STUDIES ON ZINC AND MOLYBDENUM NUTRITION OF BLACK PEPPER IN RELATION TO YIELD AND QUALITY

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DOCTOR OF PHILOSOPHY
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By

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2000

Certificate

I hereby certify that the thesis entitled "Studies on Zinc and Molybdenum Nutrition of Black pepper in Relation to Yield and Quality" (*Piper nigrum* L.), submitted by Mr. Hamza Srambikkal, Technical Officer, IISR, Calicut for the award of the degree of the Doctor of Philosophy in Chemistry at the University of Calicut, contains the results of bonafide research work carried out by him at the Indian Institute of Spices Research, Calicut under my supervision and guidance. No part of this thesis has been submitted to any other university for the award of any other degree or diploma. All sources of help received by him during the course of this study has been duly acknowledged

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Declaration

I, Hamza Srambikkal, do hereby declare that the thesis entitled "Studies on Zinc and Molybdenum Nutrition of Black pepper in Relation to Yield and Quality" submitted by me for the award of the degree of Doctor of Philosophy in chemistry to the University of Calicut is a bonafide research work carried out by me at the Indian Institute of Spices Research, Calicut-673 012, under the supervision and guidance of Dr. A.K.Sadanandan, Principal Scientist and Head, Division of Crop Production and Post Harvest Technology (Rtd.), IISR, Calicut. This thesis and no part of it, has been submitted to any other university for the award of any other Degree or Diploma. All sources of help received by me during the study have been duly acknowledged.

22/10/12

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INTRODUCTION

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INTRODUCTION

1. INTRODUCTION

Black pepper (*Piper nigrum* L), known as "the king of spices", belongs to the family *Piperaceae*. It originated from the evergreen forest of Western Ghats of South India, which is considered as the center of origin of *Piper nigrum*.

It is cultivated in warm humid and high rainfall regions, especially on the slopes of Western Ghats of South India. The crop tolerates 10° C to 40° C and is grown in tracts that receive an annual rainfall of 1250 to 2000 mm.

Pepper vine is a perennial climber, cultivated both as mono and mixed crop. Apart to India, Indonesia, Malaysia, Brazil, Ceylon, Thailand, and Vietnam are some other countries known for its cultivation. In India, it is grown extensively over a wide range of soil and climatic conditions and is cultivated along the Malabar coast, extending to both sides of the Western Ghats from the districts of Konkan and North Canara in Karnataka state to Travancore in South Kerala. To a limited extent, it is also grown in Tamil Nadu and northeast region of India.

Kerala contributes 96 per cent of the total area under pepper cultivation, followed by Karnataka (3 per cent) and Tamil Nadu (less than one per cent). Large-scale plantations account for 40 per cent of the total area under cultivation. The small holdings (0.3 to 1.5 ha) constitute about 45 per cent and the localised backyard garden occupies the rest of the area (Dineshkumar *et al* 1986).

Black pepper is cultivated mainly on medium high and high lands of Kerala where lateritic soils (Alfisols, Ultisols, and Inceptisols) are predominant (Mathew 1984). Pepper is grown in soils generally low in CEC, and exchangeable potassium. The forest loamy soils of Western Ghats are generally shallow in nature and well drained, having high organic matter status and medium to high potassium. Though pepper is grown on a variety of soils, the best plantations are raised in well-drained virgin soils (Sadanandan 1993).

In India, pepper is grown in about 200 thousand hectares producing 57 thousand tonnes, which accounts for about 49% of world area but only 30% of the total world production. During 1999-2000 India exported 42 thousand tonnes valued Rs.865 crores, emphasizing the importance of pepper in Indian economy. The balance of production is used for internal consumption. To meet the national and international demand, an annual growth rate of 8-10% is envisaged (Sadanandan 1994).

About 80% of total production in India is from Kerala where soils are acidic, poor in Zn and Mo, but high in Cu status. Ravindran (2000) reported that productivity in India is lowest (294 kg ha^{-1}) compared to Thailand (3594 kg ha^{-1}), Malaysia (1888 kg ha^{-1}), Vietnam (1100 kg ha^{-1}) and Brazil (883 kg ha^{-1}). The low productivity in pepper is mainly attributed to imbalanced manuring, poor management practices, and disease incidence (Sadanandan 2000). In Sarawak, also the necessity for micro nutrient application to black pepper has been recognized (Pursie glove *et al* 1981).

