B application rates. The residual effect of Zn/B applied in wheat and jute was not reflected clearly on this parameter (Table 4.13).

Plant height of BRRI dhan49 was significantly higher in T2.3.1 (99 cm), T3.2 (100 cm) and T4 (99 cm) treatments than the control (93 cm), in the first year of the experiment (Table 4.13). In the second year, there was no significant effect of Zn and B on plant height, showing a range of 98 - 106 cm over the treatments.

The weight of 1000-grains of BRRI dhan49 did not vary significantly due to the application of Zn and B in either of the years (Table 4.13). The 1000-grain weight ranged from 18.8 to 23.9 g in the first year and from 21.3 to 23.9 in the second year of the experiment.

4.2.3.2 Crop yield

The grain yield of T. Aman rice (third crop of wheat-jute-rice pattern) is presented in Table 4.13. In the first year, grain yield was significantly influenced by Zn application in the previous and current crop, but the yield differences among the treatments were not significant. Fageria *et al.* (2011) also reported similar result in a pot study with rice.

The highest grain yield was observed in T4 (4.36 t/ha) which was significantly higher than the control plot (T1) only. It was observed from the Table 4.13 that, in general, grain yield of BRRI dhan49 was higher in T2.2.2 to T4 (>4 t/ha) than the treatments T2.1.1 to T2.2.1 (<4 t/ha). It was observed that grain yield gradually increased from T2.1.1 (Zn applied in the 1st crop only) to T2.3.2 (Zn and B applied in the second and third crop) due to different patterns of Zn dose in T2.

In both sets of T2.1 and T2.2 treatments, the higher grain yield was observed when Zn was freshly applied in T. Aman rice (current crop) (Table 4.13). This is in agreement with Brennan and Bolland (2006), who suggested more frequent Zn application in intensive cropping system for sustained crop yield. In this regard, Johnson-Beebout *et al.* (2009) reported that the applied Zn fertilizer might become unavailable to plants upon flooding which necessitates repeated Zn application. The grain yield further increased in the treatment T2.3, in which B was applied in addition to Zn in the second crop (jute). Thus, the application of B should not be overlooked in the intensively cropped soils of AEZ 12, particularly soils with Zn and B deficiency. Response of rice to Zn application is widely reported in Bangladesh soils (Bhuiya *et al.*, 1981; Moslehuddin *et al.*, 1997; Hossain *et al.*, 2008). Saha *et al.* (2013) found higher response of local rice varieties followed by hybrid, aromatic and HYV rice to applied Zn at different levels of its application.

Similarly, rice responded to Zn application when the soils contain less than 0.83 mg/kg DTPA extractable Zn in the calcareous soils of Ganges River Floodplain (Rahman *et al.*, 2007). According to Slaton *et al.* (2005), application of Zn significantly increased rice grain yield in four field trials with different Zn sources and different application time. Response of rice to Zn under flooded condition has also been studied by Naik and Das (2007); and Fageria *et al.* (2011).

Table 4.13 Effects of Zn and B application on the yield and yield parameters of T.Aman rice (BRRI dhan49) in the Wheat-Jute-T.Aman rice cropping pattern.

Treatments			Grains/spike[a]		Plant height (cm)[a]		1000-Grain weight (g)		Grain yield (t/ha)[a]		Straw yield (t/ha)[a]	
Wheat	Jute	T.Aman rice	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
T1= Zn_0B_0[*]	T1= Zn_0B_0	T1= Zn_0B_0	105	98bc	93ab	98	19.43	23.27	3.56bc	3.65	6.61bcd	6.17e
T2= $Zn_2B_{1.5}$	T2.1= Zn_0B_0	T2.1.1= Zn_0B_0	91	94bc	83b	104	23.90	21.30	3.02c	3.96	6.48cde	6.84bcde
		T2.1.2= Zn_2B_0	92	98bc	92ab	100	19.25	23.23	3.64abc	3.99	5.8e	7.22abcd
	T2.2= Zn_2B_0	T2.2.1= Zn_0B_0	108	103bc	95ab	98	20.00	22.80	3.65abc	4.18	6.28cde	7.91a
		T2.2.2= Zn_2B_0	95	105b	97ab	104	19.20	22.73	4.05ab	3.76	7.49a	6.29de
	T2.3= $Zn_2B_{1.5}$	T2.3.1= Zn_0B_0	91	126a	99a	101	18.90	21.83	4.30ab	3.81	7.07abc	7.77ab
		T2.3.2= Zn_2B_0	102	90cd	96ab	101	19.60	21.70	4.20ab	3.77	6.06de	7.25abcd
T3= $Zn_4B_{1.5}$	T3= Zn_0B_0	T3.1= Zn_0B_0	121	80d	92ab	106	18.90	22.13	4.08ab	4.00	7.42a	7.33abc
		T3.2= Zn_2B_0	110	78d	100a	100	18.83	23.87	4.10ab	3.87	6.52cde	6.60cde
T4= Zn_6B_3	T4= Zn_0B_0	T4= Zn_0B_0	103	101bc	99a	103	21.70	23.17	4.36a	4.23	7.35ab	7.65ab
HSD $_{(0.05)}$			NS	14.2	15	NS	NS	NS	0.79	NS	0.79	0.965
Mean			102	97.4	95	101	19.97	22.6	3.90	3.92	6.7	7.1
CV%			28.7	5.0	5.6	4.1	12.1	7.0	6.8	8.60	4.1	4.6

[a] Means followed by same letter are not significantly different.

[*] Subscripts denote rate of Zn and B (kg/ha).

Unlike the results of the 1st year, the application of Zn and B did not significantly affect the grain yield of BRRI dhan49 in the second year (Table 4.13). The highest yield was observed in T4 (4.23 t/ha). All the treated plots scored higher yield than that of control, although the yield difference was not significant. Thus, in the second year, there was a lack of consistency in the increase of rice grain yield with the increase in Zn and B application rates. Variation in climatic factors might have been responsible for the variation in the availability of the nutrients that may affect the changes in yield. Also, the dynamics of the major nutrients (N, P, K and S) may affect the responsiveness of the added Zn and B. According to Bell (1997), sites which have multiple deficiencies, the alleviation of one or some of them will not give a real indication of the responsiveness of plant growth to B supply. It was suggested that an experiment comprising a complete nutrient treatment and the omission of single nutrients can be an effective approach.

It is observed from Table 4.13 that in wheat-jute-rice pattern, the residual effect of a higher rate of Zn/B applied in wheat (1st crop) on T. Aman rice (3rd crop) was equivalent to the application of Zn (and B) in second (jute) and the third crop (rice). Thus Zn application at higher rates (4-6 kg/ha) in the first crop of a pattern seems to be sufficient for next two crops. Similar kind of residual effect using Zn and B in cauliflower, maize and T. Aus rice was reported by Sarker *et al.* (2019). Jahiruddin and Islam (2014) viewed that Zn application @ 4 kg/ha to the first crop would be sufficient to meet the Zn requirement for the subsequent two crops in a pattern. Brennan (2005) observed that only a little of the applied Zn had been removed in harvested grain of the subsequent crops over the next 14 years. However, in intensive cropping systems such as rice-wheat rotations, the removal of Zn in harvested crop may account for 0.50 kg Zn/ha in a single year, which necessitates either higher rates of Zn application as fertilizer or more frequent Zn applications to maintain adequate supply (Brennan, 2005; Bell and Dell, 2008).

The yield of rice straw as affected by Zn and B application is presented in Table 4.13. The effect of Zn and B application on straw yield was not clearly demonstrated in either years of the experiment. During the first year, T3.2 scored the highest straw yield (7.7 t/ha) followed by T2.2.2 (7.2 t/ha). Similarly, in the second year, the effect of Zn and B application on straw yield was not of any specific order. The highest yield was obtained with T2.3.1 (8.1 t/ha) followed by T2.2.1 (7.91 t/ha). Mean straw yield was considerably higher in the 2nd year (7.2

t/ha) than that in the 1st year (6.1 t/ha). This could be due to variation in other environmental factors.

Similar to grain yield, residual effect of Zn/B applied in the 1st crop (wheat) was reflected in T. Aman rice straw yield, although there was lack of uniformity (Table 4.13). Repetition of Zn application improved straw yield when it was applied in the second and/or third crop e.g., T2.2.2 or T3.2. The exception was T2.3.2, in which Zn application in three crops (in addition to B in two crops) did not increase straw yield. In the second year, application of Zn and B improved the straw yield significantly, particularly in the treatments with higher dose (T3.1 and T4) or higher frequency (T2.1.2, T2.2.1, T2.3.1 and T2.3.2) compared to control (Table 4.7). Thus, the variability of rate and frequency of Zn and B application did not have any regular and consistent effect on rice straw yield in the soil under trial. In a similar study conducted in Cumilla, Sarker *et al.* (2019) reported that in Cauliflower-Maize-T. Aus pattern, the application of 4.0 kg Zn/ha and 1.5 kg B/ha at a time to the first crop or 2.0 kg Zn/ha to each of the first two crops along with 1.5 kg B/ha to the first crop was adequate to achieve satisfactory yield of the crops.

The results suggested that the applied Zn and B were not fully utilized by the standing crops and its residue remained in the soil, which, in turn, become available to the next crops. Therefore, the excess application of Zn and B should be avoided through careful monitoring of soil and plant nutrients (Yang *et al.*, 2000).

4.2.3.3. Plant Zn concentration

The concentration of Zn in rice grain varied significantly due to the application of Zn and B either in previous crop or directly to the current crop during the first year (Table 4.14). However, Zn and B treatments were unable to increase grain Zn of rice significantly from that of control. The observed grain Zn concentration of BRRI dhan49 was above critical limit of 15 mg/kg according to Yoshida (1981). The highest grain Zn (25 mg/kg) was found in T3.1 (Zn@ 4 kg/ha in wheat). The control plot showed moderate grain Zn concentration (18.8 mg/kg) which was higher than that of some of the treated plots. In the same way, grain Zn varied significantly during the second year, but not according to the Zn and B application rate. The highest grain Zn concentration (26.3 mg/kg) was exhibited by T2.1.1 having Zn@ 2 kg/ha in wheat only. However, rice grain Zn concentration of most of the treatments did not differ significantly from the control plot. Increases in rice grain Zn upon Zn fertilization has been reported by many researchers (Slaton *et al.*, 2005; Jiang *et al.*, 2008; Fageria *et al.*, 2011; Hafeez *et al.*, 2013; Fageria, 2014).

On the other hand, inability of the added Zn to increase Zn concentration in rice grain has also been reported, particularly in Zn deficient soils (Duxbury *et al.*, 2006; Wissuwa *et al.*, 2008). Duxbury *et al.* (2006) attributed immobilization of the applied Zn in the soil after flooding for lack of increase in grain Zn, while Wissuwa *et al.* (2008) observed that the accumulated Zn in rice shoot was not translocated to grain adequately.

Straw Zn concentration of BRRI dhan49 was not strongly affected by the application of Zn and B (residual or direct) in the first year (Table 4.14). The concentration found in the control plot (32.3 mg/kg) was statistically similar to the concentration of all the other treatments. In other words, the plots with Zn and B treatments did not show any better effect than the untreated plot. Similarly, in the second year, there was no significant effect of Zn and B on straw Zn concentration. As mentioned earlier, inability of the applied Zn to increase rice tissue Zn was reported by other researchers (Duxbury *et al.*, 2006; Jiang *et al.*, 2008; Wissuwa *et al.*, 2008). The mean straw Zn of the second year (31.3 mg/kg) was slightly higher than that of the first year (28.9 mg/kg), leading to higher straw Zn uptake (Table 4.14). Higher uptake may be caused by increased availability due to variation in climatic factors.

4.2.3.4 Plant Zn uptake

The grain Zn uptake in BRRI dhan49 differed significantly among the treatments in the 1st year (Table 4.14). The highest uptake was recorded in T3.1 (97 g/ha), followed by T2.2.2 (91 g/ha). However, the difference in the grain Zn uptake was not clearly influenced by Zn application rate; either direct or residual (Table 4.14). Yet, it is observed from the Table that application of Zn@4 to 6 kg/ha in first crop (wheat) exhibited statistically similar grain Zn uptake to repeated application of Zn@2 kg/ha to the next crops. The average grain Zn uptake of BRRI dhan49 was almost similar (70 and 76 g/ha) in the two years.

Uptake of Zn in rice straw was not significantly influenced by the direct or residual application of Zn and B (Table 4.14). Some of the treated plots exhibited higher uptake than others but none was significantly different from values of the Zn-untreated plot. This could be due to translocation of most of the absorbed Zn to rice grain from rice straw.

Table 4.14 Effect of Zn and B application on Zn concentration and uptake in T.Aman rice (BRRI dhan49) in the wheat-jute-T.Aman rice cropping pattern.

Wheat	Jute	T.Aman rice	Grain Zn conc. (mg/kg)[a]		Straw Zn conc. (mg/kg)[a]		Grain Zn uptake (g/ha)[a]		Straw Zn uptake (g/ha)[a]		Total Zn uptake (g/ha)	
			Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[+]	T1=Zn_0B_0	T1=Zn_0B_0	18.8abc	20.0bc	31.6abc	33.7abc	65bcd	73bc	214abc	255a	279	328
T2=$Zn_2B_{1.5}$	T2.1=Zn_0B_0	T2.1.1=Zn_0B_0	12.3c	26.3a	27.0cd	22.7e	39d	104a	171cde	172b	210	276
		T2.1.2=Zn_2B_0	14.7bc	14.2c	25.6d	38.7a	53cd	58c	148e	268a	201	326
	T2.2=Zn_2B_0	T2.2.1=Zn_0B_0	18.0abc	16.0bc	26.0d	32.7abc	63bcd	67bc	161de	263a	224	330
		T2.2.2=Zn_2B_0	21.7ab	18.3bc	33.0ab	35.3ab	91ab	69bc	247ab	217ab	338	286
	T2.3=$Zn_2B_{1.5}$	T2.3.1=Zn_0B_0	15.3bc	19.1bc	35.7a	29.3bcd	63bcd	74bc	248a	235a	311	309
		T2.3.2=Zn_2B_0	19.0abc	18.2bc	28.7bcd	31.3bcd	78abc	69bc	166de	250a	244	319
T3=$Zn_4B_{1.5}$	T3=Zn_0B_0	T3.1=Zn_0B_0	25.0a	21.6ab	27.0cd	25.0de	97a	86ab	200cd	181b	297	267
		T3.2=Zn_2B_0	17.4abc	21.7ab	29bcd	26.7cde	71abc	81ab	188cde	180b	259	261
T4=Zn_6B_3	T4=Zn_0B_0	T4=Zn_0B_0	16.3abc	21.0ab	27.5cd	33.7abc	71abc	89ab	202bcd	268a	273	357
	$HSD_{(0.05)}$		7.7	5.7	5.2	7.0	30	25	45	54	-	-
	Mean		17.9	19.7	29.1	30.9	69	77	195	229	263.6	305.9
	CV(%)		14.7	9.9	6.2	7.7	15	11	8	8	-	-

[a] Means followed by same letter are not significantly different.
[+] Subscripts express the rate of Zn and B (kg/ha)

The average uptake in the 2nd year (229 g/ha) was higher than that of the 1st year (195 g/ha), which reflects a higher straw yield in 2nd year.
Residual effect of higher Zn application (6 kg/ha) in wheat was reflected in rice grain Zn uptake clearly in the second year (Table 4.14). Similar effect was also found on the yield of BRRI dhan49, which suggests that application of Zn @ 4-6 kg/ha in wheat is sufficient for the next crops. However, in most of the cases, repeated Zn application in the 2nd/3rd crop showed better grain Zn than application in the 1st crop only (Table 4.14). Residual effect of applied Zn is well documented. According to Brennan (2005), only 7% of the Zn applied @ 3 kg/ha had been removed in harvested grain over the subsequent 14 years. However, more frequent application of Zn is necessary in intensive cropping.

Total Zn uptake by rice (grain + straw) was found to vary between 201 - 338 g/ha in the 1st year and 261 - 357 g/ha in the 2nd year across the treatments (Table 4.14). On an average, Zn uptake in rice grain was 28% of the total uptake (Table 4.14). The rest of the tissue Zn was retained in the straw. This is in agreement with the findings of Doberman and Fairhurst (2000) who reported that a rice crop yielding 6 t/ha takes up about 0.3 kg Zn/ha, of which 60% remains in the straw at maturity. Fageria *et al.* (2011) reported that translocation of Zn in the grain was about 15% of the total Zn uptake in the plants. However, there may be variation in the quantity of Zn uptake by rice due to varietal difference.

4.2.3.5 Plant B concentration

The concentration of B in grain of BRRI dhan49 varied significantly due to the application of Zn and B either directly to rice or as residual effect of that applied in wheat and jute (Table 4.15). However, the effect did not follow the variation in the application rates of Zn and B. The highest grain B concentration (8.6 mg/kg) was observed with T2.3.1 followed by that of T4 (7.4 mg/kg). Rest of the treatments exhibited <6 mg/kg of B. In the 2nd year, the effect of immediate and repeated application of Zn and B in the crops was slightly observed in T2. Again, there was no consistency in the variation of grain B concentration among the treatments. The highest grain B (7.1 mg/kg) was found with T2.2.1. The yearly average grain B concentration was almost the similar.

Similar to grain B concentration, the effect of Zn and B application was significant on straw B concentration, but not as per the rate of application (Table 4.15).

Table 4.15 Effect of Zn and B application on B concentration and uptake of T. Aman rice (BRRI dhan49) in Wheat-Jute -T.Aman rice cropping pattern.

Treatments (kg/ha)			Grain B (mg/kg)[a]		Straw B (mg/kg)[a]		Grain B uptake (g/ha)[a]		Straw B uptake (g/ha)[a]		Total B uptake (g/ha)	
Wheat	Jute	T.Aman rice	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[+]	T1=Zn_0B_0	T1=Zn_0B_0	4.2d	4.7bc	16.7ab	12.7c	15.3c	16.0c	103abc	68cd	118.3	84.0
T2=$Zn_2B_{1.5}$	T2.1=Zn_0B_0	T2.1.1=Zn_0B_0	4.7cd	5.7bc	19.0a	13.3c	18.3bc	17.3c	130ab	70cd	148.3	87.3
		T2.1.2=Zn_2B_0	4.2d	5.8abc	15.7ab	10.7c	17.0c	22.0abc	113abc	211a	130.0	233.0
	T2.2=Zn_2B_0	T2.2.1=Zn_0B_0	5.9bc	7.1a	12.4b	24.3a	23.0abc	26.1a	100abc	154ab	123.0	180.1
		T2.2.2=Zn_2B_0	5.0cd	5.4bc	18.3a	16.3abc	18.3bc	22.1abc	115abc	120bc	133.3	142.1
	T2.3=$Zn_2B_{1.5}$	T2.3.1=Zn_0B_0	8.6a	5.1bc	12.3b	9.3c	32.7a	22.0abc	96abc	43d	128.7	65.0
		T2.3.2=Zn_2B_0	4.6cd	6.0ab	18.7a	21.7ab	17.0c	25.2ab	135a	116bc	152.0	141.2
T3=$Zn_4B_{1.5}$	T3=Zn_0B_0	T3.1=Zn_0B_0	4.8cd	4.5c	15.7ab	16.7abc	19.3bc	18.7bc	115abc	97bcd	134.3	115.7
		T3.2=Zn_2B_0	4.9cd	5.0bc	11.7b	16.0bc	19.0bc	20.3abc	77c	126bc	96.0	146.3
T4=Zn_6B_3	T4=Zn_0B_0	T4=Zn_0B_0	7.4ab	4.9bc	11.8b	11.0c	29.0ab	21.3abc	89bc	120bc	118.0	141.3
	$HSD_{(0.05)}$		1.62	1.4	5.2	18.2	11.4	6.9	41.2	52.1	-	-
	Mean		5.43	5.4	15.2	15.2	20.9	21.1	107	95	128.2	133.6
	CV(%)		10.2	9.0	11.7	8.1	18.7	11.2	13.1	19.07	-	-

[a]Means followed by same letter are not significantly different.

[+] Subscripts express rate of Zn and B (kg/ha).

In the 1st year, the highest straw B concentration was observed with T2.1.1 followed by T2.3.2 and T2.2.2 treatments, all of which were statistically similar but slightly higher than that of the control plot (16.7 mg/kg). The following year, T2.2.1 exhibited significantly higher straw B followed by T2.3.2. Here again, treatments with higher B application rates (T3 and T4) did not show better straw B than the control. The mean straw B concentrations were the same in the two years.

4.2.3.6 Plant B uptake

The effect of Zn and B application was significant on B uptake of rice grain (Table 4.15). Just like grain B concentration, uptake of B in the rice grain was the highest in T2.3.1 treatment followed by T4 (Table 4.15). In the following year, B uptake values were rather closer to each other than that of the 1st year. The uptake was the highest in T2.2.1 (Table 4.15). The yearly of average grain B uptake values were almost the same. The increase in rice grain B due to B addition has been reported by many previous researchers (Rashid *et al.*, 2004; Atique-ur-Rehman *et al.*, 2018).

The uptake of B in rice straw was significantly affected by the application of Zn and B (Table 4.15). In the first year, T2.3.2 scored the highest B uptake (135 g/ha) followed by T2.1.1 (130 g/ha). Uptake of B in the treatments with higher Zn and B rates (T3.2 and T4) was unexpectedly low. A study of the dynamics of soil Zn and B fractions may reveal some facts about lower B uptake. In the second year, T2.2.1 exhibited the highest uptake (154 g/ha). Here again, the repeated application of Zn in the crops did not make any significant change in straw B uptake. The mean straw B uptake was slightly higher in the 2nd year due to higher straw yield (Table 4.15). Total B uptake (grain + straw) varied from 96 - 152 g/ha in the 1st year and 65 - 233 g/ha in the 2nd year across the treatments (Table 4.15). The uptake of B in rice grain ranged from 15 to 25% of the total above ground uptake. Similar values were also reported in the literature (Fairhurst *et al.*, 2007; Rashid *et al.*, 2007).

4.3 FIELD EXPERIMENT - 2

Effects of Zn and B on Boro rice and T. Aman rice crops

A separate experiment was conducted in Ramkantapur of Rajbari sadar with similar Zn and B treatments but with different cropping pattern, namely Boro rice-Fallow-T.Aman rice with the same objectives. The concentrations of available Zn (1.52 mg/kg) and available B (0.41 mg/kg) in the test soil were optimum for the crops according to FRG-2012 (BARC, 2012). However, their availability might vary depending on the type of soil, since Zn and B might become unavailable to the plants due to reaction with soil components (Brennan, 1990). The findings are presented in the following sections.

4.3.1 Effects of Zn and B on Boro rice (BRRI dhan29)

4.3.1.1 Yield components

The effect of Zn and B application on the yield and yield contributing parameters are presented in Table 4.16. It was observed from the Table that, there was no significant effect of Zn and B application on the number of grains per spike of BRRI dhan29 in either year. The average grain/spike was 136 in the 1st year and 133 in the 2nd year of experiment.

Table 4.16 Effect of Zn and B on the yield components of Boro rice (BRRI dhan29) in Boro-Fallow-T.Aman cropping pattern.

Treatments[a]	Grains/spike		Plant height (cm)		1000-Grain wt. (g)[a]		Grain yield (t/ha)[a]		Straw yield (t/ha)[a]	
	Yr-1	Yr-2	Yr-1	Yr-2	Yr-1	Yr-2	Yr-1	Yr-2	Yr-1	Yr-2
T1=Zn_0B_0[+]	141	134	94	100	21.45	19.50a	6.13	6.22a	5.87	6.20b
T2=Zn_2B_0	139	123	97	102	22.31	19.24a	6.53	6.92ab	6.62	7.33a
T3=$Zn_4B_{1.5}$	131	135	95	102	21.65	19.45a	6.49	7.49b	6.01	6.71b
T4=Zn_6B_3	133	141	95	98	20.80	17.52b	6.19	7.56b	6.49	6.16b
$LSD_{(0.05)}$	NS	NS	NS	NS	NS	1.49	NS	0.36	NS	0.74
Mean	136	133	95	100	21.55	18.93	6.34	7.05	6.25	6.60
CV%	7.8	12	3.7	1.4	6.7	4.0	5.1	2.6	5.3	5.7

[a] Means followed by same letter are not significantly different.
[+] Subscripts of Zn and B denotes rate of application (kg/ha)

Similar to grains per spike, plant height of BRRI dhan29 did not respond to Zn and B application (Table 4.16). The height of the plants ranged from 94 to 97 cm and 98 to 102 cm in the 1st and 2nd year, respectively.

During the 1st year, 1000-grain weight of BRRI dhan29 was not affected by Zn and B application (Table 4.16). The range of 1000-grain weight was from 20.80 to 22.31 g. During the second year, grain weight of 1000 grains in T4 (17.52 g) was significantly lower than T1, T2 and T3 (average 19.40 g). Low 1000-grain weight in high Zn treatment is unusual. However, smaller sample size may sometime show greater variation compared to larger sample size.

4.3.1.2 Crop yield

During the first year, Zn and B application did not make any significant effect on the grain yield of BRRI dhan29 (Table 4.16). However, the highest yield (6.53 t/ha) recorded by T2 (Zn@4 kg/ha + B @ 1.5 kg/ha) was 0.4 t/ha higher than that of the control plot (no Zn or B). In contrast to the first year, application of Zn and B significantly increased the grain yield of BRRI dhan29 in the treated soils during the second year (Table 4.16). The highest yield (7.56 t/ha) was exhibited by T4 followed by T3. However, the yield difference within the treatments was not significant. Thus, although the positive effect of Zn and B application on the grain yield of BRRI dhan29 was found, the effect was not visible under field condition every year. This is noteworthy that a significant response to Zn and B application was observed in a soil where Zn/B status was sufficient for plants. This indicates the availability of Zn and B may decrease in the experimental soil due to reactions with soil components. Also, different forms of soil Zn might have been in equilibrium with each other and the solubility (intensity factor) of Zn was controlled and maintained by the activity of the labile fractions (capacity factor) in the soil.

Similar to grain yield, straw yield of BRRI dhan29 increased due to the application of B and Zn in the first year, although the variation was not significant (Table 4.16). The highest yield was observed with T2 (6.62 t/ha), followed by T4 (6.49 t/ha). In the following year, a significant increase in straw yield was observed in T2. Considering the results, it was found that the addition of 2 kg Zn with or without B is beneficial for rice straw yield.

4.3.1.3 Plant Zn concentration

The concentration of grain Zn of BRRI dhan29 was not affected by the application of Zn and B in the first year (Table 4.17). In contrast, the treated plots showed significantly higher grain Zn conc. (21.3 - 23.3 mg/kg) than that of the control (17.7 mg/kg) in the 2nd year. Thus, the benefit of applied Zn/B was observed in the 2nd year. The mean Zn conc. of the 2nd year

(20.9 mg/kg) was slightly higher than that of the 1st year (18.8 mg/kg). Increases in rice grain Zn due to Zn fertilization by previous researchers have been cited in section 4.2.3.3.

Table 4.17 Effect of Zn and B application on Zn concentration in grain and straw of Boro rice (BRRI dhan29) in Boro rice-Fallow-T. Aman rice cropping pattern.

Treatment (kg/ha)	Grain Zn conc. (mg/kg)[a]		Straw Zn conc. (mg/kg)[a]	
	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[+]	18.3	17.7b	37.3	32.7b
T2=$Zn_2B_{1.5}$	19.0	21.3a	39.7	38.3a
T3=$Zn_4B_{1.5}$	18.3	23.3a	36.7	31.3b
T4=Zn_6B_3	19.3	21.3a	40.3	30.3b
$LSD_{(0.05)}$	NS	3.3	NS	2.6
Mean	18.8	20.9	38.5	33.2
CV%	4.3	7.9	7.8	4.0

[a]Means followed by same letter are not significantly different.

[+] Subscripts express the rate of Zn and B (kg/ha)

It is noteworthy that the grain Zn of rice increased in a soil which contained optimum Zn. This implies that Zn fertilizer should be applied to rice to get enhanced grain Zn in Low Ganges River Floodplain soil.

Similar to grain Zn, straw Zn concentration of BRRI dhan29 was not affected by Zn and B treatment in the 1st year, although T4 exhibited higher Zn than control (Table 4.13). In the 2nd year, T2 ($Zn_2B_{1.5}$) exhibited significantly higher straw Zn (38.3 mg/kg) than other treatments. As mentioned earlier, increase in rice straw Zn concentration due to addition of Zn was observed by others (Slaton *et al.*, 2005; Fageria *et al.*, 2011; Hafeez *et al.*, 2013). The mean straw Zn of the 1st year (38.5 mg/kg) was higher than that of the 2nd year (33.2 mg/kg). Thus, it is evident that the concentration of Zn in rice plant tissue is a variable characteristic.

4.3.1.4 Plant uptake of Zn

Zinc uptake by grain of BRRI dhan29 increased significantly in the treated soils from the untreated soil due to the application of Zn and B, both the years (Table 4.18). During 1st year, the highest uptake was observed in T4 (147 g/ha) followed by T3 (138 g/ha), while in the following year, T3 exhibited the highest uptake (152 g/ha) followed by T2 (140 g/ha). Similar to grain Zn uptake, effect of Zn and B application on straw Zn uptake was also significant (Table 4.18). However, the effect was shown by low Zn/B dose (T2), not the higher doses (T3 and T4).

Table 4.18 Effect of Zn and B application on Zn uptake in grain and straw of Boro rice (BRRI dhan29) in Boro rice-Fallow-T. Aman rice cropping pattern.

Treatment (kg/ha)	Grain Zn uptake (g/ha)[a]		Straw Zn uptake (g/ha)[a]		Total Zn uptake (g/ha)	
	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[+]	110c	118c	231b	181b	341	299
T2=$Zn_2B_{1.5}$	126b	140ab	291a	230a	417	370
T3=$Zn_4B_{1.5}$	138ab	152a	246b	181b	384	333
T4=Zn_6B_3	147a	128bc	249b	179b	396	307
$LSD_{(0.05)}$	14.0	14.5	40	18	-	-
Mean	130	135	254	193	385	327
CV%	5.4	5.4	7.5	4.7	-	-

[a] Means followed by same letter are not significantly different.
[+] Subscripts express the rate of Zn and B (kg/ha)

In the 1st year, the highest value (291 g/ha) was exhibited by T2 which took up 60 g/ha more Zn than the control (Table 4.18). Similarly, in the following year, T2 (252 g/ha) scored significantly higher uptake than all the treated plots. Unlike grain uptake, the straw Zn uptake was higher in the 1st year than that of the 2nd year.

4.3.1.5 Plant B concentration

The effect of Zn and B application on grain and straw B concentration is presented in Table 4.19. As mentioned earlier the soil B concentration (0.26 mg/kg) was low to medium in the test soil (BARC, 2012).

Significant effect of Zn and B application was observed in grain B concentration (Table 4.19). The highest B was exhibited by T4 (4.72 mg/kg) in the 1st year and T2 (3.43 mg/kg) in the following year. Thus, the variation in grain B concentration due to Zn and B application on Boro rice was not consistent always. Similar to grain B, straw B also varied significantly due to Zn and B application (Table 4.19). Both and T2 and T4 showed the highest straw B (52 mg/kg) in the 1st year. In the following year, T2 showed the highest B (31 mg/kg).

The mean B concentration in rice straw was much lower in the 2nd year (23 mg B/kg) than that of the 1st year (41 mg/kg). A lower concentration of straw B in the 2nd year indicates its lower availability in soil due to the effects of soil or environmental factors.

Table 4.19 Effect of Zn and B application on concentration of B in Boro rice (BRRI dhan29) in Boro-Fallow-T. Aman rice pattern.

Treatment	Grain B conc. (mg/kg)[a]		Straw B conc. (mg/kg)[a]	
	Year1	Year2	Year1	Year2
T1=Zn_0B_0[+]	3.20b	2.57b	28b	20bc
T2=Zn_2B_0	3.30b	3.43a	52a	31a
T3=$Zn_4B_{1.5}$	3.17b	2.83b	32b	18c
T4=Zn_6B_3	4.72a	2.45b	51a	23b
$LSD_{(0.05)}$	0.50	0.59	5.7	3.4
Mean	3.60	2.82	41	23
CV%	7.0	10.4	7.0	7.5

[a] Means followed by same letter are not significantly different.
[+] Subscripts express rate of Zn and B (kg/ha).

The concentration of B in rice straw was higher than optimum but not toxic for rice. Optimum leaf tissue B of rice has been reported to be 6 - 15 mg/kg while critical level for B deficiency is <3 mg/kg at maturity of rice (Doberman and Fairhurst, 2000). According to Doberman and Fairhurst (2000), the toxic level of tissue B in rice is 100 mg/kg at maturity. They also reported that excess B appears to retard grain filling of rice but with normal vegetative growth. Gupta and Cutcliffe (1984) observed that leaf tissue B of bean increased due to B application in one year but decreased in the next year and that yield reduction of bean is expected at leaf B concentration > 109 mg/kg.

4.3.1.6 Plant B uptake

In accordance with B concentration in grain, the uptake of B in Boro rice grain was the highest in T4 (36 g/ha) in the 1st year (Table 4.20). In the second year, T2 scored the highest grain uptake. Here again, the effect of higher Zn and B application rates was not equal in the two years.

In the 1st year, T2 exhibited the highest straw uptake (383 g/ha) followed by T4 (313 g/ha) (Table 4.20), both of which were significantly higher than the control. Similar to grain uptake, the highest B uptake in the 2nd year was observed in T2. Thus, there was good agreement between grain and straw B uptake.

Table 4.20 Effect of Zn and B application on uptake of B in Boro rice (BRRI dhan29) in Boro rice-Fallow-T. Aman rice pattern.

Treatment	Grain B uptake (g/ha)[a]		Straw B uptake (g/ha)[a]		Total B uptake (g/ha)[a]	
	Year1	Year2	Year1	Year2	Year1	Year2
T1=Zn_0B_0[+]	19c	17bc	176c	111c	195c	128c
T2=Zn_2B_0	22bc	23a	383a	186a	406a	208a
T3=$Zn_4B_{1.5}$	24b	19b	218c	102c	241c	120c
T4=Zn_6B_3	36a	14c	313b	138b	349b	152b
$LSD_{(0.05)}$	3.8	3.7	52	18.5	49	17
Mean	25	18	272	134	298	152
CV%	7.4	10.2	9.5	6.9	8.2	5.8

[a] Means followed by same letter are not significantly different.

[+] Subscripts express rate of Zn and B (kg/ha).

Total B uptake (grain + straw) varied from 195 - 406 g/ha in the 1st year and 120 - 208 g/ha in the 2nd year (Table 4.20). The uptake of B in rice grain ranged from 5 to 16% of the total B uptake in the shoot.

4.3.2 Effects of Zn and B on T. Aman rice (BRRI dhan49)

4.3.2.1 Yield components

The effect of Zn and B on T. Aman rice (BRRI dhan49), the second crop of the cropping pattern, is shown in Table 4.21. Descriptions of the parameters are as follows.

Application of Zn and B significantly affected the number of grains/spike of BRRI dhan49 in the first year (Table 4.21). The highest number of grains (143) was observed in T2.1 followed by T2.2. The higher rates of Zn (T3 and T4 applied to Boro rice) did not affect the number of grains in comparison to control. In the second year, grains/spike did not respond to the Zn and B application significantly. However, T3 (119) showed considerably higher grains than control (100). The mean grains/spike of the second year was much lower than that of the 1st year. Variation in the environmental factors like rainfall and temperature might be responsible for the decreased number of grains in the second year.

Plant height of BRRI dhan49 was unaffected by Zn and B application in the first year (Table 4.21). On the contrary, some effects of the nutrients on plant height were observed in the second year.

Significant difference was observed between the plant height of the control (96 cm) and treatments T2.1, T2.2 and T3.1 (105 - 109 cm).

Table 4.21 Effect of Zn and B application on the yield parameters of T. Aman rice (BRRI dhan49) in Boro-Fallow-T.Aman cropping pattern.

Treatment		Grains/spike[a]		Plant height (cm)[a]		1000-grain weight (g)		Grain yield (t/ha)[a]		Straw yield (t/ha)[a]	
Boro[*]	T. Aman	Year1	Year2	Year1	Year2	Year1	Year2	Year1	Year2	Year1	Year2
T1=Zn_0B_0	T1=Zn_0B_0	118bc	100	112	96c	19.40	23.25	3.82ab	3.87b	5.41	5.35b
T2=Zn_2B_0	T2.1=Zn_0B_0	143a	105	106	105ab	17.67	24.17	4.67ab	4.58ab	5.64	5.96b
	T2.2=Zn_2B_0	135ab	106	113	109a	17.60	23.64	4.84a	4.19ab	5.48	5.69b
T3=$Zn_4B_{1.5}$	T3.1=Zn_0B_0	101cd	119	113	105ab	20.53	24.65	4.54ab	3.72b	5.79	5.64b
	T3.2=Zn_2B_0	89d	104	112	98c	23.23	23.27	3.59b	4.47ab	4.98	7.26a
T4=Zn_6B_3	Zn_0B_0	117bc	101	115	100bc	20.83	23.44	4.17ab	5.06a	6.22	7.30a
HSD (0.05)		24	NS	NS	5.1	NS	NS	1.08	0.89	NS	0.79
Mean		117	106	112	102	19.9	23.74	4.27	4.31	5.59	6.24
CV%		7.3	12	3.0	1.8	13.0	3.9	8.95	7.3	11.8	4.5

[a] Means followed by same letter are not significantly different.

[*]Subscripts denote rates of Zn and B in kg/ha

The mean plant height of the 2nd year was considerably lower than that of the 1st year which might be due to other environmental factors.

The weight of 1000-grains of BRRI dhan49 did not respond to Zn and B application in either year (Table 4.21). The range of grain weight was 17.6 to 23.23 g with a mean of 19.9 g in the first year. In the second year, the range of grain weight was 23.25 to 24.65 g. The mean grain weight of the second year was slightly higher than that of the first year.

4.3.2.2. Crop yield

In the first year, grain yield of BRRI dhan49 increased in all the Zn and B treated plots (except T3) from that of the control, but not significantly (Table 4.21). The highest yield (4.84 t/ha) was obtained with T2.2, followed by T2.1. Similarly, in the second year, the yield of the treated plots was higher than that of the control. Unlike the first year, yield of T4 (5.06 t/ah) was significantly higher than the control (3.87 t/ha). Thus, in general, the effect of Zn and B on the grain yield of BRRI dhan49 was not consistently established. This could be due to an optimum level of Zn and B in the test soil for rice.

Straw yield of BRRI dhan49 did not show any significant effect of Zn and B application in the first year (Table 4.21). However, T4 produced considerably higher straw (6.2 t/ha) than control (5.4 t/ha). In the second year, straw yields with T3 and T4 treatments were significantly higher than the control with a yield difference of 2 t/ha. Thus, there was considerable variation in the response of the crop to Zn and B in the two years.

Similar to the Wheat-Jute-T. Aman rice cropping pattern, the residual effect of Zn and B added in Boro rice was reflected in the yield contributing parameters of succeeding T. Aman rice, particularly in the significant increase of grain and straw yield of rice in the second year (Table 4.21). Thus, it was obvious that the residue of the applied Zn remained in the soil, which, in turn, became available to the next crop. Hence, excess application should be avoided in the later crops of the pattern for economic and rational use of the micronutrient fertilizer. Jahiruddin and Islam (2014) suggested that Zn should be applied at 2 kg/ha to each crop in a rice-rice cropping pattern.

4.3.2.3 Plant Zn concentration

The effect of Zn and B application was not clearly reflected in grain Zn concentration of T. Aman rice (BRRI dhan49) in the 1st year of experiment (Table 4.22). The highest grain concentration was observed in T2.1 (24.4 mg/kg) which was similar to that of control plot.

Table 4.22 Effect of Zn and B application on Zn concentration of T.Aman rice (BRRI dhan49) in Boro-Fallow -T.Aman rice cropping pattern.