The importance of zinc as an essential element, required for plant growth is well known. It is a component in several dehydrogenises, proteinases and peptidases (Hemantharanjan 1988). Many agricultural soils are incapable of meeting even a small demand of zinc; consequently, the standard fertilizer recommendation of N, P, and K is sometimes inadequate in today's quest for higher crop production. Researchers have established that in many such instances, zinc treatment could bring about a striking improvement in crop yield. Work on Zn, in nutrition of pepper, is scarce. It is reported that foliar spray of 0.5% $ZnSO_4$ reduced spike shedding in black pepper by 48.4% (Geetha and Sivaraman Nair 1990). Interaction of zinc with N, P, Ca, and Mn are known (Hemantharanjan 1996).

Molybdenum is known as an essential micronutrient (Bortel, 1930). Molybdenum acts, as a metal component of enzymes, nitrate reductase and nitrogenase and thus, it is closely associated with nitrogen metabolism. Woodruff (1990) reported that Mo is required by all leguminous plants because, nitrogenase, a molybdenum containing enzyme, requires Mo to fix atmospheric nitrogen and for nitrate reductase production. A positive interaction between Mo availability and N assimilation by pepper will increase the N use efficiency, thereby economising N fertilization.

Pepper growing soils under investigation were found to be high in Cu (due to application of Bordeaux mixture/Copper oxychloride drenching to control *Phytophthora*). Antagonistic interaction of Cu with Mo, results in low utilization of N, which predominantly exist as NO_3-N in the black pepper growing soils. The use of Mo to facilitate absorption of NO_3-N and significant increase in the protein and amino acid contents due to application of Mo have been documented.

The proposed study is, therefore, a new important area of work as regards pepper nutrition is concerned since black pepper growing soils are reported to be poor in micro nutrient status, especially zinc (Sadanandan 1993, 1994). There is no systematic work on micronutrient fertilization in black pepper. Work during 1980-95 at IISR brought some basic information only. Response to micronutrients, including Zn and Mo application in soil, and foliar spray in red and lateritic soils, were reported (Sadanandan and Hamza 1993). Further, it was reported that micronutrients are removed continuously from the soil by the crops and their replenishment, especially Zn and Mo, in balanced form, will go a long way in sustaining soil fertility, crop production, and quality. Hence the study on the nutrition Zn and Mo on black pepper was taken up with the following objectives:

- Survey of major pepper growing soils for evaluating the total and available Zn and Mo and their relationship with other nutrients,
- Study of the adsorption-desorption and transformation of applied Zn and Mo in major pepper growing soils,
- Enhancement of Zn and Mo availability/use efficiency in pepper-growing soils through application of soil amendments, and
- Determination of the optimum level of Zn and molybdenum to fertilize black pepper for increasing yields, nutrient uptake and quality of pepper.

REVIEW OF LITERATURE

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REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

2.1 MOLYBDENUM

Molybdenum is one of the nutrient elements considered essential for plant growth. It is necessary for the fixation of nitrogen. Arnon and Stout (1939) established the essentiality of Mo for higher plants. Response to Mo has since been reported in a variety of crops in various countries of the world. Of the annual crops, tomatoes, lettuce, all the *brassica* species (cauliflower, broccoli, and rape) are very sensitive to restricted Mo supply (Johnson 1980). Molybdenum is an exception among micronutrients, in that, it is readily translocated in anionic form and its deficiency symptoms are generally yellowing and stunting of the plant like N deficiency and interveinal mottling and cupping of the older leaves followed by leaf tips and margins. Root interception and mass flow are considered to be the important mechanisms controlling the movement of Mo to plant roots. Plants appear to absorb Mo in the form of the anion MoO_4^{2-}. Mo occurs in the following forms: (1) water-soluble (2) adsorbed by soil, (3) held in the crystal lattice of minerals, (4) present in organic matter. Forms most available for plant use are the soluble forms present in the soil solution and Mo adsorbed by soil colloids. Highly weathered acid soils are apt to be more deficient in Mo. Large quantities of Mo in plants generally do not produce harmful effects or yield reductions in crops. Molybdenum can be applied to crops in the form of different fertilizer sources and most commonly used sources are $Na_2MoO_4 .2H_2O$ and $(NH_4)_2MoO_4$. Another source of Mo is ammonium phosphomolybdate. Molybdenum can be applied as seed treated, added to soil, as a foliar spray or in combination with superphosphates. Molybdenum is a component of various enzymes that catalyze diverse and unrelated reactions, namely nitrogenase, nitrate reductase and sulfite oxidase, which are found in plants. The principal functions of Mo in plants are implicated in the electron-transfer system; for nitrate reductase and nitrogenase in the reduction of NO_3^- and in the fixation of N, respectively.