Treatment		Grain Zn conc. (mg/kg)[a]		Straw Zn conc. (mg/kg)[a]	
Boro	T.Aman	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[+]	Zn_0B_0	24.4a	19.7	23.4cd	38.3
T2=$Zn_2B_{1.5}$	Zn_0B_0	24.4a	18.7	17.7d	35.4
	Zn_2B_0	17.7cd	15.7	23.7bcd	32.2
T3=$Zn_4B_{1.5}$	Zn_0B_0	16.8d	18.3	34.8b	34.5
	Zn_2B_0	20.8bc	17.7	29.9bc	39.1
T4=Zn_6B_3	Zn_0B_0	22.9ab	19.0	54.8a	37.3
LSD $_{(0.05)}$		3.3	NS	11.3	NS
Mean		21.2	18.17	30.7	36.2
CV%		5.6	8.4	13	6.9

[a] Means followed by same letter are not significantly different.
[+] Subscripts express the rate of Zn and B (kg/ha).

Some of the treated plots showed lower grain Zn than the untreated plot. This is not usually observed. However, it is to be noted that Zn and B was applied in the previous crop (Boro rice), which may not influence the nutrition of the crop in the following season. Moreover, multiple factors under the complex environment in the field condition (like rainfall quantity and frequency and variation in temperature) may be responsible for the changes in the effects of the applied nutrients (Moraghan and Mascagni Jr, 1991). Similarly, in the 2nd year, there was no significant difference between the concentration of grain Zn in the control and the treated plots. The conc. of grain Zn ranged from 15.7 mg/kg to 19.7 mg/kg.

On the contrary to grain Zn, the concentration of straw Zn of BRRI dhan49 differed significantly in the 1st year, due to the application of Zn and B (Table 4.22). The highest Zn concentration was observed in T4 (55 mg/kg) followed by T3 (30-35 mg/kg), both being significantly higher than the control. The range of Zn concentration was much wide, starting from 17.7 to 54.8 mg/kg. This is in agreement with the findings of Rengel *et al.* (1999) who reported a wide variation in Zn concentration of cereal grains, e.g., 17 - 52 mg/kg in rice and 25 - 64 mg/kg in wheat.

In comparison to the 1st year, straw Zn concentration in the 2nd year varied only slightly ranging from 32 to 39 mg/kg and the difference was not significant.

4.3.2.4 Plant uptake of zinc

Uptake of Zn in rice grain was significantly influenced by the Zn and B application in the 1st year (Table 4.23). The highest uptake was observed in T2.1 (109 g/ha) followed by T4 (102 g/ha), both of which were statistically similar to control (100 g/ha).

Table 4.23 Effect of Zn and B application on Zn uptake by T.Aman rice (BRRI dhan49) in Boro-Fallow -T.Aman rice cropping pattern.

Treatment		Grain Zn uptake (g/ha)[a]		Straw Zn uptake (g/ha)[a]		Total Zn uptake (g/ha)	
Boro	T.Aman	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
T1=Zn_0B_0[+]	Zn_0B_0	89ab	100	152c	205b	241	305
T2=$Zn_2B_{1.5}$	Zn_0B_0	109a	99	112c	211b	221	310
	Zn_2B_0	73bc	82	172bc	184b	245	266
T3=$Zn_4B_{1.5}$	Zn_0B_0	59c	97	233ab	194b	292	291
	Zn_2B_0	90ab	98	236ab	292a	326	390
T4=Zn_6B_3	Zn_0B_0	102a	104	286a	274a	388	378
LSD $_{(0.05)}$		26	NS	68	32	-	-
Mean		87	98	198	227	286	323
CV%		10.7	8.6	12.2	5.0	-	-

[a]Means followed by same letter are not significantly different.

[+] Subscripts express the rate of Zn and B (kg/ha).

Moreover, the uptake of Zn by some treatments was even lower than that of the control. The findings are in agreement with that of Duxbury *et al.* (2006) who attributed immobilization of the applied Zn for non-response of the crop. As mentioned earlier, complex factors that are active under field conditions might have caused micronutrient application to be less effective. Likewise, in the following year, the effect of Zn and B on grain Zn uptake was not significant (Table 4.23)

The effect of Zn and B application was more clearly observed in rice straw Zn uptake than grain in both the years (Table 4.23). Usually the higher doses of Zn and B i.e., T3 and T4 caused significantly higher straw Zn uptake than the control. In the 1st year, T4 showed the highest while in the 2nd year, T3.2 exhibited the highest straw Zn uptake. Increased straw Zn uptake in rice due to Zn addition is consistent with the findings of the previous researchers

(Fageria *et al.*, 2011; Hafeez *et al.*, 2013). Also, the residual effect of higher Zn rates (4-6 kg/ha) applied in Boro rice was reflected in Zn uptake by straw of T. Aman rice (Table 4.23). However, Zn taken up by rice straw was not translocated to its grain in accordance to the uptake rate as reflected by unchanged rice grain Zn concentration after Zn application (Table 4.23).

The average total uptake Zn by Boro rice (BRRI dhan29) (356 mg/kg) was higher than by T. Aman rice (BRRI dhan49) (304 mg/kg) in the Boro-Fallow-T. Aman rice pattern (Tables 4.18 and 4.23). This could be due to many reasons including the variation in grain yield, grain size, field duration of the two crops, frequency of irrigation and seasonal climatic conditions affecting soil Zn availability.

4.3.2.5 Plant B concentration

The effect of Zn and B addition in Boro rice was tested in T. Aman rice. There was no application of B in T. Aman rice. Rather, addition of Zn @ 2 kg/ha was repeated in two treatments (Table 4.24). In the 1st year, Zn and B addition increased grain B concentration significantly in T2 (Zn_2B_0) and T3 ($Zn_4B_{1.5}$), with T3 exhibiting the highest B concentration (4.37 mg/kg) (Table 4.24). In the following year, significant increase in grain B was also observed in T3, although the highest grain B concentration was exhibited by T2.1 (5.53 mg/kg).

Significant effect of Zn and B was observed on straw B concentration of BRRI dhan49 (Table 4.19). The highest straw B was observed in T3 in both the years. The difference between the control (no Zn or B) and T3 was more distinct in the 1st year compared to the following year. The effect of residual and direct application of Zn was slightly observed in T2 and T3. Straw B concentration in T4 was much lower compared to those of other Zn added plots (T2 and T3). The average straw B was much higher in the 2nd year (41 mg/kg) than that of the 1st year (21 mg/kg). A higher availability of soil B in the following year due to climatic variation might be the reason for higher straw B.

4.3.2.6 Plant B uptake

Likewise, the uptake of B in grain increased significantly due to the addition of Zn and B, both in T3 and T2 in the two years of experiment (Table 4.24). Thus, the applications of Zn @ 2 and 4 kg/ha in Boro rice with or without B @ 1.5kg/ha were found to be efficient in increasing T. Aman rice grain B compared to treatment with Zn @ 6 kg/ha plus B @ 3 kg/ha in T. Aman. The residue of B fertilizer applied in Boro rice provided B for T. Aman rice crop, also.

Uptake of B in straw of BRRI dhan49 varied significantly due to Zn and B addition (Table 4.24). The highest uptake was observed in T3.2 both the years. However, the average uptake was much higher in the 2nd year (271 g/ha) than that of the 1st year (132 g/ha). The yearly variation of B uptake might be due to soil and environmental factors that improved B availability to rice.

It is noteworthy that the uptake of B in straw in treatment T4 (Zn_6B_3 in Boro rice) was not higher than the treatments with lower rates of Zn+B. This might be due to interaction between Zn and B in the soil that influenced B uptake. Singh *et al.* (1990) reported that Zn alleviates B activity in crop due to a protective mechanism in the root cell of wheat works against excessive B uptake.

The total uptake of B ranged from 69 to 255 g/ha in the 1st year and 167 to 437 g/ha in the 2nd year. The proportion of grain B uptake in total uptake ranged from 5 to 10%, which was lower than that of Boro rice. A lower uptake of boron in T. Aman rice than in Boro was expected, since the yield and growth duration of T. Aman rice (BRRI dhan49) were quite lower than Boro rice (BRRI dhan29) (Tables 4.16 and 4.21).

According to the treatment plan, there was no B application in T. Aman rice. Still, residual effect of the B applied in Boro rice was observed in T. Aman rice (Table 4.24). Residual effect of B applied in rapeseed or soybean has been reported in rice crop by others (Yang *et al.*, 2000; Slaton *et al.*, 2005; Atique-ur-Rehman *et al.*, 2018). However, it was observed previously in the Wheat-Jute-T. Aman rice pattern (Table 4.15), that the concentration of B in the grain and straw of BRRI dhan49 increased considerably (with few exceptions) in the treatments in which B was applied repeatedly in each crop of the pattern.

Table 4.24 Effect of Zn and B application on B concentration and uptake in T. Aman rice (BRRI dhan49) in Boro rice-Fallow-T.Aman rice cropping pattern.

Treatments (kg/ha)		Grain B conc. (mg/kg)^{a}		Straw B conc. (mg/kg)^{a}		Grain B uptake (g/ha)^{a}		Straw B uptake (g/ha)^{a}		Total B uptake (g/ha)^{a}	
Boro	T.Aman	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
$T1=Zn_0B_0^{+}$	$T1= Zn_0B_0$	1.83c	1.73d	18b	42b	9.3c	6.27c	98b	254b	107	260
$T2=Zn_2B_0$	$T2.1= Zn_0B_0$	1.90c	5.53a	10b	25c	10.2bc	24.7a	59b	158c	69	183
	$T2.2= Zn_2B_0$	2.87b	1.87d	18b	44ab	14.9b	7.7c	104b	321b	119	329
$T3=Zn_4B_{1.5}$	$T3.1= Zn_0B_0$	4.37a	3.63b	33a	48ab	23.0a	12.9b	188a	313b	211	325
	$T3.2= Zn_2B_0$	1.47c	3.2bc	35a	54a	8.1c	13.8b	257a	423a	265	437
$T4=Zn_6B_3$	$T4= Zn_0B_0$	1.93c	2.73c	12b	30c	10.6bc	12.2b	86b	155c	97	167
	$LSD_{(0.05)}$	0.81	0.83	10.1	11.3	5.3	3.9	70	67	-	-
	Mean	2.4	3.1	21	41	12.7	13	132	271	145	283
	CV%	12	9.2	17	9.8	14.7	11	19	9	-	-

[a] Means followed by same letter are not significantly different.
[+] Subscripts express rate of Zn and B (kg/ha).

4.4 Effect of Zn and B addition on their fractions in soil (Incubation study)

4.4.1 Effect of added Zn on soil Zn fractions

To observe the pattern of Zn redistribution after Zn application, the initial soil from the WJR experiment was incubated with added Zn under field capacity and submerged conditions. The soil was incubated with 5 mg Zn/kg soil as $ZnSO_4$. The average Zn concentrations as percent of total Zn after 28 days of incubation are presented in Fig. 4.4.

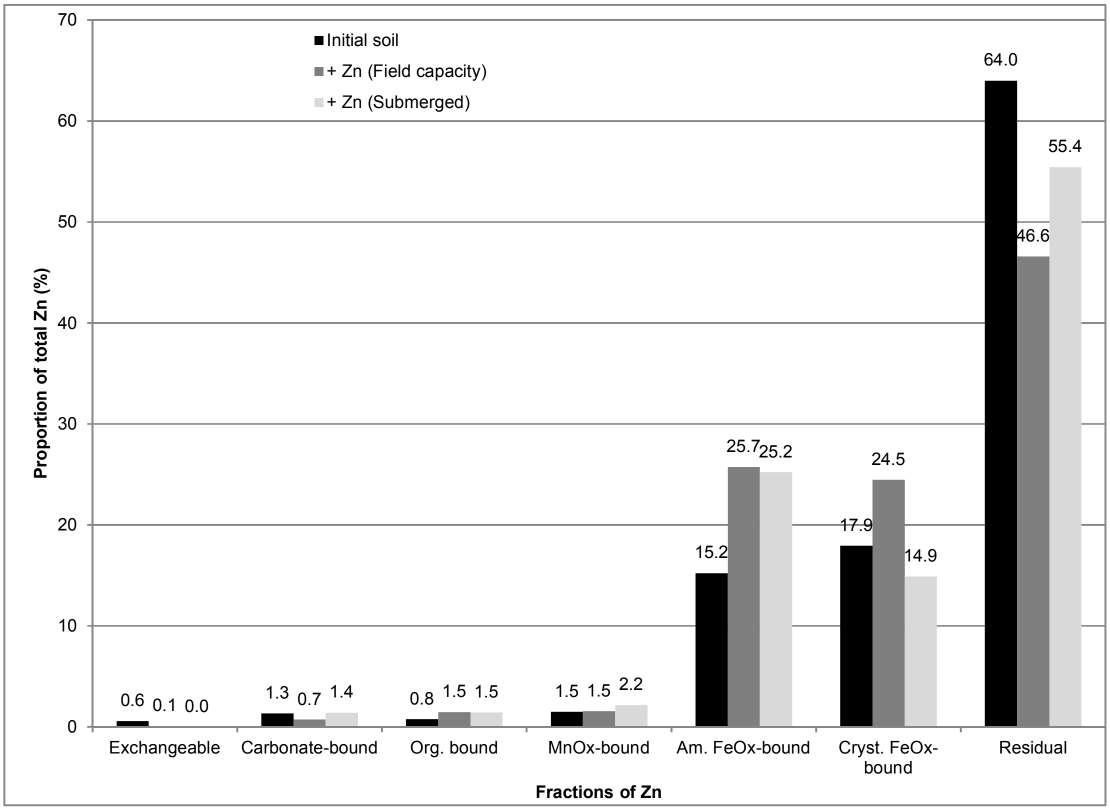


Fig. 4.4 Distribution of native and added Zn in different fractions (as % of total Zn) of the field soil incubated under field capacity and submerged conditions.

The distribution of the Zn fractions in the incubated soils followed the order Residual Zn >> Amorphous Fe-oxide (Am. FeOx) bound Zn > Crystalline Fe-oxide (Cryst. FeOx) bound Zn > Mn-oxide bound Zn > Organically bound Zn > Carbonate-bound Zn > Exchangeable Zn.

Percent of exchangeable Zn did not change considerably due to Zn addition compared to that of the initial soil under any of the moisture conditions (Fig. 4.4). The organically bound Zn increased slightly (0.72%) both under field moist and submerged conditions from that of the initial soil. There are contrasting reports of the effect of flooding on the changes and redistribution of Zn forms (Shuman, 1991). Mandal and Mandal (1987) found that waterlogging or alternate wet and dry conditions decreased the exchangeable, organic, and amorphous Fe-Ox fraction of Zn. However, earlier, they reported increase in organic and amorph.FeOx-Zn due to submergence (Mandal and Mandal, 1986).

Hazra *et al.* (1987) reported that reducing conditions of soil decreased exchangeable and organic Zn, at the same time increased amorph. FeOx- and cryst. FeOx-Zn. In contrast, Sims and Patrick (1978) found that reducing conditions caused increase in the exchangeable and organic Zn fractions and decrease in the oxide fractions. Thus, although there are contradictions, Shuman (1991) commented that usually reducing conditions increases Zn availability.

Percent carbonate bound-Zn in the submerged soil remained almost similar to the initial percentage (Fig. 4.4). However, its content decreased slightly in the field moist soil. Decreasing carbonate-bound Zn indicates increase in the reactivity of solution Zn. Ma and Uren (1997) observed that the proportions of added Zn in carbonate bound Zn decreased with Zn addition, suggesting that the reactivity of Zn increased with Zn addition.

The percent of Mn-oxide bound Zn increased slightly (0.66%) from the initial soil under submerged condition (Fig. 4.4). Usually, a decrease in the redox potential of soil due to flooding causes dissolution of Mn-oxide (Norvell, 1988; Scheinost, 2005; Bunquin *et al.*, 2017). However, the incubation period of 28 days might not be sufficient enough to get a complete picture of the Mn-oxide breakdwon.

A striking re-distribution was observed in the Fe oxide bound and in the residual Zn due to application of Zn (Fig 4.4). The percent of amorphous FeOx-bound Zn increased about 10% from that of the initial soil both under field capacity and submerged soil conditions. In the same way, the proportion of crystalline FeOx-bound Zn increased in the field moist soil due to addition of Zn. However, in the submerged soil, its proportion decreased from the initial soil. Duxbury *et al.* (2006) reported inability of soil Zn addition to increase Zn conc. in rice grain caused by a reversible decrease in Zn availability following flooding of soil. This was due to precipitation of Zn as a non-crystalline mixed Zn/Fe sulfide under reduced soil conditions.

Ma and Uren (1997) observed an increase of Am. FeOx-bound Zn in the Zn added incubated soil. Kamali *et al.* (2011) reported an increase in Am. FeOx and Cryst. FeOx bound Zn due to addition of Zn in soil under incubation. From the plant nutrition point of view, amorphous Fe-oxide fraction seems to act as a potential source of Zn both in field moist and submerged soils that may contribute more than the organic and MnOx bound forms. Torri and Lavado (2008) also observed increase in inorganic component of Zn in organic amended soil.

Similarly, a considerable decrease in the residual Zn fraction of the treated soils, particularly in the field moist soil, is also favourable for plant nutrition. It indicates that the Zn in the mineral fraction may weather into other forms upon addition of Zn. Mandal *et al.* (1988) observed a transformation of mineral Zn to Fe-oxide and other labile pools upon addition of organic matter in submerged soil. They opined that this may be due to the release of Zn from the more resistant mineral fractions as a result of decomposition of added organic matter under anaerobic conditions.

4.4.2 Effect of added boron on soil boron fractions

Laboratory incubation study was also conducted with added B to observe the changes occurred in B distribution of the soil under field moisture capacity and submerged conditions. The soil from the field under wheat-jute-rice crop experiment was incubated with 3 mg B/kg soil as H_3BO_3. The average B concentrations after 28 days of incubation as percent of total B are presented in Fig 4.5.

The general distribution of the applied B in the incubated soils changed from that of the initial soil (Fig. 4.5). In the incubated soils, B fractions followed the order: Residual B >> oxide bound B > specifically adsorbed B > readily soluble B. The majority (70%) of the B was found in the residual (occluded in mineral) fraction, both in the initial and added B conditions.

The added B has been re-distributed to soluble and specifically adsorbed B and seemed to favour B nutrition of plant, since B distributed in the available pool increased remarkably while that of the residual / mineral bound fraction decreased significantly compared to the initial soil (Fig. 4.5). Percent readily soluble (plus non-specifically adsorbed) B increased substantially (8.5%) in the B added soils.

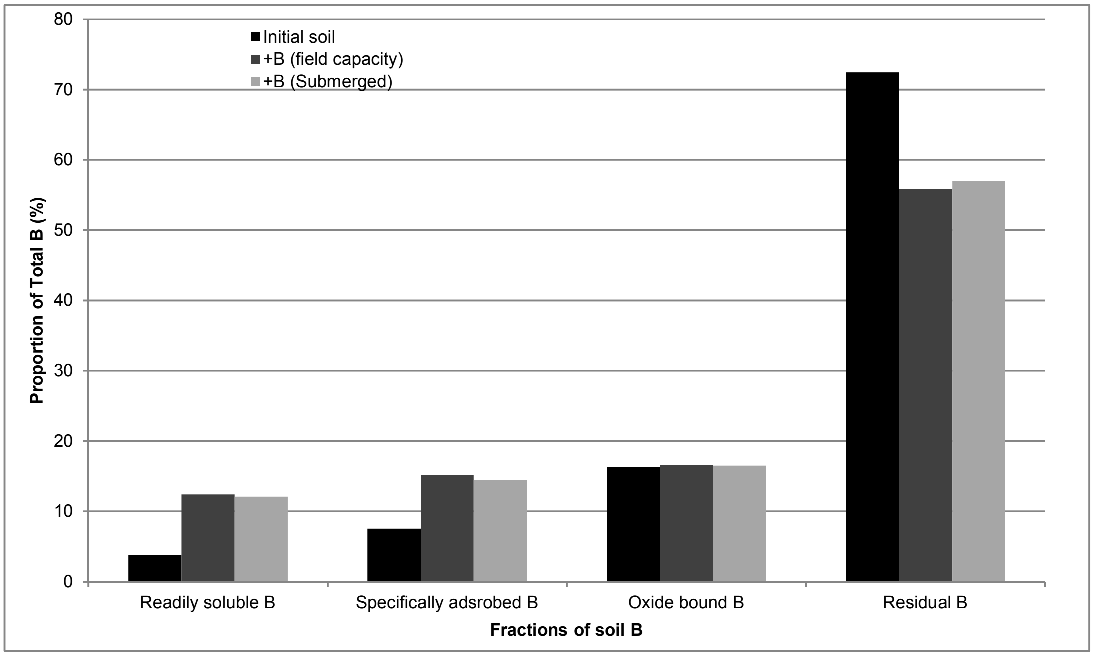


Fig. 4.5 Distribution of native and added B in different fractions (as % of total B) of the field soil incubated under field capacity and submerged conditions.