2.1.2 Molybdenum Response to Crops

The criterion for response to an added nutrient in agricultural terms is usually an increase in growth of the plant, or in final yields. It might be expected that supplying N predominantly as NH_4^+ would lessen the demand for Mo and the response of Mo to yield will be accompanied by an increase in Mo content, as applied Mo is readily taken by plants. The response of molybdenum on yield, quality and other parameters in various crops are detailed below.

Crop	Method/Rate of application	Effect on yield and quality	References
Alfalfa	Lime and Mo application	Increased dry matter and N content	Somner, 1928
"	Mo application	Increased its concentration	Pierzynski and Jacob, 1986
Bajra	Foliar spray of Mo	No influence on yield but increased protein content	Sasirekha *et al* 1998
Black gram	Mo application in sandy loam soil	Response on yield	Jongruaysup *et al* 1994
Beans	Seed soaking with sodium molybdate solution	Increased dry matter, yield and N content	Mohandas, 1985
Cauliflower	Mo application	Increased yield	Gupta *et al* 1990
"	Mo @ 0.25 kg/ha in soil of pH 5.6	Produced optimum yield	Sharma *et al* 1988
Cowpea	Mo application	Increased yield and protein content	Bladeo Singh *et al* 1992
Groundnut	Mo application	Increased N uptake by 55% and yield by 24%	Hafner *et al* 1992
"	P as triple superphosphate	Increased N and Mo uptake	Rebafka *et al* 1993
"	P as Single superphosphate	Decreased N and Mo content in shoot	Rebafka *et al* 1993
"	Mo @ 1 kg/ha or foliar	Increased protein and yield	Zade *et al* 1998

Crop	Method/Rate of application	Effect on yield and quality	References
Green gram	Mo application	Yield and N content of module increased	Banasridas et al 1989
”	Mo application	No effect on yield	Sarkar and Banik 991
Horse gram	Mo @ 100g ha^{-1} in laterite soil	Superior to foliar or seed treatment for response	Pradhan and Sarkar 1985
Lentil	P+Mo application	Increased yield	Pal 1986
Maize	Mo application	Increased Mo content and not yield	Quggio *et al* 1991
”	Lime application	Increased root growth, N absorption and NRA	”
Phaseolus Vulgaris. L	Mo application	Stimulated protein and inhibited carbohydrate synthesis of aerial part	Gomez *et al* 1985
”	Residual effect of Mo to previous cabbage crop	Increased yield and protein content	Domska *et al* 1989, Hiev and Ivaniv 1988
Peas	Mo @ 0.5 kg ha^{-1}in sandy loam soil	Optimum for economic yield	Kovalevich 1991
”	Seed treatment by Mo	Increased yield and protein content	Guseva 1991
Potato	Mo application	Increased N metabolism, N and P content of leaf	Esteban *et al* 1986
Red gram	Mo @ 0.5 kg ha^{-1}or 1% foliar soil molybdates	No effect	Subbian *et al* 1989
Rice	Foliar molybdenum	Stimulated proliferation of Azatobacter in rhizosphere of soil	Dey and Ghosh 1986
”	Lime @ 0.5 t + Mo @ 0.5 kg ha^{-1} in acidic soil	Increased yield	Dar *et al* 1989, Sheudzhen 1991
”	Mo with blue green	Increased yield	Raju and Reddy 1989
Raya	Mo application in sand and sandy loam soil	Increased yield	Dhankar *et al* 1993
Sugarcane	Mo application	Response to yield	Hague 1987
Strawberry and raspberry	Mo application	Increased yield and quality	Cheng 1994