Similarly, the specifically adsorbed B increased remarkably (7.5%) due to B addition. In contrast, the percent of residual B, which is mainly the B present in the minerals, decreased greatly (16%) in the B added soils, both under field moist and submerged conditions. It should be noted here that, in addition to silicate mineral B, the residual fraction includes organically bound B, since it was not possible to determine organically bound B. Thus, decrease of organic B along with decreasing residual B cannot be ruled out.

The percent of oxide bound B remained quite unchanged throughout the incubation period (Fig. 4.5). Olykan *et al.* (1995) observed increase in non-specifically adsorbed, specifically adsorbed and amorphous Fe/Al oxide B due to B addition under field condition. Ranjbar and Jalali (2013) found an increase of all B fractions due to B spiking. Similarly, Padbhushan and Kumar (2015) observed increases in oxide bound B fractions due to B addition. The pH of the studied soil were very high (>8.0), which might have led to higher B adsorption to the oxides of Al and Fe, clay minerals, carbonates and organic matter as observed by other researchers (Goldberg, 1997; Goldberg and Su, 2007). According to Goldberg and Su (2007), adsorption to these surfaces is considered as strong specific adsorption due to ligand exchange with the surface hydroxyl groups.

4.5 TRANSFORMATION OF ZINC AND BORON IN SOIL UNDER WHEAT-JUTE-T.AMAN-RICE CROPPING PATTERN

4.5.1 Transformation of soil Zn

To study the transformation and redistribution of different Zn fractions due to the application of Zn and B, the plot soils of the Wheat-Jute-T. Aman rice (W-J-R) cropping experiment were analyzed. The plots in which Zn and B were applied only in wheat crop were selected for fractionation and transformation study. The distribution of the different fractions of soil Zn in the initial soil and in the post-harvest soil after two years of cropping with added Zn are shown in Table 4.25 and Fig. 4.6.

Table 4.25 Distribution of Zn fractions in the initial and post-harvest soils under Wheat-Jute-Rice cropping pattern after two years of cropping**.**

Rate of Zn/B added in Wheat	Concentration of Zn (mg/kg)						
	Exch. Zn	Org. Zn	MnOx- Zn	Amorph. FeOx-Zn	Cryst. FeOx-Zn	Residual Zn	Total Zn
Initial soil	0.61a	0.98d	1.58a	16.0b	18.8a	67c	105
$Zn_0B_0^+$	0.22b	3.78bc	0.87d	16.5b	18.2a	68c	107
Zn_2B_0	0.27b	3.46c	1.10c	21.7a	7.9c	79b	114
$Zn_4B_{1.5}$	0.27b	4.57a	1.02c	7.5c	2.5d	97a	112
Zn_6B_3	0.31b	4.07ab	1.21b	19.2ab	9.5b	79b	113
$LSD_{(0.05)}$	0.18	0.53	0.11	3.2	1.1	4.7	NS
Mean	0.33	3.33	1.16	16.2	11.4	78	110

+ Subscripts express rate of Zn and B (kg/ha).

Most of the Zn (64 - 87%) both in the initial and fertilized soil was found to be in residual form which is made up of the primary and the silicate clay minerals and unavailable to the plants (Table 4.20; Fig. 4.6). In general, the quantities of different forms of Zn under this study were in the following order: Residual Zn>> Amorph. Fe-oxide bound Zn > Cryst. Fe-oxide bound Zn > Organic Zn> Mn-oxide bound Zn> Exchangeable Zn. The values of the different fractions observed were within the range of the values usually reported by others (Iyengar *et al.*, 1981; Hazra *et al.*, 1987; Mandal and Mandal, 1987). The mean Zn conc. of the control plot remained quite unchanged in case of amorph. FeOx, cryst. FeOx and residual Zn compared to the initial soil Zn (Table 4.25). Significant variations in the initial and control plot were observed in exchangeable, organic and MnOx-bound Zn (which are comparatively labile) after two years of cropping. A discussion on the redistribution of the Zn fractions is presented in the following sections.

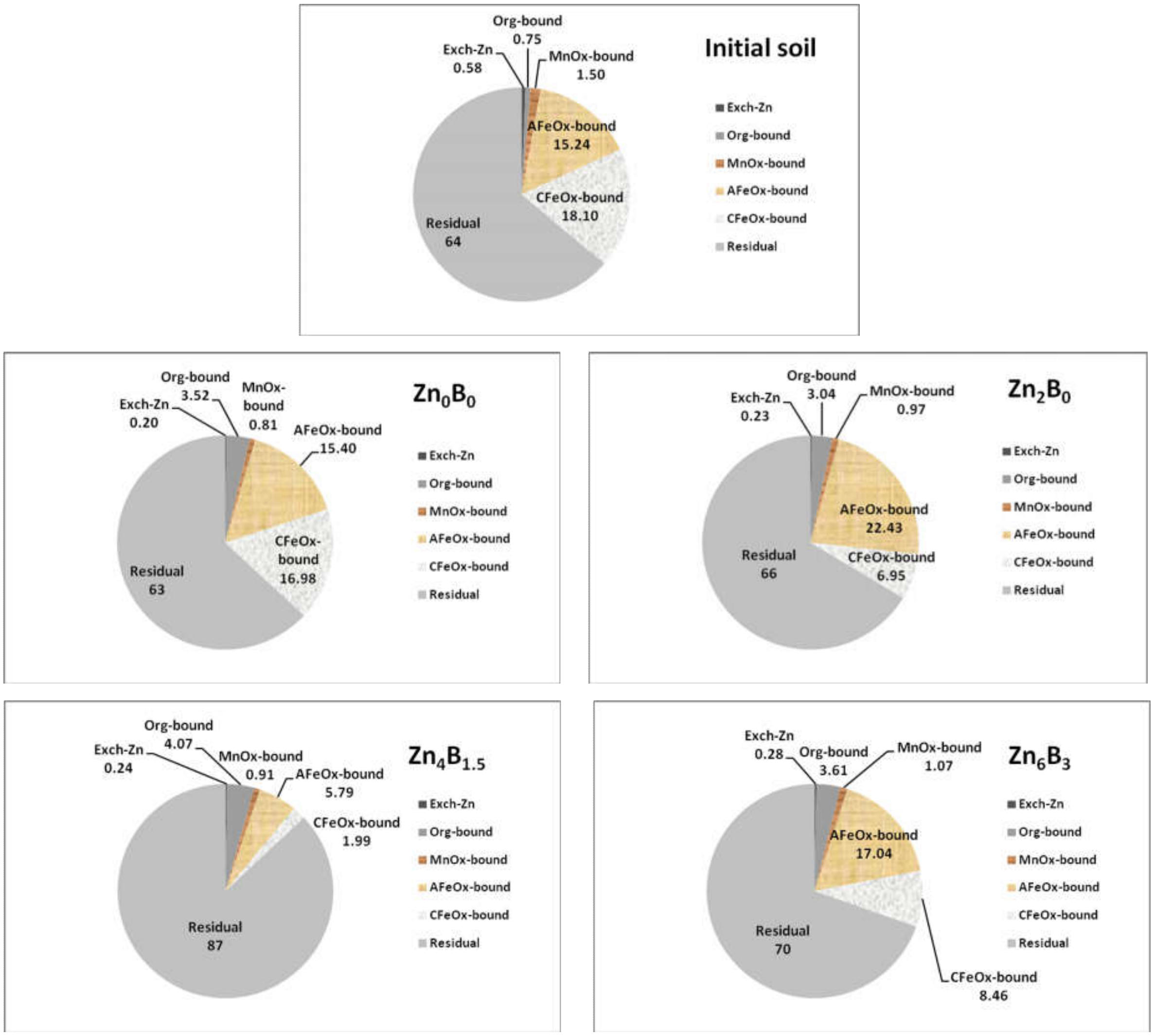


Fig. 4.6 Percent distribution of Zn fractions in the post-harvest soils as affected by Zn and B application in Wheat-Jute-Rice cropping pattern after two years of cropping**.**

4.5.1.1 Exchangeable Zn

The concentration of exchangeable Zn was found to be the lowest among all the fractions in all the treatments (Table 4.25). The lowest proportion of exchangeable Zn agrees with the values reported in many studies involving fractionation of Zn (Shuman, 1985; Mandal and Mandal, 1986; Ma and Uren, 1997). Poor release of available Zn due to less weathering of the parent materials of the study area (Inceptisols) might be attributed to lower exchangeable Zn. Moreover, soils with high pH (calcareous soils) were found to possess low exchangeable Zn due to fixation by carbonate (McBride, 1989).

The percent of exchangeable Zn in the total Zn reduced significantly in the Zn added soils from that of the initial soil (Fig. 4.6). Application of Zn and B did not significantly influence the amount of exchangeable Zn. It is possible that the exchangeable fraction of the added Zn transformed to other forms due to variation in soil properties as a result of cropping practice. Torres-Martin and Gallardo-Lara (1991) reported a steady increase of exchangeable Zn in soil due to successive cropping. Singh *et al.* (1999) observed that exchangeable and soluble form of native Zn recorded a decrease upon submergence in a rice soil. Similarly, Sarkar and Deb (1985) found exchangeable Zn transformed to complexed forms, with time, in an Indian Vertisols. In the same way, Ma and Uren (1997) observed that upon addition of Zn to the soil, more reactive forms (including the exchangeable form) converted to non-reactive (unavailable) forms with time.

4.5.1.2 Organically bound Zn

The percentage of the organically bound Zn was much lower in the initial soil (Table 4.25; Fig. 4.6). It increased 4-5 times higher in the Zn treated soils than in those of the untreated soils. It is interesting to note that the content of organically bound Zn increased several fold even in the control plots (with no added Zn) than the initial soil (Table 4.25). This could be an impact of cultivation of wheat, jute and rice crops as well as the application of N, P, K and S fertilizers during the cropping period. Torres-Martin and Gallardo-Lara (1991) reported a significant increase of organic Zn fractions in cultivated soil under alfalfa crops. Also, the crop residues may contribute to the organic Zn. Norouzi *et al.* (2014) reported that preceding crops (sunflower, sorghum, clover and safflower) influenced the increase of Zn in the exchangeable, organic and Fe- and Mn-oxide bound fractions significantly over the fallow treatment. Zinc mobilization in the various fractions was attributed to the activities of microbes and organic ligands released from the root exudates previous crops. According to Shuman (1999) organic materials high in Zn can increase Zn in exchangeable, organic and MnOx fractions. Also, a higher pH of the soil (> 8.0) may have fovoured Zn redistribution in organic fraction. Sims (1986) reported that organically complexed and Fe oxide bound Zn were dominant forms at higher soil pH (~7.7). Keefer and Estepp (1971) found in a pot experiment that the added Zn initially existed in the acid-soluble or clay fraction which decreased with time while the organic Zn increased, indicating a shift to more available forms.

Among the treated soils, the plots with higher Zn application rates (4 and 6 kg Zn/ha) showed higher amount of organic Zn than those with lower or no Zn application. However, the concentration of organic Zn in the plot with 4 kg Zn/ha was higher than that of the 6 kg

Zn/ha. Increase in organic Zn fraction upon Zn addition is well documented and desirable for plant nutrition since this form acts as labile pool of soluble Zn (Mandal *et al.*, 1988; Shuman, 1991). The organically bound Zn plays an important role in Zn nutrition of lowland rice and other crops (Iyengar *et al.*, 1981; Mandal and Mandal, 1986; Banjoko and McGrath, 1991).

4.5.1.3 Manganese oxide (MnOx) bound Zn

The concentration of MnOx bound Zn was lower than organically bound and iron oxide bound Zn fractions in the experimental plots (Table 4.25). This is consistent with the findings of other studies (Shuman, 1985; Mandal and Mandal, 1986; Chowdhury *et al.*, 1997). The MnOx-Zn fraction decreased slightly but significantly in the Zn and B treated soils (avg. 1.05 mg/kg) compared to the initial soil (1.58 mg/kg) (Table 4.25). A reduction of MnOx-bound Zn may indicate release of the bound Zn. The sample was collected from the soil after harvest of flooded rice cultivation which might have favoured the dissolution of Mn-oxides. It is well documented that the reductive dissolution of MnOx under anaerobic condition when the soil is flooded for rice cultivation releases Zn to soil solution (Gambrell, 1996; Scheinost, 2005; Bunquin *et al.*, 2017). On the other hand, cultivation of upland crops and drying of the soil may also favour release of Zn due to reduction of Mn in hydrous oxides (Reed and Martens, 1996). Also, in calcareous soils, Ca^{2+} ion competes for adsorption sites at high Zn concentration in MnOx and thus may be responsible for increase in solution Zn in the soil (Zasoski and Burau, 1988).

Thus, the soil underwent an array of dynamic processes due to cultivation of wheat, jute and rice crops, such as flooding and drying cycle and crop management practices that brought about changes in soil pH, temperature and moisture status and influenced the microbial activities that mediate the formation and breakdown of Mn-oxides.

Among the Zn treated plots, application of Zn and B was found to influence the increase in MnOx fraction significantly compared to the plot with no added Zn (Table 4.25). This finding agreed with Ma and Uren (1997) who observed that most of the added Zn was found predominantly as specifically adsorbed Zn and as Zn associated with oxides of Fe, Al and Mn. They also reported that the available forms (soluble and exchangeable) transformed to Fe and Mn-oxide bound Zn with time.

4.5.1.4 Iron oxide bound Zn

A large proportion (33%) of the total Zn was found in the iron oxide bound fraction of the initial soil (Fig. 4.6). Large amounts Zn associated with iron oxide in native or applied Zn have also been reported by several workers (Iyengar *et al.*, 1981; Mandal *et al.*, 1988). Ma and Uren (1997) found that the indigenous Zn was largely present in the residual and Fe-oxide fractions. Oxides and hydrous oxides of Fe and Mn have been named as the principal factor for fixation of Zn and other trace elements in soils (Shuman, 1991). The common occurrence of these oxides makes them important in retention and release of trace elements like Zn. A large fraction of Fe-oxide bound Zn implies their importance in Zn chemistry of Bangladesh soils and in controlling Zn availability to the plants. The ineffectiveness of the applied Zn in increasing crop yield and nutrient uptake may be related to the existence of a large quantity of iron oxide in the soil that are responsible for adsorption/ fixation/ retention/ occlusion of the applied Zn.

Of the oxides/ hydrous oxides of iron, amorphous or non-crystalline forms are most reactive in fixing trace elements due to their higher surface area (Loeppert and Inskeep, 1996). Detail descriptions of the results are presented in the following sections.

4.5.1.4.1 Amorphous Fe-oxide bound Zn

The fraction of Zn associated with amorphous iron oxide increased significantly due to the application of Zn and B from that of the initial soil, except T3 (Zn @ 4 kg and B @ 1.5 kg/ha) (Table 4.25). This treatment showed significantly lower concentration (7.5 mg/kg) of this fraction. Thus, the redistribution of this form of Zn was not consistent with Zn application rate, although the general tendency was to increase with increasing rate.

The increase in the concentration of amorphous FeOx-bound Zn is in agreement with others. Ahmed and Rahman (1990) observed that the applied Zn was distributed largely in the complexed, amorphous and crystalline sesquioxides. These forms comprised the bulk of the Zn fractions. Kamali *et al.* (2011) observed that applied Zn was highly extracted in carbonate, amorphous and crystalline Fe oxides and residual forms. Ma and Uren (1997) found that the added Zn was mainly associated with amorphous FeOx and crystalline FeOx forms. They also reported that with long term Zn application, significant increase was observed in EDTA-Zn, MnOx-Zn and amorphous FeOx form of Zn in most of the soils tested.

Addition of Zn and B along with major nutrients, addition of crop residues and the variation of soil properties like pH and redox potential due to cultivation of wheat, jute and rice crops might have influenced the redistribution of iron oxide bound Zn fraction. Mandal *et al.* (1988) found that added organic matter caused applied Zn to increase in all fractions, except the crystalline Fe oxides and the residual, indicating an increase in bioavailability. In contrast, Shuman (1991) reported that organic matter additions resulted in Zn redistribution from the oxide to the organic fraction. Similarly, Torres-Martin and Gallardo-Lara (1991) reported that cropping led to a reduction of Zn associated with Fe oxides.

High soil pH of the tested soil may also affect the concentration of amorphous FeOxide bound Zn as observed by Xiang *et al.* (1995). They observed, while working with acid, neutral and calcareous soils of China, that the proportion of added Zn in amorph. FeOx and cryst. FeOx was much higher in calcareous soils than those in acidic and neutral soils. Jahiruddin *et al.* (1986) found greater adsorption of Zn on Fe-oxides due to an increase of soil pH.

Amorphous Ferrihydrite is a common mineral of younger soils and gradually transforms to stable crystalline Goethite or Hematite by pedogenic processes (Scheinost, 2005). In the poorly drained soils of Ganges River Floodplain, the *in situ* formation of free Fe-oxide (both amorphous and crystalline) is favoured (Hussain, 1992; Hassan, 1999). It is reported that amorphous Fe oxides present as coatings on the calcite (a common feature of calcareous soil) or as separate phase have larger specific adsorption capacity for Zn than free oxides (Uygur and Rimmer, 2000).

Both increase and decrease in retention or occlusion of Zn by Fe oxide/hydroxides was found due to submergence of soil. Hazra *et al.* (1987) found that submergence of rice soils caused an increase in amorphous FeOx bound Zn and decrease in crystalline FeOx bound form. They explained that due to the increase in the formation of fresh oxides of Fe with a large surface area, more Zn was adsorbed in the amorphous Fe-oxides and resulted in higher concentration of this form. Similarly, Mandal *et al.* (2000) observed increased Zn desorption accompanied with increase in amorphous Fe-oxide in a soil which was pre-flooded before growing rice. They opined that the changes in soil chemical properties due to flooding were responsible for Zn desorption.

In contrast, Mandal and Mandal (1987) reported that waterlogging or alternate wet and dry conditions caused decreases in the amorphous Fe oxide bound Zn. Decrease in oxide bound Zn due to soil submergence has also been reported by others (Ghanem and Mikkelsen, 1987; Singh *et al.*, 1999). McBride (1989) reported desorption of Zn from amorphous Fe oxide during its transformation and crystallization to stable oxide forms.

4.5.1.4.2 Crystalline Fe-oxide bound Zn

Unlike amorphous FeOx-bound Zn, application of Zn and B effectively and significantly decreased Zn in the crystalline Fe-oxide fraction from that of control plot (Fig. 4.6, Table 4.25). The magnitude of decrease varied with Zn application rate. Greater reduction was observed in the plots with lower rates (2 and 4 kg Zn/ha) compared to higher rate (6 kg Zn/ha) (Table 4.25). Thus, it may be assumed that the applied Zn transformed mainly to FeOx-bound and the residual forms.

Decrease of Fe oxide bound Zn due to Zn application did not agreed with the findings of others (Ma and Uren, 1997; Kamali *et al.*, 2011). The decrease of crystalline FeOx bound Zn might be due to the submergence of the soil during rice cultivation, as observed by Hazra *et al.* (1987).

Declining of the crystalline Fe-oxide bound Zn forms is, however, desirable from plant nutritional point of view, since nutrients in this form are found to be quite unavailable to the plants compared to exchangeable, adsrobed or organic fractions. Based on plant uptake, Iyengar *et al.* (1981) found that adsorbed and organically bound Zn was more available compared to Zn occluded in Fe and Mn oxides. Sims (1986) reported that Fe and Mn oxide bound Zn was poorly correlated with plant uptake.

Increasing of amorphous FeOx-Zn and decreasing of crystalline FeOx-Zn is in favour of plant nutrition since Zn in the amorphous Fe-oxide fraction has been found to contribute more to uptake by rice plant compared to other forms (Singh and Abrol, 1986). Retention of Zn by amorphous Fe oxide may not be as problematic as crystalline Fe oxide since Zn is more strongly adsorbed in the latter than the former. According to Trivedi *et al.* (2001), Zn is only physically sorbed on amorphous hydrated ferric oxide (HFO) on the microporous surfaces and does not form any solid state with Fe^{3+}. On the other hand, Zn ions are chemically sorbed and forms strongly bonded mono-nuclear complexes with goethite (crystalline Fe-oxide) with structural changes upon adsorption.

The concentration of FeOx bound Zn found in the studied soil was higher than those reported in many research articles (Shuman, 1979; Iyengar *et al.*, 1981; Mandal and Mandal, 1986; Mandal and Mandal, 1987). There may be several reasons supporting the findings, including:

- the soil (Ganges River Floodplain, Recent Floodplain) is less weathered (and less developed) compared to the soils mentioned in the literature and that the parent material of the soil may have a higher Zn occluded in FeOx.
- Zinc might have been highly adsorbed/ retained in the FeOx compounds (both amorphous and crystalline) due to a higher pH of the soil since high pH favours adsorption of Zn to Fe oxides as described earlier.

4.4.1.5 Residual fraction

The highest proportion of Zn was found in the residual fraction (Table 4.25). The large percentage of residual Zn composed mainly of the soil minerals is consistent with the findings mentioned in the literature (Ahmed and Rahman, 1990; Shuman, 1991; Chowdhury *et al.*, 1997; Ma and Uren, 1997). A large residual Zn fraction indicates that the soils are relatively young and unweathered alluvial soils (Chowdhury *et al.*, 1997).

After redistribution, the percentage of the residual Zn increased greatly from 63% in the Zn control plot to as high as 87% in 4 kg Zn/ha plot (Fig. 4.6). The redistribution was exceptionally high in 4 kg Zn/ha plot. Thus, the application of Zn and B seems to cause Zn to be accumulated in the residual fraction. With time, Zn from the residual fraction may become available to the plants through weathering (Iyengar *et al.*, 1981).

The parent material of the soils of Ganges River Floodplain is composed of substantial quantity of smectite in the fine clay fraction (Brammer, 1971; Hassan, 1999; Rahman *et al.*, 2005; Kader *et al.*, 2015). According to Moslehuddin and Egashira (1997), the smectite of Ganges River Floodplain soils (AEZs 11 and 12) is composed of iron-rich high charge biedellite with high inherent potentiality. The presence of biedellite in these soils (AEZ 12) may be highly responsible for the fixation of Zn in reversible or irreversible forms. Rahmatullah *et al.* (1985) observed that on an average 57% of the applied Zn was unextractable and considered fixed, and that the biedellite clay systems possessed the highest (70%) Zn-fixing capacity. Similarly, Bradl (2004) reported that the sorption of Zn by 2:1 type clay minerals exhibit greater fixing capacity than 1:1 clays e.g., Kaolinite.

However, the Zn was applied in the 1st crop (wheat), while the soil was analysed after the harvest of the 3rd crop (rice) of the cropping cycle. In the interim period, various factors may act upon Zn to make it available. The reactive and available forms of Zn (soluble, exchangeable and adsorbed) have been found by others to be transformed to the unavailable and unreactive forms (oxide and residual) with time (Ma and Uren, 1997; Kamali *et al.*, 2011).

4.4.2 TRANSFORMATION OF SOIL BORON

The distribution of different B fractions in the harvested soil after two years of cropping is presented in Table 4.26 and their percentage in total B is presented in Fig. 4.7. Application of Zn and B made a redistribution of the B fractions, although not significantly in every cases. The concentration of B decreased from that of the initial soil. The added B was traced only in the oxide bound and the residual fractions practically.

Table 4.26 Fractionation of soil B in the post-harvest soil under wheat-jute-rice cropping pattern after two years of cropping.

Treatments	Concentration of B (mg/kg)*			
	Exchangeable B	Specifically adsorbed B	Oxide bound B	Residual
Initial soil	0.94a	1.89a	4.07b	18.1
Zn_0B_0	0.28b	0.44b	3.63b	19.0
Zn_2B_0	0.38b	0.64b	1.79c	20.8
$Zn_4B_{1.5}$	0.09c	0.45b	3.26b	19.2
Zn_6B_3	0.10c	0.57b	5.63a	17.7
$LSD_{(0.05)}$	0.12	0.41	0.94	NS
Mean	0.36	0.80	3.68	19.0

* Values followed by same letter in a column are not statistically different.

4.4.2.1 Soluble/ Exchangeable B

Exchangeable B reduced significantly in the treated soils from that of the initial soil (Table 4.26). Among the treated soils, significantly higher exchangeable B (0.28 mg/kg) was observed in the plot with no added B than the plots with added B (T3 and T4), indicating that the applied B might have been transformed from exchangeable to other forms during the cropping period. Adsorption to oxides surfaces and clay minerals is among the major causes of decrease in availability of B in soil (Goldberg, 1997).

Absorption by the cultivated crops might also be the reason for reduced exchangeable B. Sims and Johnson (1991) reported that hot water soluble B was not correlated with plant B concentration suggesting the need for a better understanding of the soil B pools and their availability to the plants.

4.4.2.2 Specifically adsorbed B

Like the exchangeable B, the concentration of specifically adsorbed B decreased significantly in the treated plots compared to the initial soil (Table 4.26). Among the treated plots, no significant changes were observed due to the application of B. It is noteworthy that the concentration of specifically adsorbed B in the control plot was much lower than the initial soil. In this plot, major nutrients (N, P, K and S) other than Zn and B were applied. Application of major nutrients in wheat, jute and rice crops along with the changes in soil properties might have caused the adsorbed B to be redistributed to other forms especially the organic, oxide bound and the residual forms as stated by Atique-ur-Rehman *et al.* (2018).

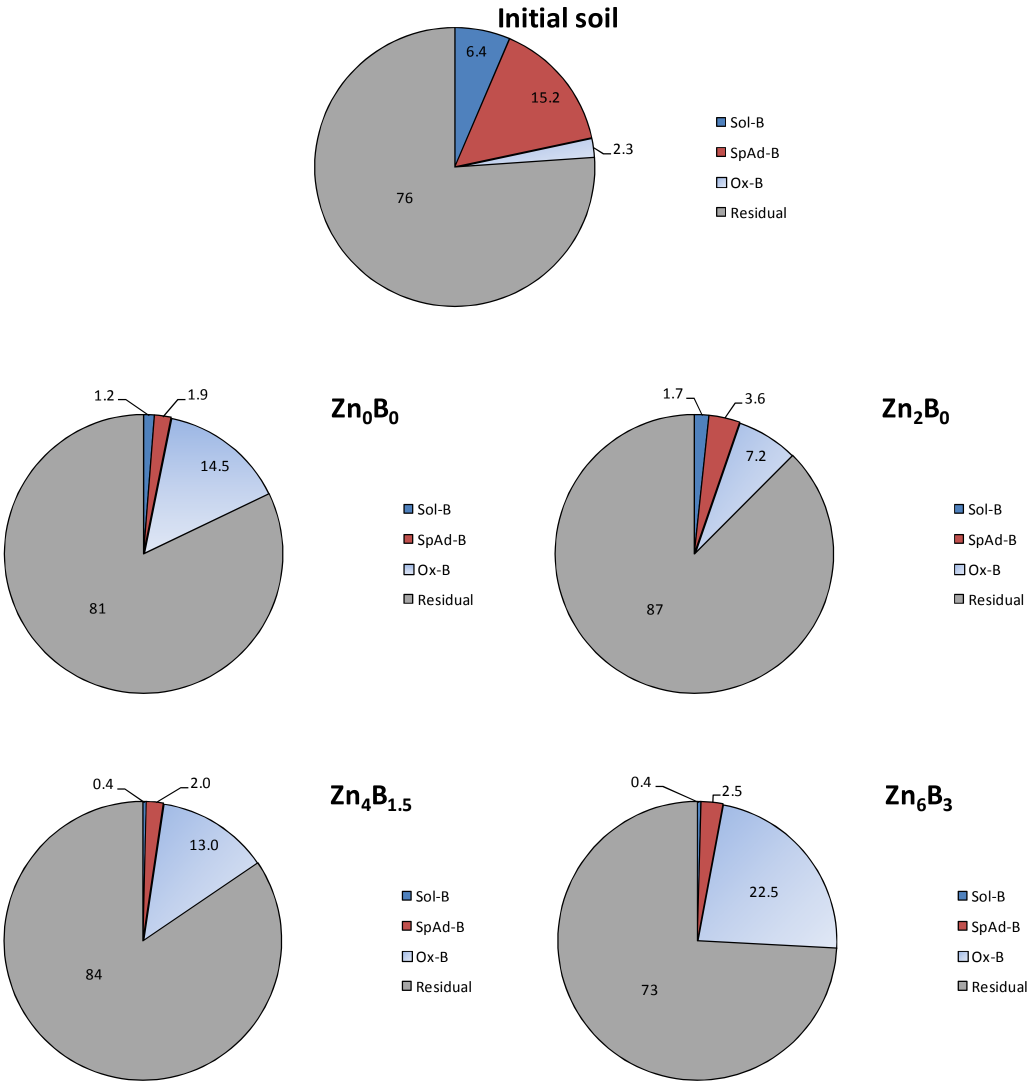


Fig. 4.7 Changes in B fractions in the post-harvest soil as percent of total B due to the application of Zn and B under wheat-jute-rice cropping pattern.

4.4.2.3 Oxide bound B

The concentration of oxide bound B (extracted by ammonium oxalate) remained more or less similar to the values of initial soil, with a few exception (Table 4.26). The concentration of oxide-B was the highest in the plot with the highest B application. It is possible that the applied B has been transformed to oxide bound B with the passage of time. The effect is more obvious in the plots with higher B rate than those with low or no B. Higher pH of the test soil might be responsible for higher B adsorption in the oxide surfaces. Goldberg and Su (2007) showed that B adsorption on Goethite (Fe-oxide) increased with soil pH.

4.4.2.4 Residual B

The concentration of residual B did not change significantly due to Zn and B application (Table 4.26). However, the concentration was slightly lower in the treatment with highest Zn and B application. This may indicate the transformation of the residual B to other forms, particularly, to oxide bound B with the increase in B application. It is to be mentioned here that, in the present study, the organic B fraction is included in the residual fraction. Thus the scenario of B adsorption/ complexation by organic substances is not very clear in this study.

4.5 Correlation between soil Zn fractions and crop Zn

The relationship between Zn concentration and uptake of the crops in the experimental plots and the fractions of Zn in the corresponding plot soils is shown in Tables 4.27 and 4.28, respectively. It appears from Table 4.27 that, wheat grain Zn correlated significantly with Mn-oxide bound Zn fraction. On the other hand, wheat straw Zn conc. correlated significantly positively with the organic and residual Zn, but negatively with amorphous FeOx and crystalline FeOx-bound Zn fractions (Table 4.27). The uptake of Zn in wheat grain did not correlate with any of the Zn fractions significantly (Table 4.28). In case of straw Zn uptake, significant positive and negative relationships were found with residual and crystalline FeOx Zn, respectively.

Table 4.27 Correlation coefficient between Zn concentrations of crops grown in the test soil and soil Zn fractions of the same soil.

Soil Zn fractions	Wheat		Jute	T. Aman rice	
	Grain Zn	Straw Zn	Stick Zn	Grain Zn	Straw Zn
Exchangeable Zn	0.28	0.13	0.50	-0.15	-0.31
Organically bound Zn	0.17	0.59*	0.24	0.73**	0.13
Mn-oxide bound Zn	0.66*	-0.12	0.77**	-0.38	-0.61*
Amorph. Fe-oxide bound Zn	0.36	-0.85**	0.07	-0.87**	0.15
Crystalline Fe-oxide bound Zn	-0.05	-0.60*	-0.10	-0.18	0.75**
Residual Zn	0.04	0.79**	0.33	0.47	-0.65*
Total Zn	0.39	0.13	0.62*	-0.18	-0.53

*=significant at 5% prob. level, **= significant at 1% prob. level

Table 4.28 Correlation coefficient between Zn uptake by crops grown in the test soil and soil Zn fractions.

Soil Zn fractions	Wheat		Jute	T. Aman rice	
	Grain Zn uptake	Straw Zn uptake	Stick Zn uptake	Grain Zn uptake	Straw Zn uptake
Exchangeable Zn	-0.33	-0.06	0.47	0.04	-0.43
Organically bound Zn	-0.07	-0.04	0.34	0.82^{**}	0.43
Mn-oxide bound Zn	0.19	-0.11	0.73^{**}	-0.09	-0.71^{**}
Amorph. Fe-oxide bound Zn	0.51	-0.38	0.01	-0.79^{**}	-0.63^{**}
Crystalline Fe-oxide bound Zn	0.10	-0.58^{*}	-0.35	-0.28	0.19
Residual Zn	-0.14	0.60^{*}	0.27	0.49	0.07
Total Zn	0.50	0.27	0.31	-0.11	-0.46

*=significant at 5% prob. level, **= significant at 1% prob. level.

The positive relationship of wheat tissue Zn with exchangeable and organic Zn and negative association with oxide bound or non-exchangeable Zn is well documented. However, positive relationship of crop Zn with oxide bound Zn is less usual. Norouzi *et al.* (2014) found significant positive correlation between exchangeable and organic Zn with Zn uptake by wheat and negative correlation with carbonate bound and residual Zn. Likewise, Iyengar *et al.* (1981) and Yoo and James (2003) observed negative relationship between Mn-oxide bound Zn or non-exchangeable Zn and tissue Zn of cereal crops. In contrast, Ahumada *et al.* (2009) reported positive correlation of ryegrass shoot Zn with soil MnOx and FeOx-bound Zn.

In the present study, it is possible that the Mn-oxide bound Zn fraction was transformed into bioavailable forms during the growing period of wheat. Behera *et al.* (2008) reported that Zn associated with easily reducible Mn, carbonate, Fe- and Al-oxide contributed directly to DTPA extractable Zn in wheat grown soil. In the same way, Chowdhury *et al.* (1997) found that the plant available Zn extracted from soil with DTPA and other reagents was significantly correlated with Mn-oxide bound Zn fraction.

A positive relationship between wheat straw Zn concentration and its uptake and the residual Zn (composed mainly of silicate minerals) is not expected (Tables 4.27 and 4.28). Jin *et al.* (1987) remarked that a strong correlation between plant availability and total content of the element would not be expected since the total content consists of relatively higher percent of the plant unavailable forms that are associated with the primary and secondary minerals. However, weathering of the parent material may contribute to the labile and, in turn, the available pool of the nutrient. According to Iyengar *et al.* (1981), parent materials with high Zn concentrations could weather into soils with high amount of both plant available and residual Zn. The relationship between plant Zn uptake and soil Zn fractions was further analyzed by fitting them in linear regression models as discussed later.

Jute stick Zn concentration and its uptake strongly correlated with Mn-oxide bound Zn (Tables 4.27 and 4.28). Also, jute stick Zn correlated significantly with the total Zn (Table 4.28). Thus, Zn associated with Mn-oxide was found to be an important source of Zn in this soil for jute. As mentioned earlier, this fraction of Zn might have transformed into bioavailable forms slowly during the growing period of the crops. Linear regression model also depicted the contribution of MnOx-bound Zn to jute plant tissue Zn (section 4.5.1.1).

In case of rice, grain Zn concentration and its uptake strongly positively correlated with organically bound Zn and negatively with amorph. FeOx bound Zn (Tables 4.27 and 4.29). On the other hand, straw Zn concentration was significantly and negatively correlated with Zn associated with Mn-oxide and residual Zn, and positively with cryst. FeOx bound Zn. Likewise, straw Zn uptake was significantly related to both MnOx- and amorph. FeOx bound Zn (Table 4.28). The relationship of rice tissue Zn with organic Zn agrees with the findings cited in the literature. Mandal and Mandal (1986) found strong correlation between organic complexed Zn and rice plant Zn. Liang *et al.* (1990) observed that Zn taken up by plants in high pH (calcareous) soil was from exchangeable, acid-soluble and residual Zn. Ahmed and Rahman (1990) found the highest contribution of complexed and residual Zn to Zn uptake by rice. A negative relationship between oxide Zn and plant Zn indicates that, Zn associated with these compounds are quite unavailable. Iyengar *et al.* (1981) also found negative correlation between oxide Zn and maize Zn uptake. Likewise, Yoo and James (2003) reported that leaf Zn of rice, wheat and barley was negatively correlated with non-exchangeable Zn.

It can be concluded that the relationship between plant Zn and the soil Zn fractions varies with plant types, seasons and soil properties. For instance, the fractions of Zn that are positively related to wheat tissue Zn (e.g., amorphous FeOx-Zn) were negatively correlated to rice tissue Zn, while organic Zn was negatively related to wheat grain but positively related to rice grain Zn. Ahumada *et al.* (2009) reported similar type of variation between the soil Zn and ryegrass and clover plant Zn relationship.

4.5.1.1 Contribution of Zn fractions to crop Zn nutrition: Multiple regression models

In order to quantify the contribution of soil Zn fractions to plant Zn nutrition, multivariate linear regression analysis was carried out by forward stepwise method (Table 4.29).

Table 4.29 Regression models between soil Zn fractions and plant Zn uptake.

Sl.	Crop	Regression Model	r^2
1	Wheat	Grain Zn uptake = -64.09 - 206.3 Exch. Zn + 23.05 Org. Zn + 4.05 Amorphous FeOx-Zn + 0.91 Residual Zn	0.68
2		Straw Zn uptake = 0.104 - 0.023 Org. Zn+0.002 Residual Zn	0.50
3	Jute	Stick Zn conc. = - 27.9 + 54.66 MnOx-Zn	0.55
4	Rice	Grain Zn uptake = 21.375 Org. Zn - 1.60 Amorph. FeOx-Zn	0.79
5		Straw Zn uptake = 198.85 + 19.92 Org. Zn - 107.613 MnOx-Zn	0.67

The estimation by the regression models reveals that the variability of crop Zn uptake was moderately influenced by the different soil Zn fractions. However, the magnitude of variation differed from crop to crop. A brief description is presented in the following sections.

Wheat

According to the model, 68% of the variation of grain Zn uptake in wheat was due to the soil Zn fractions (Table 4.29). The fractions that positively influenced the grain Zn uptake were the organic and Amorphous FeOx-bound Zn, along with residual Zn, to some extent. The negative contribution by exchangeable Zn may indicate that Zn was not translocated to wheat grain from this fraction during the growing period. The variation of wheat straw Zn uptake was weakly predicted (r^2=0.5) by the regression model. Mainly, the organic and residual Zn fractions explained 50% of straw Zn variation and the remaining 50% variation might have been due to factors other than soil Zn.

The present findings that soil Zn fractions influence the plant Zn uptake is consistent with those reported by other researchers (Murthy, 1982; Torri and Lavado, 2008; Ahumada *et al.*, 2009). A positive relationship with amorphous Fe oxide bound Zn and residual Zn reflected that Zn from these fractions might become available to the plants through weathering processes. According to Iyengar *et al.* (1981), Zn is released from the residual (mineral) fraction upon weathering. The inverse relationship between straw Zn uptake and organic Zn deserves attention. In Table 4.20, it was observed that the concentration of organic Zn increased due to addition of Zn and B. Thus, although organic Zn increased due to added Zn, this form might not be available to wheat. This might be due to the transformation of organic fraction to other forms before taking up by wheat. Redistribution of organically bound Zn to inorganic and unavailable forms has been described earlier by many researchers (Shuman, 1999; Torri and Lavado, 2008). Crop residue and organic matter addition may enhance this kind of transformation. Shuman (1999) reported that some of the organic amendments lowered the potential availability of Zn in soil by redistributing it from exchangeable to less soluble fraction like MnOx bound or organically bound forms.

Jute

Variation in jute stick Zn uptake could not be predicted by the regression model. Stick Zn concentration was modeled instead (Table 4.29). Variation of jute stick Zn concentration was weakly explained by positive relationship with MnOx bound Zn (r^2=0.55) (eq. 3). A variation in the soil oxidation-reduction status due to changes in crop management practices might have caused MnOx bound Zn to be bioavailable and be the principal contributor of jute stick Zn.