Crop	Method/Rate of application	Effect on yield and quality	References
Sunflower	Mo @ 0.1kg ha^{-1}	Increased seed yield	Sarkar and Ghosh 1992
”	Mo @ 0.2 kg ha^{-1}	Decreased seed yield	”
”	Mo application	Increased seed yield and quality	Toma *et al* 1990
Soybean	Mo application	Increased yield and leaf N content	Adams *et al* 1990
”	Lime application with Mo	No response to lime	”
Soybean	Lime application without Mo	Response to lime	”
”	Seed treated of 30g ha^{-1} sodium molybdenate	Increased growth and yield	Nayak *et al* 1989
”	Mo application in Alluvial soil	Response to yield	Ali *et al* 1993
”	Mo /Lime	Increased yield	Burmester *et al*
”	Mo application in Ultisol	Increased yield and protein content	Sharma and Minhas 1988
”	Mo as soil or foliar	Increased dry matter and N content	Walworth and Sumner 1990
Sorghum	Mo or Lime application	Good response	Quaggio *et al* 1998
Timothy	Mo fertilization in peat soil	Doubled the yield	Urvas 1989
Toria	S, B, Mo application	Increased oil content	Patgiri 1995
Tobacco	Mo @ 1.1 kg ha $^{-1}$with lime in sandy loam soil	Increased yield by 22%	Kham *et al* 1994, Liu *et al*1996
Tomato	Mo application	Increased Ca uptake	Kheshem *et al* 1990
Viciafaba	Mo or lime application	Response to yield	Byhad 1988

2.1.3 Molybdenum in the Soil

Information on the levels of Mo in different soils is limited. Normal level is 0.5-5 mg kg^{-1}. Soil pH, organic matter, clay content, drainage, and nutrient interactions are the main factors affecting the availability of Mo to plants. High concentrations of Mo seldom retard plant growth (Hague 1987). The average amount of soil Mo extracted by ammonium oxalate decreased with increasing pH of extractant

(Liu *et al* 1996). Acid ammonium oxalate extractable molybdenum ranged from 0.10 to 1.39 in topsoil and 0.12 to 1.31 mg kg^{-1} in the sub soil and it is correlated positively with electrical conductivity (Ahamed *et al* 1991). Available and total Mo content of Malaysian soils ranged from 1.13 mg kg^{-1} to 10.53 mg kg^{-1} and 155 mg kg^{-1} to 721 mg kg^{-1} respectively. Mitra *et al* (1993) after extracting 56 soil representing eight soil groups in Orissa reported that 59% of the soils contained less than 0.05 mg kg^{-1} acid ammonium oxalate extractable Mo and were considered as deficient. Further average Mo content obtained was in the order Saline>mixed red and black=black>brown forest>alluvial>red>mixed red and yellow> lateritic soils. Molybdenum availability in soil and plants, including functions, factors affecting its availability to plant, and its interaction were reviewed by Das and Kumar (1993). Available Mo in acid alluvial surface soils (Entisols, Inceptisols and Alfisols) of the sub Himalayan plains of West Bengal ranged from traces to 0.54 mg kg^{-1} (Mukhopadhyay and Halder 1992). They also got significant positive correlation of available Mo with pH and exchangeable base. Application of Mo @ 5kg ha^{-1} in a sandy soil was sufficient to raise the soil test value of Mo from low to medium and was expected to guarantee safe value for human and animal consumption of crops. Application of long-term NPK (16 years) decreased soil pH, reduced the content of soluble Mo, the uptake of which was improved by higher P or lime application (Gezenchova *et al* 1987). Sharma *et al* (1988) after conducting a survey in Himachal Pradesh soils of pH varying from 4.8 to 7.1 reported that acid ammonium oxalate extractable Mo content was in the range of 0.02 to 0.4 mg kg^{-1} and 70% samples had Mo content below critical level of 0.15 mg kg^{-1}. They also reported that total Mo content of surface horizons varied from 0.20 to 0.90 mg kg^{-1} while that of ammonium oxalate extractable Mo was in the range of 0.02 to 0.25 mg kg^{-1} and total Mo was significantly related to available molybdenum.