Rice

The model accounted for 79% of the variability of grain Zn concentration of T. Aman rice mainly by the variation of organic and amorphous FeOx bound Zn (Eq. 4; Table 4.29). Similarly, rice straw Zn uptake variation was explained by the relationship with organic and MnOx bound Zn (Eq. 5; Table 4.24). Negative relationships of rice grain and straw Zn uptake with the oxide bound Zn (FeOx and MnOx) implies that Zn from these sources is difficultly available or unavailable to rice because of strong bonding between Zn and oxide surfaces. This is in accordance with the findings of Singh and Abrol (1986).

In contrast to the negative relationship between wheat plant Zn and organic Zn, rice plant Zn uptake was positively related to the same. This observation suggests that the organic Zn prevailed in a dynamic state in the soil, being unavailable during wheat cultivation but became available to rice crop later. Redistribution of organic Zn was attributed to this type of variation (Shuman, 1999).

4.5.2 Correlation between soil B fractions and crop B

Wheat grain B concentration and uptake showed strong correlation with soil exchangeable B (Tables 4.30 & 4.31). Wheat tissue B was not related to specifically adsorbed, oxide bound and residual B. The negative and insignificant correlation between plant B and residual B is well documented (Jin *et al.*, 1987; Tsadilas *et al.*, 1994; Badr-Uz-Zaman and Salim, 1999; Ren *et al.*, 2014; Padbhushan and Kumar, 2017).

Table 4.30 Correlation coefficient between B concentrations of crops grown in the test soil and soil B fractions in the same soil.

Soil B fractions	Wheat	Jute	T. Aman rice
	Grain B	Stick B	Grain B
Exchangeable B	0.78**	0.36	0.65*
Specifically adsorbed B	0.35	0.59*	0.59*
Oxide bound B	-0.21	-0.29	-0.43
Residual B	-0.52	0.02	0.05

*= significant at 5% probability level, **= significant at 1% prob. level

The reason behind poor correlation of plant B with residual B is that this fraction is composed of the primary and secondary silicate minerals and is unavailable to the plants. The correlation matrix reveals that wheat absorbed B only from the exchangeable B pool in the soil studied (Table 4.31).

Table 4.31 Correlation coefficient between B uptake of crops grown in the test soil and soil B fractions of the same soil.

Soil B fractions	Wheat	Jute	T. Aman rice
	Grain B uptake	Stick B uptake	Grain B uptake
Exchangeable B	0.88**	0.24	-0.54
Specifically adsorbed B	0.34	0.43	0.16
Oxide bound B	-0.41	-0.15	0.51
Residual B	-0.41	-0.14	-0.02

*=significant at 5% prob. level, **= significant at 1% prob. level

Jute stick B concentration was found to be significantly positively correlated with specifically adsorbed B (Table 4.30). Similar findings were also observed by others. Jin *et al.* (1987) found that B in corn tissue was related to water soluble, specifically adsorbed and Mn-oxyhydroxide B. Ren *et al.* (2014) reported that B concentration of rapeseed significantly correlated with soluble, specifically adsorbed and oxide bound B. Diana and Beni (2006) observed that B content in lettuce correlated positively only with the specifically adsorbed B.

In case of T. Aman rice, significant positive correlation was observed between B concentration of grain and the exchangeable and specifically adsorbed B (Table 4.30), which was in accordance with wheat grain and jute stick B concentration. As mentioned earlier, several authors reported positive correlation of plant B with exchangeable, specifically adsorbed and oxide B (Tsadilas *et al.*, 1994; Ren *et al.*, 2014). However, B uptake in rice grain was not related to any of the soil B fractions (Table 4.31). On the contrary, Jin *et al.* (1987) found that oxide B was unrelated to plant B. Researchers attributed the difference between the observations to difference in soil fertility and plant species. Also, equilibrium among the soil B fractions might have existed that influenced the availability of B. According to Ren *et al.* (2014) the soluble and exchangeable B pool has been found to be controlled by the B pools in other soil fractions and their equilibrium.

4.5.2.1 Multiple regression models: Soil B fractions vs. plant B uptake

Multiple linear regression models can only be constructed between grain B (wheat and rice) and soil B fractions. The variation in straw B of the wheat, rice or jute crops could not be predicted by the models. In case of wheat, grain B uptake was strongly (r^2=0.85) explained by the positive relationship with readily soluble and oxide bound B (Table. 4.32).

Table 4.32 Regression models between soil B fractions and grain B uptake.

Crop	Regression Model	r^2
Wheat	Grain B uptake = -1.83 + 49.28 Soluble B + 1.57 Oxide-B	0.85
Rice	Grain B uptake = 9.373 + 6.765 Spec. adsorbed B + 1.368 Oxide-B	0.53

The relationship between soil B fractions and rice grain B uptake was weakly explained by the regression model with r^2= 0.53 (Table 4.32). The main contributors of rice grain B variation were specifically adsorbed B and oxide bound B.

In the incubation experiment with added B (section 4.4.2), it was observed that the added B was mainly distributed to soluble and specifically adsorbed fractions, which indicates that plants may absorb B from these pools.

The flooded soil conditions for rice cultivation may be responsible for a large concentration of oxide-bound B. A positive relation of the plant B with oxide bound B fractions indicates this B fraction may become available to the plants through desorption under various soil conditions. Plant uptake of B depends on its concentration in soil solution which, in turn, is regulated by soil pH, initial B content, sorption and desorption of B from adsorption sites (clays and oxides), types of exchangeable ions, soil minerals, SOM content, the wetting and drying cycle, and soil:water ratio (Keren, 1996; Hu and Brown, 1997; Goldberg *et al.*, 2002).

Ren *et al.* (2009) reported that B-containing oxides improved B supplying capacity of the soil and provided more B to rape seedlings than control treatment. They remarked that B desorbed from metal oxides is an important source of B for plants in acid soils. Similarly, Padbhushan and Kumar (2017) reported that most readily available forms of B for plants are soluble B, specifically adsorbed B and Mn-oxide B. On the other hand, Jin *et al.* (1987) reported that corn tissue B were positively correlated with Mn oxide-bound B, but B in the Fe and Al-oxides was not available to plants. Thus, the forms of B may vary in their availability to the plants depending on the species of plant.

4.6 Fractionation of zinc and boron in the soils from different AEZs of Bangladesh

4.6.1 Fractionation of Zn in the soil

In order to quantify different fractions of Zn and their relationship with plant nutrition, selected samples from five Agroecological Zones of Bangladesh were analyzed. The AEZs were: AEZ 1: Old Himalyan Piedmont Plain; AEZ 9: Old Brahmaputra Floodplain, AEZ 11: High Ganges River Floodplain and AEZ 12: Low Ganges River Floodplain and AEZ 28: Madhupur Tract. The quantities of different Zn fractions along with the percentage of total Zn is presented in Table 4.28. It was found that the concentration of different Zn fractions in the samples varied in the following order: Residual > Amorphous FeOx-bound > Crystalline FeOx bound > MnOx bound > Organically bound > Carbonate-bound > Exchangeable Zn (Table 4.33). There were substantial variations in the quantities of Zn fractions among the samples. A detailed description is presented in the following sections.

4.6.1.1 Exchangeable Zn

The concentration of exchangeable Zn (Exch-Zn) constituted only 0.7% of the total Zn on an average (Table 4.33). Among the 10 soil series analyzed, the concentration of Exch-Zn was significantly lower (0.11 to 0.19 mg/kg) in the calcareous soils of Gopalpur, Sara and Ishurdi series representing AEZ 11 and 12, which was 0.09 to 0.18% of total Zn. The highest level of exch. Zn (1.46 to 1.75%) was observed both in Gangachara and Laskara soil series from AEZ 1 (Table 4.33). Ahmed (1993) observed that the content of Exch-Zn fraction ranged from 0.07 to 1.2% of total Zn in 15 different soils collected from all over the country. The variation among the Exch-Zn concentration might be due to variation in the soil properties and the parent materials of the contrasting soils (Jahiruddin *et al.*, 1992; Moslehuddin *et al.*, 1997; Hassan, 1999; Soltani *et al.*, 2015). The concentration of Exch-Zn decreased with the increase in soil pH (Table 4.33). This is in accordance with the findings of Iyengar *et al.* (1981) and Neilsen *et al.* (1986) who reported that increase in exchangeable Zn was accompanied by decline in soil pH. The Ganges River Floodplain soils occurring in the calcareous Gangetic Alluvium containing variable quantities of calcite are prone to Zn deficiency (Jahiruddin *et al.*, 2000).

Table 4.33 Fractionation of Zn in the soils sampled from different AEZs of Bangladesh

AEZ	Soil series	Location	Soil Zn fractions (mg/kg)[*]							Total Zn (mg/kg)[a]	DTPA Zn (mg/kg)	Soil pH[a]
			Exchangeable[a]	Carbonate -bound[a]	Org. bound[a]	MnOx bound[a]	Am.FeOx bound[a]	Cryst.FeOx bound[a]	Residual[a]			
1	Gangachara	Kaharol, Dinajpur	1.11a (1.75)		3.58b (5.64)	7.8b (12.3)	20.0b (31.6)	13.3cd (21.3)	17f (27.4)	64e	1.65	5.13f
1	Laskara	Ghoria, Thakurgaon	1.12a (1.46)		3.65b (4.78)	6.1c (8.0)	5.5c (7.2)	13.0cd (17.0)	47bcd (62.0)	77de	1.23	4.75g
9	Silmondi	Fulbaria, Mymensingh	0.60ab (0.72)		5.12ab (6.13)	4.7d (5.6)	24.1b (29.4)	20.0abcd (23.9)	29def (34.7)	84cd	0.61	6.64d
9	Silmondi	Trishal, Mymensingh	0.49b (0.57)		4.39ab (5.08)	6.2c (7.1)	16.0bc (18.5)	22.2abc (26.0)	37cde (42.8)	87cd	0.99	6.54d
11	Gopalpur	Sadar, Kushtia	0.11b (0.12)	0.60d (0.67)	6.32a (7.03)	1.7e (1.9)	16.4bc (18.4)	12.5cd (13.9)	52bc (57.8)	90cd	0.66	8.05a
11	Sara	Damurhuda, Chuadanga	0.11b (0.09)	1.00c (0.82)	6.13a (4.98)	5.1cd (4.1)	21.2b (17.5)	11.0d (9.0)	78a (63.3)	123a	0.63	7.35c
12	Ishurdi	Sadar, Rajbari	0.61ab (0.57)	1.65b (1.55)	0.98c (0.92)	1.6e (1.5)	18.2b (17.4)	27.5a (25.8)	56b (52.1)	107b	0.52	8.20a
12	Ishurdi	Sadar, Rajbari	0.19b (0.18)	2.10a (2.01)	1.25c (1.20)	1.9e (1.8)	27.0b (25.9)	25.0ab (23.9)	47bc (44.9)	105b	1.43	7.69b
28	Kalma	Sadar, Gazipur	0.52ab (0.66)		4.14ab (5.35)	9.8a (12.7)	24.6b (31.8)	12.0cd (15.6)	27ef (34.6)	78de	3.45	6.58d
28	Dhamrai	Kapasia, Gazipur	0.68ab (0.73)		6.46a (5.96)	5.3cd (5.7)	39.3a (42.4)	16.4bcd (17.7)	26ef (27.5)	93bc	0.71	6.25e
Minimum			0.11	0.6	0.96	1.6	5.5	11.0	17	64	0.52	4.75
Maximum			1.12	2.10	6.46	9.8	39.3	27.5	78	123	3.45	8.20
Mean			0.55	1.34	4.20	5.0	21.2	17.3	41	90	1.19	6.72

[*] Values in the parentheses represent percent of the total Zn.

[a] Means followed by a common letter in a column are not significantly different at 5% level.

4.6.1.2 Organically bound Zn

Organically bound Zn (Org-Zn) ranged from 0.98 to 6.5 mg/kg comprising 0.9 to 7.0% of the total Zn, respectively (Table 4.33). The lowest Org-Zn concentration (0.98 - 1.25 mg/kg) was observed in Ishurdi series (Rajbari) of AEZ 12. Ahmed (1993) also observed that, among diverse types of soils of the country, the soils from Ishurdi series contained the lowest quantity of organic Zn. In the same way, Rouf *et al.* (1998) reported that the organically bound Zn was the lowest of all the fractions in Khilgaon and Kalma series of Gazipur. These findings suggest that in the Low Ganges River Floodplain soils, Zn fractions that are potentially bioavailable represent only a negligible fraction of total soil content while most of the Zn is distributed in forms that might be difficult to be available to the plants. This is in agreement with the findings of others. Banjoko and McGrath (1991) reported the lowest percentage of organic Zn among all the Zn fractions in the soils of Nigeria and UK. In China, Han *et al.* (2011) reported much smaller concentration of organic Zn (~2%) in soils having carbonate minerals and a lower content of organic matter. In a study conducted in India, only a small content of Zn (<0.1 mg/kg) was found in the organic fraction which was attributed to lower content of SOM and a predominance of Fe-oxides in retaining Zn (Singh *et al.*, 1988). Iyengar *et al.* (1981) reported wide variation in the magnitude of Zn fractions among 19 soils with different chemical and physical properties. On an average, most of the Zn was found in the Fe oxide (25%) and residual (70%) fractions and the Exch-Zn, Org-Zn and Mn oxide bound Zn averaged 3.7, 2.5 and 2% of total Zn, respectively.

4.6.1.3 Carbonate-bound Zn

Carbonate-bound Zn was studied only in the Ganges River Floodplain soils which represent the calcareous region of the country (Table 4.33). The concentration of Carb-Zn was significantly higher in AEZ 12 (1.65-2.10 mg/kg) than that of AEZ 11 (0.6-1.0 mg/kg). Dolomite is a diagnostic mineral of Ganges sediment (Hassan, 1999). This dolomite and other carbonate minerals may fix Zn in an unavailable form. Adsorption of Zn by carbonates or precipitation of $Zn(OH)_2$ or $ZnCO_3$ in calcareous soils is believed to be partly responsible for unavailability of Zn in those soils (Udo *et al.*, 1970; Kalbasi *et al.*, 1978; Singh and Singh, 1980). Uygur and Rimmer (2000) showed that in calcareous soils with pH values 8 or above, Fe-oxides readily precipitate out and form coatings on the carbonate minerals. They found that an increase in pH from 8 to 8.3 can double the strength of bonding of Zn to calcite, but with a 0.05% Fe oxide coating on the calcite the bonding increases 7-fold over this pH range.

Therefore, in calcareous soils, the occurrence of calcite in coatings of Fe oxide results in even less availability of Zn to plants than with pure calcite (Alloway, 2009).

4.6.1.4 Manganese oxide (MnOx) bound Zn

The content of MnOx-bound Zn ranged from 1.1 to 9.6 mg/kg comprising 1.5 to 12.3% of the total Zn (Table 4.33). The highest proportion (12.3 - 12.7%) was observed in Kalma series (AEZ 28) and Gangachara series (AEZ 28) located in Gazipur and Thakurgaon, respectively. The lowest percentage (~1.6%) of MnOx-Zn was observed in Ishurdi series (AEZs 11 & 12) located in Kushtia and Rajbari. Similar results were observed in the soils of Bangladesh by Rouf *et al.* (1998), who found 10 to 28% of MnOx-Zn in Khilgaon and Kalma series (AEZ 28). The quantity of this fraction was quite lower than FeOx-bound Zn which is usually observed in most of the soils (Iyengar *et al.*, 1981; Chowdhury *et al.*, 1997). The reason of lower quantity of MnOx-Zn is less abundance of Mn-oxides, usually 1/50 part of Fe oxides even though they may exhibit greater chemical reactivity (Scheinost, 2005). Although the size of the fraction was small, the reactivity of MnOx was reflected in its proportional increase with the increase DTPA Zn of the soils (Table 4.28). This implies that MnOx-bound Zn may act as an important source of DTPA Zn in Bangladesh soils. Positive and significant correlation between MnOx-Zn and plant available Zn was also reported by others (Liang *et al.*, 1990; Behera *et al.*, 2008). In addition, MnOx bound Zn was inversely related to pH (Table 4.28). According to McBride (1989) the activity of Mn decreases as pH rises. As a result, sorption of Zn on Mn-oxides decreases with decrease in soil pH.

4.6.1.5 Iron oxide (amorphous and crystalline FeOx)-bound Zn

A substantial portion of soil Zn was associated with Fe oxides (Table 4.33). In some soils, FeOx-bound Zn was higher than residual or mineral bound Zn. Higher FeOx-bound Zn was also reported by others (Kalbasi *et al.*, 1978; Shuman, 1979; Mandal and Mandal, 1986; Ahmed, 1993). The calcareous soils (e.g., Ganges River Floodplain soils) with higher pH usually show higher FeOx bound Zn (Uygur and Rimmer, 2000; Alloway, 2009). Among the two iron oxide bound forms, the average concentration of amorphous Fe oxide bound Zn was higher than that of the crystalline Fe oxide bound Zn (Table 4.33).

The highest percentage (42%) of amorphous FeOx-bound Zn was observed in AEZ 28 (Kalma series, Gazipur). The Ganges River Floodplain soils (AEZ 11 and 12) showed comparatively lower amorph. FeOx-Zn than other parts of the country. Ahmed (1993) reported that amorphous- and crystalline sesquioxide-bound Zn ranged from 2.03 to 8.91 and 1.86 to 5.12%, respectively in 15 contrasting types of soils of the country. Rouf *et al.* (1998) and Singh *et al.* (1988) also observed much higher quantity of amorph. FeOx-Zn compared to cryst. FeOx-Zn that usually exists as surface coating of finer particles in the soils. Also, this finding indicates that Fe-oxides are of greater concern in Zn chemistry of the soil than Mn-oxides.

4.6.1.6 Residual Zn

The residual Zn is the fraction occluded or fixed in the primary and secondary alumino-silicate minerals. In most of the samples, soil Zn was predominantly in the residual fraction ranging from 17 to 78 mg/kg and constituted 27 to 63% of the total soil Zn (Table 4.33). This is well documented that usually more than half of total soil Zn is associated with the residual fraction and is unavailable to the plants (Mandal *et al.*, 1988; Liang *et al.*, 1990; Shuman, 1991; Chowdhury *et al.*, 1997; Ma and Uren, 1997).

In general, the Ganges River Floodplain soils (Sara and Ishurdi series) contained larger proportion (average 55%) of residual Zn than the rest of the soils studied (average 38%). Higher percent of residual or mineral-bound Zn in Ganges River Floodplain soils might be due to fixation by clay minerals, particularly, biedellite and similar type of minerals, which are distinct in this region (Egashira and Yasmin, 1990; Moslehuddin and Egashira, 1997; Hossain *et al.*, 2011). Fixation of Zn by clay minerals is evident in the literature. Rahmatullah *et al.* (1985) observed that biedellite fixed the highest (70%) amount of applied Zn in the soils of Pakistan followed by vermicullite and montmorillonite (55 - 59%).

4.6.1.7 Total Zn

Total Zn content was characteristically higher (90-123 mg Zn/kg) in the High and Low Ganges River Floodplain soils (AEZs 11 and 12) than that of the other AEZ soils (64 to 93 mg Zn/kg) (Table 4.33). Madhupur Tract soils (AEZ 28) and Old Brahmaputra Floodplain (AEZ 9) soils exhibited almost similar quantities of total Zn averaging 85 mg/kg. The lowest quantity of total Zn (on an average 70 mg/kg) was found in the Old Himalayan Piedmont Plain soils (AEZ 1).

The concentration of total Zn found in the present study agreed well with those reported by others. For instance, Jahiruddin *et al.* (2000) reported that total Zn content of non-calcareous soils ranged from 45 to 94 mg/kg while that of calcareous soils from 51 to 111 mg/kg. The mean concentration of total Zn in Old Brahmaputra Floodplain (AEZ 9) and High Ganges River Floodplain (AEZ 11) were 66 and 79 mg/kg, respectively. Domingo and Kyuma (1983) found 10 to 110 mg/kg total Zn with a mean of 68 mg/kg in 53 soils of Bangladesh, while Khan *et al.* (1997) found 97 to 447 mg/kg of total Zn in floodplain top soils of Bangladesh. Likewise, Begum *et al.* (2016) observed that the mean total Zn content of the highland soils of Gazipur (AEZ 28) was 112 mg/kg. On the other hand, Rouf *et al.* (1998) found 103 to 136 mg/kg of soil total Zn in Khilgaon and Kalma series located in Gazipur (AEZ 28). Similarly, Hassan (1999) reported 105 mg/kg and 141 mg/kg total Zn in Ishurdi and Ghior series, respectively. In his study, the average total Zn concentration of recent floodplain soils in Bangladesh was 105 mg/kg. The mean total Zn contents in Ganges River Floodplain soils were higher compared to terrace or hill soils (Hassan, 1999). Higher contents of trace elements in the floodplain soils may be due to higher clay contents (Moslehuddin *et al.*, 1997). Also, the higher contents of primary minerals present in the silt fractions probably contribute to the high content of trace elements in these soils (Huizing, 1971; Hassan, 1999) thus reflecting differences in parent materials.