Nature of parent rock, the form of Mo in the soil, soil pH, drainage, the presence of organic matter, the status of P, S, N, Mn and Cl in the soil, variation in plant species and part of plant samples etc are the major factors that affects Mo uptake by plants (Gupta 1997). Leaching losses could affect Mo availability in soil (Leu and Lim 1992). Leaching does not appear to be an important factor in the occurrence and recurrence of molybdenum deficiency on yellow-brown acidic sandy soils of Western Australia (Riky *et al* 1987). Different forage legumes grown on the same soil have nearly the same amounts of Mo. Well-drained soils are likely to be low in Mo, and there is little enrichment in any layer. Significant increase in Mo accumulation in corn, soybeans, and alfalfa was reported by Pierzynski and Jacob (1986) due to increase in soil pH. They found ammonium bicarbonate DTPA (AB-DTPA) as better extractant for predicting Mo concentration in plant tissue than Tamm's acid. They recommended 1.0 M NH_4HCO_3+0.005 M DTPA for predicting Mo concentration in soil because of its potential for simultaneous use with other plant nutrients and heavy metals in the soil during multi element analysis as well as the analysis using plasma emission. Wang *et al* (1994) compared three extractants *viz., a*mmonium bicarbonate DTPA, ammonium carbonate and ammonium oxalate and reported that all extractants were not significantly different in extracting Mo and were considered suitable for assessing Mo availability though Ammonium oxalate extracted the greatest amounts of Mo out of the three extractants used.

Verma and Jha (1970) reported that bulk of the total molybdenum was concentrated in the sand fraction of soil. Soil moisture content also seems to affect the availability of molybdenum to plants. Highest amount of extractable molybdenum was recorded in treatments at Yield Capacity moisture level, followed by 50 per cent Field Capacity (FC) and at saturation. Relatively more extractable molybdenum at high moisture level may be due to reduction in the ferric form of iron mainly responsible for fixation of molybdenum. Generally, the acid-oxalate extractable molybdenum is used as a measure of available molybdenum in the soils. Molybdenum up to 100 mg kg^{-1} did not affect adversely the ammonification of organic nitrogen, but caused an accumulation of nitrite. The contents of the HNO_3 and EDTA extractable Co, Cu, Mn and Mo decreased at deeper depth in Danish spodozols and ultisols (Bibak *et al* 1994). They also got highly significant correlations between HNO_3 extractable micronutrients and the clay content.

The reduced availability of molybdenum in acid soils is well known. Anderson (1956) has quoted several workers who were able to increase molybdenum availability in acid soils by liming. The increase in molybdenum availability in acid soils by liming is because of exchange of MoO_4^{2-} and $HMoO_4^-$ anion for OH groups of clay. The role of organic matter in increasing the availability of molybdenum, especially in acid soils, seems to be due to protection of molybdenum from anion adsorption. Soil pH is one of the most important single factors affecting the uptake of

Mo in plants. The beneficial effects of liming on Mo solubility are obvious. Liming increased Mo availability in a sandy soil. The MoO_4^{2-} concentration increases 100-fold for each unit increase in pH (Lindsay, 1972). With increase in pH, the soluble MoO_4^{2-} in equilibrium with soil Mo is much greater than for $HMoO_4^-$. At a pH of 5 or 6, the ion $HMoO_4^-$ becomes dominant and at very low pH values, the unionized acid H_2MoO_4 is the principal species present. The MoO_4^{2-} anion exists in an exchangeable form in the soil. Because of this fact, Mo availability to plants increases with increasing pH. The behavior of Mo in soil is strongly influenced by its tendency to form aqueous anionic species. Mo is generally least soluble in acid soils, but is relatively mobile under oxidizing alkaline condition (Smith *et al* 1997).

Plant uptake of Mo is usually enhanced by soluble P and decreased by available S. Higher P levels in culture solutions increased Mo uptake as much as tenfold and therefore soil applications of Mo with P fertilizers may be effective. The effect of P in increasing the concentration of Mo in plants has been reported to be associated with the formation of a complex phosphomolybdate anion, which is absorbed more readily by the plants. Addition of S has been found to decrease the Mo content of crops. The inhibitory antagonistic effects of $S0_4^{2-}$ on Mo content have been suggested to occur primarily during the absorption process, with some antagonistic mechanism involved during translocation from roots to leaves. Mo requirement of plants can be met by liming the soil. Because of the low requirements, the deficiency and sufficiency levels in most plants are extremely narrow. Application of casein and orange peel promoted fixation of Mo in soil and observed difference in the amount of soluble Mo in a leachate between cattle manure- amended soil and non-amended soil (Caldernone and Franken Berger 1990). Fielder *et al* (1987) reported reduction of Mo uptake by trees because of soil acidification and excess sulphate in forest eco system. S and Mo had antagonistic effect on each other with reference to concentration; uptake and percentage utilization of S, which increased with higher, levels of S. Increased Mo application decreases copper availability and vice versa. Mo and Fe are antagonistic (Kumar *et al* 1993). Mo and Ca have synergic relationship (Kheshen *et al* 1990).

2.1.4 Molybdenum Deficiency in Crops

Molybdenum deficiency as marginal and interveinal chlorosis, necrosis and downward curling in deficient leaf and leaf tissue contained Mo below critical level of 0.5 mg g^{-1} and NO_3-N more than 1% in poinsettia, was reported (Cox 1992). Agarwal *et al* (1988) induced Mo deficiency in sorghum, which showed interveinal chlorosis of leaves at start, and the plant collapse during severe case. The activity of catalase peroxides, aldofase and nitrogen reductase was also reduced in Mo deficient leaves. Mo deficiency causes interveinal chlorisis and reduction in shoot and root DW of cauliflower (Drew and Bain 1986). Symptoms of Mo deficiency were reported in wheat, barley, sunflower, maize, tomato, brassica, lucerne, pea, and soybean grown in grey forest soil poor in Mo (Gezenchova 1988). Mo deficiency in tomatoes decreased organic nitrogen content of the leaves to the same degree as decrease in the organic anion content of the leaves. Deficiency of Mo can cause plant chlorosis, due to the inability of the plants to form chlorophyll. The deficiency of Mo reduces the rate of NO_3^- reduction in plants, photosynthesis decreases because the end products are not removed by combination with nitrogenous compounds; hence the symptoms associated with deficiency of Mo are closely related to metabolism of N and accumulation of NO_3^- in plants.

2.1.5 Molybdenum Sorption- Desorption Studies

Molybdenum in soil occurs as Mo dissolved in the soil solution, occluded with oxides, solid phase and associated with organic compounds. Dissolved Mo in soil solution results from ion complexation, adsorption-desorption precipitation, and dissolution process. Al and Fe oxides and organic matter play vital role for soil Mo adsorption. Adsorption of Mo is highly pH dependent and is also affected by the contents of soil Fe and Al oxides and organic matter (Reddy *et al* 1997). Bibak and Borggaard (1994) observed good relationship between measured Mo adsorption in a sandy soil and the amount calculated from the adsorption capacities of the pure oxides and humic acids and the contents oxalate and dithionite extractable Mo. Sorption desorption of Mo as a function of added P was studied in a clay and a loam soil by Xie and Mackenzie (1991). Samples were shaken for 72hrs with solution containing varying amount of phosphates and molybdates in 0.03 M $KClO_4$. The first equilibration measured P sorption, the second Mo sorption and P desorption, the third Mo desorption, and further P desorption. Initial pH of the solution was held at 6.0. Sorbed P reduced Mo sorption at high P addition level and the experimental data fitted Temkin isotherm best rather than the Freundlich, Langmuir, and Gunary. The presence of P reduced the intercept values of Tamkin equation indicating a reduced affinity of surfaces for Mo. In the presence of various amount of sorbed P, Mo sorption was described best by Gunary isotherm that included a P term. Goldberg *et al* (1996) reported from an adsorption studies that molybdenum adsorption was higher for the oxide minerals having higher specific surface area and lower in crystalline. Molybdenum adsorption on the clay minerals exhibited a peak near pH 3 which decreased rapidly with increasing pH until adsorption was virtually zero near pH 7.0.

2.1.6 Molybdenum Correlations

Soil total Mo had significant positive correlation with available Mo. Mo availability in soil tended to increase with rise in pH values. Available Mo showed non-significant positive correlation with $CaCO_3$ (r = 0.09), organic. C (r = 0.38**) available N (r = 0.66**) and P (r =0.49**) and negative correlations with available S (r = 0.30**) (Vinay Singh *et al* 1995).