According to Jahiruddin *et al.* (2000) the level of total Zn varied considerably between the locations irrespective of land type. They reported that total Zn content of non-calcareous soils were much lower than that of calcareous soils. They also observed positive relationship between total Zn and other elements with organic matter and clay content of the soils studied.

4.6.1.8 Regression model to predict Zn availability in soil

A multiple linear regression model was constructed by forward stepwise method to predict the variation of DTPA Zn in the soil due to the dynamics of the different Zn fractions, org. C, clay content and pH of the soils with contrasting properties. The regression equation is as follows:

$$\text{DTPA Zn} = 1.79 + 0.26\ \text{MnOx-Zn} - 0.22\ \text{Org. Zn} - 1.19\ \text{Exch. Zn} + 0.57\ \text{CFeOx-Zn} - 0.14\ \text{Residual Zn} \ldots\ldots (r^2=0.79) \ldots\ldots\ldots\ldots \text{(Eq. 1)}$$

The model (Eq. 1) accounted for 79% of the variation of DTPA Zn in these diverse types of soils. The main contributor of the variation was MnOx bound Zn. Organic and exchangeable

Zn contributed negatively to DTPA Zn. Minor contributions of cryst. FeOx and residual Zn was also observed. Contribution of MnOx and FeOx bound Zn is consistent with the findings of Behera *et al.* (2008), who reported that MnOx, FeOx-bound and carbonate bound Zn directly contributed to DTPA Zn. Similarly, Liang *et al.* (1990) found that DTPA Zn contains Zn from Mn oxides and organic matter associations in addition to the exchangeable and adsorbed forms. However, negative relationship of DTPA Zn with exchangeable and organic Zn is unusual in light of the previous reports (Chowdhury *et al.*, 1997; Shuman, 1999). According to Kaplan *et al.* (1990) it is possible that the variation in the soil properties, parent materials and climate of the studied samples was too wide which decreased the likelihood of observing a strong positive relations between DTPA Zn and organic matter or exchange sites.

4.6.2 Fractionation of boron in the soils

Fractions of soil B were also quantified in the selected soil samples of contrasting origin from five Agroecological Zones of Bangladesh. The results are presented in Table 4.34. Details of findings are discussed in the following sections.

Soils from AEZ 1 (Dinajpur and Thakurgaon) contained the highest quantities (3.0 - 4.2) of readily soluble B extracted by cold $CaCl_2$, among the soils from different AEZs analyzed (Table 4.34). Similarly, the specifically adsorbed B and oxide bound B (Ox-B) were comparatively higher in the Ganges River Floodplain soils than the other soils. This was accompanied by a higher quantity of total B in the Ganges River Floodplain soils.

The range of readily soluble B was consistent with those reported in the literature. Domingo and Kyuma (1984) reported that the content of extractable B in the soils of Bangladesh was below 1 mg/kg. Badr-Uz-Zaman and Salim (1999) found that the proportion of total soil B in the soluble and nonspecifically adsorbed fractions of calcareous soils of Pakistan ranged from 0.4 to 2.3%, with an average value of 1.2%.

The soils from AEZ 1 (Old Himalayan Piedmont Plain) were acidic (pH 4.7 - 5.1) where higher amount of soluble B was observed (Table 4.34). It is reported that the concentration. of solution B and the plant availability of B decreases as soil pH increases due to higher adsorption in higher pH (Keren and Bingham, 1985; Goldberg, 1997). Hou *et al.* (1994) found strong significant positive correlation between readily soluble B and soil pH. However, the cold $CaCl_2$ extractable B (used in the fractionation scheme) is not a practical index of plant available B in comparison to hot water soluble B (Diana, 2008).

Table 4.34 Fractionation of B in soils sampled from different AEZs of Bangladesh

AEZ	Soil series	Location	Soil B fractions (mg/kg)* Readily soluble B^a	Specifically adsorbed B^a	Oxide bound B^a	Residual B^a	Total B (mg/kg)^a	HWS B (mg/kg)^a
1	Gangachara	Kaharol, Dinajpur	4.22a (4.9)	1.36cd (1.6)	7.5a (8.8)	72a (85)	86a	0.45ab
1	Laskara	Ghoria, Thakurgaon	3.07b (5.9)	1.64bc (3.2)	3.9b (7.5)	43c (83)	52c	0.24cde
9	Silmondi	Fulbaria, Mymensingh	0.92cd (4.8)	0.63e (3.3)	2.5b (13.2)	15e (79)	19e	0.17de
9	Silmondi	Trishal, Mymensingh	0.38d (0.6)	0.49e (0.8)	3.3b (5.1)	61b (94)	65b	0.53a
11	Gopalpur	Sadar, Kushtia	0.71d (2.9)	0.98de (4.0)	9.3a (38)	13.5e (55)	25e	0.15 e
11	Sara	Damurhuda, Chuadanga	0.54d (2.5)	0.73e (3.4)	2.75b (12.8)	17.45e (81)	22e	0.27cd
12	Ishurdi	Sadar, Rajbari	1.7c (9.2)	2.41a (13.0)	4.1b (22)	8.9e (48)	19e	0.42b
12	Ishurdi	Sadar, Rajbari	1.0cd (4.5)	2.18ab (9.9)	4.1b (18.6)	14e (64)	22e	0.30c
28	Kalma	Sadar, Gazipur	0.43d (2.4)	0.9de (5.0)	3.45b (19.2)	13.25e 74()	18e	0.26cd
28	Dhamrai	Kapasia, Gazipur	0.45c (1.2)	0.9de (2.3)	3.15b (8.2)	34.05d (88)	39d	0.18de

[*] Values in the parentheses represent percent of the total B.

[a] Means followed by a common letter in a column are not significantly different at 5% level.

In general, the soil samples of AEZ 12 showed larger proportion (9-13%) specifically adsorbed B in total B than other soils (up to 5%). This might be due to amount and type of clay of those soils that are major adsorbent of this B fraction (Evans and Sparks, 1983; Goldberg, 1997). As mentioned in Table 3.5 (Chapter 3) that the soils of Ganges River Floodplain contains mica and smectite clay minerals. Among the clay minerals, smectite (montmorillonite) has been reported to adsorb B stronger than kaolinite (Singh, 1971).

Higher oxide bound B in the piedmont soil may be due to presence of higher level of Fe and Al oxides in those soils (Hassan, 1999) that are responsible for B adsorption in soil. Sesquioxides have been reported to be responsible for strong retention of B in the soils and tend to reduce the easily available B to plants (Tsadilas *et al.*, 1994).

4.6.2.1 Regression model to predict boron availability in soils

A multiple regression model was constructed by forward stepwise method to predict the variation of hot water soluble (HWS) B due to the dynamics of the different B fractions, and soil properties of the soils from the different AEZ. The model is presented in the following equation:

$$\text{HWS B} = -0.915 + 0.006\ \text{Resid. B} + 0.11\ \text{soil pH} + 0.298\ \text{Org. C} - 0.02\ \text{Ox. B} \quad (r^2 = 0.68)$$

The model accounted for 68% of the variation of HWS B in these contrasting soil types. The main contributor of variation was residual B, soil pH and organic C. Oxide B was negatively related to available B.

Since organic B could not be separated out like the other fractions in this study, it is believed there were some effects of this fraction which might have been nested in that of residual B. Besides, the effect of soil organic matter (i.e., organic C) on available B was also visible in the model. This finding agrees well with those reported by others. Raza *et al.* (2002) observed that organic C was significantly related to HWS B suggesting that SOM may be a source of labile B in the soil. Jin *et al.* (1988) reported that soil organic matter plays an important role in B availability and can minimize B leaching from soil and maintain B in a relatively available form (Berger and Truog, 1945; Page and Paden, 1954).

The negative relationship of HWS B with Ox-B observed in the model was discussed in the previous section. In fact, B can be adsorbed by sesquioxides by ligand exchange mechanism making it less available for the plants (Yermiyahu *et al.*, 1988; Keren, 1996).

In can be briefly summerized from the discussions, that significant effect of Zn and B was observed in grain yield of wheat (BARI Gom 26) in the W-J-R pattern. The Zn effect was dominant over B effect. However, the stick and fiber yield of jute (JRO 524) and grain yield of T. Aman rice increased inconsistently with Zn and B application. Similar trend of inconsistent yield response was also observed in Boro and T. Aman rice crops of R-F-R pattern. The residual effect of Zn and B applied in wheat was realized in the yields and nutrient uptake of jute and T. Aman rice crops, suggesting that all of the applied Zn and B are not utilized by the current crop and their residue remains in the soil. However, a fresh addition of the nutrients yielded more jute or rice grain than that of the residual nutrients. The positive response of T. Aman rice to B applied in jute indicates that B application should not be ignored in Low Ganges River Floodplain soils. Similar to grain yield, the effect of Zn and B on the uptake of Zn and B in wheat, jute and rice crops were insignificant, although some remarkable variation was observed.

Striking re-distributions in the amorphous and crystalline Fe-oxide bound Zn and the residual Zn was observed in the incubation study with added Zn indicating a transformation of the added Zn. In the incubation of the soil with added B, the readily soluble and specifically adsorbed B increased substantially and residual B, decreased greatly implying a shift of added B to plant available forms. Fractionation of the field soil under W-J-R soil revealed significant variations in the exchangeable, organic and Mn oxide-bound Zn forms (comparatively labile) due to application of Zn and B implying changes in the chemistry of native soil components. The increase in organically bound Zn in the native soil could be a contribution of the crop residue or the impact of applying fertilizers. The fractionation of B revealed that the concentration of B in the various soil fractions decreased from that of the initial soil and the added B could not be traced out in any of the B fractions practically.

Correlation between plant tissue Zn and the soil Zn fractions varied with plant type, season and soil properties. Concentration and uptake of grain B in wheat and rice were significantly correlated with exchangeable and specifically adsorbed B.

The fractionation of Zn in the soils from different AEZs indicated that MnOx-bound Zn acts as an important source of available Zn in Bangladesh soils. Higher residual Zn was observed in Ganges River Floodplain soils indicating fixation by clay minerals. Likewise greater quantity of specifically adsorbed B in Ganges River Floodplain indicates adsorption of B by smectite type clay minerals.

CHAPTER V

SUMMARY AND CONCLUSION

Deficiencies of micronutrients have long been established in the intensive cropping practices. Since intensive cropping is a common picture of most of the cultivated areas of Bangladesh, application of micronutrients is emphasized equally as that of the major nutrients to sustain the crop productivity. Thus, it would be appropriate to have a closer look on the various aspects of micronutrients with special emphasis on zinc (Zn) and boron (B), particularly, in the areas with known deficiency, e.g., Ganges River Floodplain soils. Investigations were, therefore, carried out to delineate the status of Zn and B as well as some other micronutrients of 25 soils from each of High and Low Ganges River Floodplain soils (AEZs 11 and 12). Laboratory experiments were conducted to study the fractionation and transformation of native and applied Zn and B in soils. Field experiments were also conducted to study the response of wheat, jute and rice crops to various rates of Zn and B as well as the relationship of Zn and B fractions with crop uptake. In addition, fractionations of Zn and B in soils from different AEZs of Bangladesh were also done. The results are summarized below:

1) The study of the micronutrient status revealed that quite a large number of soil samples of AEZ 11 and 12 had low concentration of plant available Zn and B. This is more noticeable in Low Ganges River Floodplain (AEZ 12), with most of the topsoils of the region being deficient in Zn. Similarly, about 66% of the samples of AEZ 12 were deficient in B. The average concentration of available iron (Fe), copper (Cu) and manganese (Mn) in the Ganges River Floodplain soils was much higher than the optimum concentration for plant growth. Too much solution Fe may inhibit the uptake and utilization of other nutrients by plants like rice. However, there was no report of micronutrient-toxicity in these regions.

2) A significant and strong correlation was observed between DTPA Zn and Fe concentration suggesting that Zn may be closely associated with iron rich compounds like oxides and hydroxides in the study area. In the same way, a positive significant relationship of organic C with Cu and B was observed implying that these micronutrients may have been released from soil organic matter.

   Among the soil series of the Ganges River Floodplain, the Sara, Gopalpur and Ishurdi series exhibited higher available Zn, while Gopalpur and Ghior series were rich in B.

3) It was observed from the field experiments that there were some variation in the response to Zn and B application among the crops. In the wheat-jute-T. Aman rice (W-J-R) cropping pattern, the grain yield of BARI Gom 26 was significantly influenced by

Zn and B application at farmer's field at Rajbari sadar upazila. The Zn effect was dominant over B effect. The soil was low in Zn and B. Straw yield remained unaffected by Zn and/ B application. The yield of jute (JRO 524) stick and fiber increased but not consistently with the rate of Zn and B application.

The residual effect of Zn and B applied in wheat was realized in the yield of jute. However, a fresh addition of the nutrients returned better jute yield than that of the residual effect. In general, application of Zn @ 4-6 kg/ha in wheat was sufficient for all the crops in the cropping pattern. However, fresh addition of Zn and B produced better yield than the residual effect. Moreover, frequent application helps build up of soil Zn.

In T. Aman rice (BRRI dhan49), the third crop in the W-J-R pattern, although the grain yield was significantly influenced by the application of Zn and B in the previous or current crop, the effect was not as per the rate of Zn and B application. Usually, higher grain yield was observed when Zn was freshly applied.

4) A positive response of B was observed in T. Aman rice when it was applied in addition to Zn in the second crop (jute) of the pattern. Hence, the application of B should not be overlooked in the intensively cropped soils of AEZ 12.

5) In Boro rice-Fallow-T. Aman rice cropping pattern, some positive effect of Zn and B application on the grain yield of Boro rice (BRRI dhan29) was found, but the effect was not visible under field condition every year. The second crop of the pattern, i.e., T. Aman rice (BRRI dhan49) responded to Zn and B application, to some extent. This was mainly the residual effect of their application in Boro rice.

This is noteworthy that a significant response to Zn and B application was observed in a soil (in the rice-rice pattern field) where the soil available Zn/B status was sufficient for plant requirement. This indicates the availability of Zn and B may decrease in the studied soil due to various soil chemical reactions and that the different forms of soil Zn/B are in equilibrium with each other and their solubility (intensity factor) is controlled by the activity of the labile fractions (capacity factor) in the soil.

It can be opined from the above findings that, since the applied Zn and B were not fully utilized by the standing crops and their residue remained in the soil for the next crops, requirement of Zn and B application in crops should be determined through monitoring of their dynamics in the soil.

6) Wheat grain Zn concentration and its uptake increased remarkably due to Zn and B application. Similarly, straw Zn increased significantly with few exceptions.

   The effect of Zn and B application on the concentration and uptake of Zn and B in jute and rice crops was not consistent. In some cases, the highest Zn and B application did not show the highest plant Zn and B. This may be attributed to the variation of soil properties in the field conditions influencing availability of Zn and B for the crops in question. In case of rice, immobilization of the applied Zn in the soil by soil components after flooding or the lack of translocation of the accumulated Zn in rice shoot to grain have been attributed for non-response to applied Zn.

   Yearly difference of Zn and B uptake was sometimes strikingly visible. Variation in soil properties due to seasonal climatic changes may affect the availability of the nutrients.

7) Application of Zn and B may not always increase grain yield of rice and wheat but the grain quality (grain Zn and B) may be enhanced by their application. For rice-rice cropping pattern, 2 kg Zn/ha in each crop is sufficient for satisfactory yield and grain Zn concentration.

   The average Zn uptake by Boro rice (~130 mg/kg) was higher than that of T. Aman rice (~92 mg/kg) which may be due to the variation in grain yield, field duration of the crop, and seasonal climatic conditions.

8) Similar to Zn, the concentration and uptake of boron was not sharply visible in the crops. However, some positive responses were observed in jute and rice crops.

9) In the incubation study using the field soil of Rajbari experimental site, a striking re-distribution was observed in the Fe-oxide bound Zn and in the residual Zn due to application of Zn. The percent of amorphous Fe-oxide bound Zn increased from that of the initial soil both under field capacity and submerged soil conditions indicating that the added Zn may have transformed to amorphous FeOx-Zn. In the same way, the proportion of crystalline Fe-oxide bound Zn increased in the field moist soil due to addition of Zn. However, in the submerged soil, the proportion of crystalline FeOx-Zn decreased from the initial soil, which implies that under submerged and reduced soil conditions, Zn may be released from the cryst. FeOx-Zn. From the plant nutrition point of view, increase in amorph. FeOx-Zn fraction is beneficial in the long run, since it acts as a potential source of Zn both in field moist and submerged soils. A substantial decrease in the residual Zn fraction of the incubated soils, particularly in the field moist

soil, is also favourable for plant nutrition. It indicates that the Zn in the mineral fraction may weather into bioavailable forms.

10) In the incubation study with added B, the major portion (70%) of the B was found in the residual (occluded in mineral) fraction, both in the initial and added B conditions. Percent of readily soluble and specifically adsorbed B increased substantially in the B added incubated soils. In contrast, the percent of residual B, which is mainly the B present in the minerals, decreased greatly in the B added soils, both under field moist and submerged conditions. The pH of the studied soil were very high (>8.0), which might have led to higher 'specific' B adsorption to the oxides of Al and Fe, clay minerals and organic matter in soil. However, increase in readily soluble B and decrease in residual B is obviously favourable for plant nutrition.

11) The fractionation study of Zn under the field condition reveals that the mean amorph. FeOx, cryst. FeOx and residual Zn concentration of the control plot (without Zn and B) remained quite unchanged. Significant variations were observed in exchangeable, organic and MnOx-bound Zn (which are comparatively labile) after two years of cropping both in the initial and control plot implying changes in the chemistry of native soil components.

    Percent of exchangeable Zn reduced significantly in the Zn treated soils from that of the initial soil which was probably due to the reason that the exchangeable fraction of the added Zn was transformed to other forms caused by the variation in soil properties.

    The percent organically bound Zn increased several folds in the Zn treated soils than those of the untreated soils. Also, the inherent content of organically bound Zn increased in the plot with no added Zn. This could be a contribution of the crop residue of the cultivated crops (wheat, jute and rice) or the impact of the application of N, P, K and S fertilizers during the cropping. A high soil pH (> 8.0) may also fovour Zn redistribution to organic fraction. Among the treated soils, the plots with higher Zn application rates (4 and 6 kg Zn/ha) showed higher amount of organic Zn than those with lower (2 kg/ha) or no Zn application. Increase in organic Zn fraction upon Zn addition is desirable for plant nutrition since this form acts as labile pool of soluble Zn.

    The MnOx-Zn fraction reduced slightly but significantly in the Zn and B treated soils from that of the initial soil. A reduction of MnOx-bound Zn may indicate release of the bound Zn. Flooding of soil for rice cultivation might have favoured the dissolution of Mn-oxides.

Amorphous Fe oxide bound Zn increased significantly due to the application of Zn and B from that of the initial soil. This is attributed to an increased adsorption of Zn by amorphous FeOx in submerged soil. Under submerged soil condition, increase in fresh Fe oxide/hydroxides with large surface area are formed which are responsible for adsorption of higher amount of Zn.

Unlike amorphous FeOx-bound Zn, application of Zn and B effectively and significantly decreased the crystalline Fe-oxide bound Zn fraction. Greater reduction was observed in the plots with lower added Zn (2 and 4 kg Zn/ha) compared to higher rate (6 kg Zn/ha). Thus the added Zn was transformed more to fractions other than crystalline FeOx-Zn. Retention of Zn by amorphous Fe oxide may not be as problematic as crystalline Fe oxide, since Zn is more strongly adsorbed in the latter than the former. Hence, the increase of amorphous FeOx-Zn and the decrease of crystalline FeOx-Zn is favourable for plant nutrition, since Zn in the amorphous FeOx fraction contributes more to uptake by the crop compared to other forms.