2.2 ZINC

Zinc (Zn) content of the lithosphere is about 80 mg kg^{-1}, and Zn in soil ranges from 10 to 300 mg kg^{-1} and averages approximately 50 mg kg^{-1}. Zn deficiencies are widespread throughout the world, especially in the rice cropland of Asia. Soil conditions mostly associated with Zn deficiencies are acid sandy soils. Maze (1914) furnished first convincing evidence that zinc is essential for higher plants. Zinc is mainly required in plant system for Tryptophan synthesis. Its essential nature was not generally accepted until Sommer and Lipman (1926), and Somner (1928) showed that zinc was indispensable for normal growth of plants. Among different micronutrients, zinc deficiencies are more widespread in fruit crops, in different parts of India.

Depending upon type of extractant used, available zinc content, water soluble, exchangeable and 0.1N HCI soluble zinc in some of the Indian soils, vary from traces to 0.41 mg kg^{-1}, traces to 16.0 mg kg^{-1} and 0.1 to 20.9 mg kg^{-1} respectively. The forms of Zn in soils are: divalent zinc in soil solution, adsorbed divalent zinc on clay surfaces, organically complexed zinc, carbonates, and oxides of zinc and Zn^{2+} substituted for Mg^{2+} of clay minerals; and Zn existing in primary and secondary minerals. Zinc in the soil solution is very low, ranging between 2 and 70 mg kg^{-1}, with over half of the Zn^{2+} in solution complexed by organic matter. Several Zn hydrolysis species exist in solution with Zn^{2+} predominating below pH 7.7. Diffusion is the dominant mechanism for transporting Zn^{2+} to plant roots. Complexing agents or chelates from exudates or from decomposing organic residues, facilitate the diffusion of Zn^{2+} to a root. Diffusion of chelated Zn^{2+} can be significantly greater than that of unchelated Zn^{2+}. Zinc sulfate ($ZnSO_4$), containing about 35% Zn, is the most common Zn fertilizer source. Rate of Zn application depends on the crop, Zn source, methods of application, and severity of Zn deficiency. Because of limited Zn mobility in soils, broadcast Zn should be thoroughly incorporated into the soil. In the case of long-term perennials such as hops, grapes, and tree fruits, preplanting soil applications of Zn are effective. Foliar applications are used primarily for tree crops. Foliar applications of chelates and natural organics are suitable for quick recovery of Zn. Chelatesuch as Zn-EDTA is mobile and fit for soil application.

2.2.1 Soil Availability of Zinc

Availability of zinc in soil decreases with increased soil pH. At high pH, Zn precipitates as insoluble amorphous $ZnFe_2O_4$ and/or $ZnSiO_4$. Red lateritic soils of West Bengal were deficient in available Zn (Karan *et al* 1993). Liz and Shuman (1996) reported that EDTA application significantly increased DTPA extractability of Zn. Hydrogen ion concentrations accounted for most changes in DTPA extractable Mn, Cu, and Zn. Application of the respective cations increased their availability while lime reduced availability (Li and Mahler 1993). Liang *et al* (1991) reported that DTPA extraction was not a successful method for soils with diverse soil properties based on correlation analysis. Rathore (1992) reported that soil of Madhya Pradesh was widely deficient in Zn and deficiency was greatest (87%) in alluvial soil, followed by red soil (65%) and yellow soil (63%) in mixed red and black soils and 59% in black soils. He also reported that zinc application to soil, before sowing, was most successful method to control Zn deficiency. In standing crop, the deficiency could be cured by foliar spray of zinc sulfate. It was reported that an average 57% of the applied Zn was unextractable by 0.05M DTPA and considered fixed (Rahmatullah *et al,* 1985). The magnitude of response to Zn progressively increased with increasing levels of soil fertility. The depletion in soil available Zn was enhanced with increasing soil fertility levels (Sakal *et al* 1988). Chauhan (1995) reported that about 50% cultivated Indian soil is deficient in Zn and need Zn dressing in variable quantities for crop production. Dutta and Barua (1992) reported that 34% out of 12,165 soil samples collected from five districts of Assam (Alluvial soil) were deficient in zinc. Deb and Leelabhai (1988) reported that calcareous soils showed a significantly lower recovery of fertilizer Zn than non-calcareous soils. El Fouly *et al* (1984) after collecting and analyzing 6000 soil and 4000 leaf samples of oranges, grapes, cereals, legumes and potatoes from Nile valley reported wide spread deficiencies of iron, manganese and zinc. Iron deficiency dominated in calcareous soil, zinc deficiency in sandy soil and manganese deficiency in alluvial soils (Figlielia *et al* 1993). The occurrence of panicle malformation in mango was attributed to a decrease in the availability of Cu and Zn in sub surface soil layers especially on sandy soils and/ or poor soil and poor water management (Abdel Mottaleb *et al,* 1983). Wide spread Zn deficiency was reported in Assam, Bihar, MP, Orissa, U.P. and West Bengal (Ali, 1992). Ghosh *et al* (1992) reported that zinc deficiency occurred in 56.6% of the state of Orissa and zinc deficiency increased with soil pH and decreased with increasing organic carbon and available P. Coorg soils are low in base saturation, slightly to strongly acidic, low in CEC, high in N, low to medium in P, medium to high in K and deficient in zinc (NBSS & LUP, Annual Report, 1997).