The bulk of the Zn was observed in the residual (mineral-bound) fraction. A large residual Zn fraction indicates that the soils are relatively young and unweathered alluvial soils. The residual fraction increased greatly from 63% in the soil without Zn to as high as 87% in 4 kg Zn/ha plot after two years of cropping. Thus, the application of Zn and B seems to cause Zn to be transformed primarily in the residual fraction. The presence of Fe-rich high charge biedellite clay minerals in these soils (AEZ 12) with higher fixing capacity may be largely responsible for the fixation of Zn in reversible or irreversible forms. Also, the reactive and available forms of Zn (soluble, exchangeable and adsorbed) have been reported to be transformed to the unavailable and unreactive forms (oxide and residual) with time.

12) The fractionation study for B in the same soil revealed that the concentration of B in the various soil fractions decreased from that of the initial soil. Thus, the added B could not be traced out in any of the B fractions practically.

Exchangeable B reduced significantly in the treated soils from that of the initial soil, indicating that the applied B may have been transformed from exchangeable to other forms during the cropping period. Adsorption to oxides surfaces and clay minerals is among the major causes of decrease in B availability in soil.

Likewise, specifically adsorbed B decreased significantly in the treated plots compared to the initial soil. Application of major nutrients in the crops along with the changes in soil properties might have caused the specifically adsorbed B to be redistributed to other forms especially the organic, oxide bound and the residual forms.

The concentration of oxide-B increased in the plot with highest B application. It is possible that the applied B has been transformed to oxide bound B with time. The effect is more obvious in the plots with higher B rate than those with low or no B. Higher pH of the test soil may be responsible for higher B adsorption in the oxide surfaces.

Residual B did not change significantly due to Zn and B application indicating that an equilibrium may exist in the soil B fractions and that the exchangeable, specifically adsorbed and oxide bound B may be transformed to residual B with the increase in B application.

13) Correlation study between Zn uptake by crops and soil Zn fractions revealed that wheat grain Zn concentration correlated significantly with Mn-oxide bound Zn fraction, while the Zn uptake by grain did not correlate with any of the fractions, significantly. It is possible that the Mn-oxide bound Zn fraction had transformed and contributed to plant available forms of Zn in soil during the growing period of wheat. Similarly, jute stick Zn concentration and its uptake were significantly positively correlated with Mn-oxide bound Zn and total Zn in soil. Thus, Mn-oxide bound Zn appears to be an important source of Zn for jute in this soil.

A positive relationship was also observed between wheat straw Zn concentration and its uptake with the residual Zn which implies that weathering of the parent material may contribute to the labile and, in turn, the available pool of the nutrient.

Rice grain Zn concentration and uptake were strongly positively correlated with organically bound Zn and negatively with amorphous FeOx bound Zn. A negative relationship between oxide Zn and plant Zn indicates that amorphous FeOx-Zn was not available to rice during the growing period.

Thus, it is observed that the relationship between plant tissue Zn and the soil Zn fractions varies with plant type, season and soil properties. For instance, the fractions of

Zn that are positively correlated with wheat tissue Zn (e.g., amorphous FeOx-Zn) was negatively correlated with rice tissue Zn, while organic Zn was negatively correlated to wheat grain but not with rice grain Zn.

14) Multiple linear regression model predicted 68% of the variation of wheat grain Zn uptake due to the dynamics of organically bound, amorph. FeOx-bound and residual Zn fractions in soil, implying that, Zn from these fractions becomes available to wheat plant through dynamic equilibrium with the solution Zn.

    In T. Aman rice, 79% of the variability of grain Zn uptake was accounted for by the positive association with organic Zn and negative with amorph. FeOx-Zn fractions of soil. Similarly, 67% of the variation in rice straw Zn uptake was explained mainly by a positive relationship with organic and a negative relationship with MnOx bound Zn. Negative relationships of rice plant Zn uptake with the oxide bound Zn (FeOx and MnOx) implies that Zn from these sources was unavailable or marginally available to rice because of strong bonding between Zn and oxide surfaces.

    In contrast to the negative relationship between organic Zn and wheat plant Zn, uptake of Zn by rice plant was positively correlated. This observation suggests that the organic Zn prevailed in a dynamic state in the soil, being unavailable during wheat cultivation but became available to rice crop later. Redistribution of organic Zn under dynamic soil conditions has been attributed to this type of variation.

15) Correlation study of crop tissue B and soil B fractions reveals that wheat grain B concentration and uptake were strongly correlated with soil exchangeable B and not related to specifically adsorbed, oxide bound and residual B, implying that wheat takes up B only from the exchangeable B pool in the soil studied. Likewise, T. Aman rice grain B concentration was related to exchangeable and specifically adsorbed B fractions. However, rice grain B uptake was not related to any of the soil B fractions. Researchers attributed the difference between the relationships to the difference in soil fertility and plant species.

    Linear regression models were able to predict only the variation of grain B of wheat and rice and soil B fractions. The variation in straw B of the wheat, rice or jute crops could not be predicted by the models. In case of wheat, grain B uptake was strongly (r^2=0.85) explained by the positive relationship with readily soluble and oxide bound B. The relationship between soil B fractions and rice grain B uptake was weakly explained by the regression model with $r^2= 0.53$. The main contributors of rice grain B variation were specifically adsorbed B and oxide bound B, implying that in addition to readily soluble fraction, B from specifically adsorbed and oxide bound fractions may also become available to crops as affected by various soil properties and processes.

16) Fractionation study conducted with contrasting soils of different AEZ of Bangladesh reveals that there was substantial variation in the quantities of Zn fractions among the locations. Among the 10 soil series analyzed, exchangeable-Zn was significantly lower in Gopalpur, Sara and Ishurdi series from AEZ 11 and 12. The highest level of exch. Zn was observed both in Gangachara and Laskara series of Old Himalyan Piedmont plain (AEZ 1). The concentration of exchangeable-Zn decreased with the increase in soil pH of the studied soils.

The content of MnOx-bound Zn ranged from 1.1 to 9.6 mg/kg comprising 1.5 to 12.3% of the total Zn. The highest proportion (12.3-12.7%) was observed in Kalma (Gazipur) and Gangachara series (Thakurgaon) while the lowest (~1.6%) was in Ishurdi series (from Kushtia and Rajbari). The quantity of this fraction was quite lower than FeOx-bound Zn, but the reactivity of MnOx was reflected in its proportional increase with the increase DTPA Zn of the soils. This implies that MnOx-bound Zn may act as an important source of DTPA Zn in Bangladesh soils.

A considerable portion of soil Zn was associated with Fe oxides. In some soils, FeOx-bound Zn was larger than residual or mineral bound Zn. The average concentration of amorph. FeOx-bound Zn was higher than that of cryst. FeOx-bound Zn in the studied soils. In most of the samples, soil Zn was predominantly in the residual fraction ranging from 17 to 78 mg/kg which consituted 27 to 63% of the total soil Zn. Among the soils studied, higher residual or mineral-bound Zn was generally observed in Ganges River Floodplain soils indicating fixation by clay minerals, particularly, biedellite and similar type of minerals, which are distinct in this region.

Total Zn content was characteristically higher (90 - 123 mg/kg) in the High and Low Ganges River Floodplain soils than other AEZ soils (64 to 93 mg Zn/kg). Madhupur Tract soils and Old Brahmaputra Floodplain soils exhibited an average of 85 mg/kg of total Zn. The lowest quantity of total Zn was found in the Old Himalayan Piedmontplain soils (average=70 mg/kg). Higher Zn contents in the floodplain soils have been attributed to higher clay contents, higher contents of primary minerals present in the silt fractions, presence of carbonate minerals and organic matter content of the soils, all of which reflect the differences in parent materials.

These findings suggest that most of the Zn in the soils is generally resides in the oxide bound and residual forms. The other forms that are potentially bioavailable represent only a negligible fraction of total soil Zn content.

17) A multiple linear regression model accounted for 79% of the variation of DTPA Zn in the diverse types of soils of Bangladesh. The main contributor of the variation was MnOx bound Zn. Organic and exchangeable Zn contributed negatively to DTPA Zn. Negative relationship of DTPA Zn with exchangeable and organic Zn is unusual. Probably the variation in the soil properties, parent material and climate of the studied samples was too wide that decrease the likelihood of observing strong positive relationships between DTPA Zn and organic matter or cation exchange sites.

18) Fractions of soil B were quantified in the aforementioned contrasting soils from five AEZs. Soils from AEZ 1 (Dinajpur and Thakurgaon districts) contained the highest quantities (3.0 - 4.2) of readily soluble B. Specifically adsorbed B and oxide bound B were comparatively higher in the Ganges River Floodplain soils than the other soils. In general, the samples of AEZ 12 showed larger percent (9-13%) of spec. adsorbed B than other soils (<5%). This may be due to the fact that the soils of Ganges River Floodplain contain smectite clay minerals which have been reported to adsorb B stronger than kaolinite. Likewise, higher oxide-B in the piedmont soil may be due to presence of higher level of Fe and Al oxides in those soils that are responsible for B adsorption in soil.

19) Multiple linear models were developed to predict B availability as influenced by soil B fractions and other soil properties, in these diverse types of soil. The model accounted for 68% of the variation of hot water soluble (HWS) B with main contributor being residual B, soil pH and organic C. Oxide B was negatively related to available B. negative relations of HWS-B with Ox-B reflects B adsorption by sesquioxides by ligand exchange mechanism making it less available for the plants.

Future research

In the context of the results obtained from the present study, further investigations should be conducted on soil Zn and soil B fractions in the intensively cropped areas, both in the laboratory and in the field to acquire more understanding of the micronutrients' dynamics as they relate to crop nutrition and yield. Likewise, soil test-crop response studies should be carried out under diverse types of soils of the country to upgrade the critical levels of Zn and B in soils, taking into account of the factors under consideration that interacts with the fractions of Zn and B.

Future research needs to be directed towards the fate of Zn and B in the soils using tracer (isotopic) techniques covering the major soil groups of Bangladesh. Particular attention should be given to elucidate the mechanism of adsorption/fixation of the applied Zn and B by the oxides and hydroxides of iron and manganese under flooded and upland soil conditions and other relevant factors in soil that may render Zn and B unavailable for the plants.

Studies should be conducted to develop appropriate soil management practices that can make use of the potential sources (e.g., labile pool) of these micronutrients for increased crop yield, particularly in the deficient areas. Studies should also be carried out to increase and sustain the Zn concentration in food grain through effective soil fertilization (or agronomic bio-fortification) to reduce dietary Zn deficiency in human.

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APPENDIX I

Description of the soils from High and Low Ganges River Floodplain (AEZ 11 and 12).

Soil	AEZ	Location	Land type*	Soil series	Cropping pattern
1	11	Mollateghghoria, Mojompur, Sadar, Kushtia	MHL	Gopalpur	Mustard-Aus-T.Aman
2	11	Gobindapur, Talbaria, Mirpur, Kushtia	MHL	Ishurdi	Tobacco-T.Aus-T.Aman
3	11	Tiktikipara, Bahirchar, Bheramara, Kushtia	MHL	Sara	Boro-Fallow-T.Aman
4	11	Joyrampur, Hoglabaria, Daulatpur, Kushtia	MHL	Ishurdi	Wheat-Jute-T.Aman
5	11	Uttar Bhabanipur, Dharampur, Bheramara, Kushtia	MHL	Ishurdi	Wheat-Jute-T.Aman
6	11	Chuniapara, Baroipur, Mirpur, Kushtia	MHL	Ishurdi	Tobacco-T.Aus-T.Aman
7	11	Baradi farm (WDB), Barokhada, Sadar, Kushtia	MHL	Ishurdi	Boro-Fallow-T.Aman
8	11	Bhatpara, Ramnagar, Sadar, Jessore	MHL	Ishurdi	Boro-Fallow-T.Aman
9	11	Kuniaghara, Bhojghati, Monirampur, Jessore	MHL	Gopalpur	Sesame-Fallow-T.Aman
10	11	Shundalpur, Shyamkur, Monirampur, Jessore	MHL	Gopalpur	Boro-Fallow-T.Aman
11	11	Hashadanga, Shyamkur, Monirampur, Jessore	MHL	Ishurdi	Boro-Fallow-T.Aman
12	11	Majidpur, Majidpur, Keshobpur, Jessore	HL	Sara	Lentil-Jute-T.Aman
13	11	Sripur, Sagardari, Keshobpur, Jessore	MHL	Gopalpur	Boro-Jute-T.Aman
14	11	Rejakati, Biddanandakati, Keshobpur, Jessore	MHL	Ishurdi	Boro-Fallow-T.Aman
15	11	Shundali, Shundali, Abhoynagar, Jessore	MLL	Ghior	Boro-Fallow-B.Aman
16	11	Dhopadi, Noapara, Abhoynagar, Jessore	MHL	Gopalpur	Boro-Fallow-B.Aman
17	11	Goragachha, Narendrapur, Sadar, Jessore	MHL	Gopalpur	Boro-Fallow-B.Aman
18	11	Srirampur, Kalidashpur, Alamdanga, Chuadanga	MHL	Gopalpur	Boro-Fallow-T.Aman
19	11	Rowakuli, Jehala, Alamdanga, Chuadanga	MHL	Gopalpur	Maize-Aus-Fallow
20	11	Goalmari, Sarishadanga, Sadar, Chuadanga	HL	Gopalpur	Maize-Aus-Fallow
21	11	Bhimrulla, Pauroshabha, Sadar, Chuadanga	HL	Sara	Maize-Aus-Fallow
22	11	Joyrampur, Hauli, Damurhuda, Chuadanga	HL	Sara	Maize-Aus-Fallow

Sample no.	AEZ	Location	Land type	Soil series	Cropping pattern
23	11	Dudhpatila, Damurhuda, Chuadanga	MHL	Sara	Boro-Aus-Fallow
24	11	Uthali, Shenerhuda, Jibannagar, Chuadanga	MHL	Sara	Maize-Aus-Fallow
25	11	Peyaratala, Khoirhuda, Jibannagar, Chuadanga	HL	Gopalpur	Maize-Jute-Fallow
26	12	Goidi, Ghotmaji, Sadar, Madaripur	MHL	Gopalpur	Boro-Fallow-T.Aman
27	12	Chaturpara, Mostafapur, Sadar, Madaripur	HL	Gopalpur	Wh-Jute-T.Aman
28	12	Mazumderkandi, Rajoir, Madaripur	HL	Sara	Mustard/Khesari-Jute, Chilli-Mustard
29	12	Kashiani, Gopalganj	MLL	Ishurdi	Mustard-Jute-T.Aman
30	12	Balladdi, Saltha, Faridpur	MLL	Ghior	Onion-Jute-T.Aman
31	12	Gotter char, Dattapara, Shibchar, Madaripur	MHL	Gopalpur	Kheshari-G.nut-B.Aus
32	12	Chhalildia, Chandra, Bhanga, Faridpur	MLL	Ghior	Boro-Fallow-T.Aman (L)
33	12	Bogail, Tajarpur, Bhanga, Faridpur	LL	Ghior	Wheat-Fallow-T.Aman (L)
34	12	Dasherhat, Moksudpur, Gopalganj	MLL	Ghior	Boro-Fallow-T.Aman (L)
35	12	Mithapur, Poursabha, Alfadanga, Faridpur	MHL	Gopalpur	Onion-Fallow-T.Aman
36	12	Ramchandrapur, Chatur, Boalmari, Faridpur	MHL	Ghior	Onion Seed-Jute-T.Aman
37	12	Kamarigram, Poursabha, Boalmari, Faridpur	MHL	Sara	Fallow-Jute-T.Aman (L)
38	12	Majhkandi, Raipur, Madhukhali, Faridpur	MHL	Ghior	Khesari (relay)-Jute-T.Aman
39	12	Jhaohati, Madhukhali, Madhukhali, Faridpur	MHL	Ghior	Wheat-Jute-T.Aman
40	12	Deura, Chondoni, Sadar, Rajbari	MHL	Ghior	Wheat-Jute-T.Aman
41	12	Koya, Koya, Kumarkhali, Kushtia	HL	Sara	Lentil-Sesame-T.Aman
42	12	Nagarshaota, Chapra, Kumarkhali, Kushtia	MHL	Gopalpur	Maize-T.Aman-Fallow
43	12	Baithakhali, Matchar, Sadar, Faridpur	MHL	Gopalpur	Wheat-Jute-T.Aman
44	12	Chhonpocha, Kanaipur, Sadar, Faridpur	MHL	Gopalpur	Wheat-Mungbean-T.Aman
45	12	Mollikpur, Krishnanagar, Sadar, Faridpur	HL	Sara	Wheat/Lentil-Fallow-T.Aman
46	12	Char Moishapur, Gajna, Modhukhali, Faridpur	HL	Sara	Sugarcane

Sample no.	AEZ	Location	Land type	Soil series	Cropping pattern
47	12	Purba Moukuri, Baliakandi, Rajbari	MHL	Gopalpur	Wheat-Jute-T.Aman
48	12	Ghoramara, Sonapur, Baliakandi, Rajbari	HL	Sara	Wheat-Jute-T.Aman
49	12	Majhbari, Kalukhali, Rajbari	MHL	Gopalpur	Wheat-Jute-T.Aman
50	12	Horiana, Hat Modhapur, Kalukhali, Rajbari	HL	Sara	Wheat-Jute-T.Aman
51	12	Char bagmara, Sadar, Rajbari	MHL	Ishurdi	Wheat-Jute-T.Aman
52	12	Ramkantapur, Sadar, Rajbari	MLL	Ishurdi	Boro-Fallow-T.Aman

[*] HL = High land, MHL = Medium high land, MLL = Medium low land, LL = Low land

APPENDIX II

Basic information of the soils collected from AEZ 1, 9, 11, 12 and 28.

Sl	AEZ no.	Name of the AEZ	Location	Soil Series	Cropping pattern	Land type	GST[a]	Parent Material	Clay mineralogy	Diagnostic soil features
1	1	Old Himalayan Piedmont plain	Kaharol, Dinajpur	Gangachara	Maize-F-T.Aman	Medium Highland	NCGFP[b] soils	Old Himalayan Piedmont Plain Alluvium	Mica and chlorite*	Sandy loam to Sandy CL; very str. acidic; OM high; rapid leaching of nutrients incl. B.
2			Sadar, Thakurgaon	Laskara	Boro-F-T. Aman	Highland				
3	9	Old Brahmaputra Floodplain	Fulbaria, Mymensingh	Silmondi	Boro-F-T.Aman	Medium Highland	NCGFP soils	Old Brahmaputra Alluvium	Mica, chlorite and vermiculite*	SiL to SiCL; strongly acidic to neutral; low fertility; low B content
4			Trishal, Mymensingh	Silmondi	Boro-F-T.Aman	Medium Highland				
5	11	High Ganges River Floodplain	Sadar, Kushtia	Gopalpur	Mustard-Aus-T.Aman	Medium Highland	CDGFP and CBFP soils	Ganges River alluvium	Mica and smectite	SiL to SiCL; slightly acidic to sl. neutral; low fertility; low B & Zn content
6			Damurhuda, Chuadanga	Sara	Maize-Aus-F	Highland				
7	12	Low Ganges River Floodplain	Sadar, Rajbari	Ishurdi	Wheat-Jute-T.Aman	Medium Highland	CDGFP and CBFP soils		Mica and smectite	SiL to SiCL; calcareous; alkaline to neutral; OM low; low B content
8			Sadar, Rajbari	Ishurdi	Boro-F-T.Aman	Medium Highland				
9	28	Madhupur Tract	Sadar, Gazipur	Kalma	Boro-F-T.Aman	Lowland	SRBT soils and GV soils	Madhupur Clay	Mica, kaolinite & interstr. minerals (mica-vermi.-smect. and kaol.-smectite)	Clay to CL; well drained; sl. to str. acidic; low fertility; very low to low P & B cont.
10			Kapasia, Gazipur	Dhamrai	Boro-F-T.Aman	Medium Highland				

[a] GST= General Soil Type, [b]Abbreviations: NCGFP=Non-calcareous Grey Floodplain; CDGFP=Calcareous Dark Grey Floodplain; CBFP=Calcareous Brown Floodplain; SRBT=Shallow Red Brown Terrace; GV=Grey Valley. *Partial chloritization of some vermiculite or partial degradation of some chlorite.

Source: (FAO-UNDP, 1988; Moslehuddin *et al.*, 1999).