For the determination of zinc, Cruz *et al* (1997) recommended a soil solution ratio of 1:2 and an extraction time of 120 minute for DTPA and Na_2 DTPA. They also recommended a ratio of 1:4 and extraction time of 15 and 5 minute for HCl and Mehlich I, respectively. The most suitable extractant for predicting the Zn content of wheat was DTPA-$CaCl_2$ followed by NH_4HCO_3-DTPA and residual Zn contributed 90.7% of total Zn (Sharma *et al* 1991). DTPA extractable Zn decreased with increasing P rates. Most of the applied Zn adsorbed or precipitated and extractability decreased within 25 days of incubation. (Sadik *et al,* 1996). Most alluvial and reddish brown sandy loam soils of UP were deficient in Zn but rich in Fe, Cu and Mn (Paul *et al* 1992). Murthy and Schoen (1987) reported that Zn in soil is held by weak organic bonding and that the extraction by Cu $(OAC)_2$ and/or EUF- 5 minutes serve as a useful basis for estimating zinc availability in rice soil. Banda and Singh (1989) compared three extractants for available zinc and reported that 0.005 M DTPA and 0.1 N HCl were superior to NH_4OAC-EDTA in relating zinc concentration and 0.005 M DTPA gave highest correlation between extractable zinc and plant zinc for maize crop. Grant and Bailey (1989) reported that zinc availability to the plant increased with soil levels of Zn. DTPA extractable micronutrients increased with an increase in organic carbon, CEC, silt, and clay and decreased with an increase in sand content. Further, alluvial soil did not show any pattern of depth distribution of DTPA extractable micronutrients (Sharma *et al* 1992). Increasing application of Zn increased DTPA extractable Zn but decreased Mn and Fe contents (Antil and Dabiya 1986). Haddad and Evans (1993) reported that 0.05 M HCl was suitable for Zn extraction in acidic to near neutral soil (R^2=0.80 for soil content and 0.78 for uptake) and DTPA for calcareous soil (R^2= 0.80 for content and uptake), 0.01 M $CaCl_2$ for Mn (R^2=0.71 for content and 0.64 for uptake) and 0.31 M HNO_3 for Cu uptake (R^2=0.72). Addition of Calcium caused reprecipitation of organic matter and zinc, suggesting that Zn at high pH is primarily absorbed with organic matter where it is selectively retained as an organic complex. Brennan (1992) reported that amount of Zn extracted by DTPA after addition of Zn fertilizer was affected by clay (%), organic C (%) and $CaCO_3$ (%)

content of the soil. Fertilizer zinc applied to the surface of an acid sand of low CEC remained close to the soil surface even after 1438 mm of rain. When zinc applied at 22.5kg ha^{-1}, 95% of the applied zinc could be accounted for in the top 5cm of soil. (Brennan and Mc Grath 1988). Bansal and Sekhon (1987) reported that critical levels of available Zn in soils of SE Punjab were 0.50, 0.70, 1.50 and 2.64 mg kg^{-1} respectively for available zinc estimated by ammonium acetate-dithizone, DTPA, EDTA and 0.1N HCl. Devarajan *et al* (1989) reported that critical Zn level for sorghum was 1.5 mg kg^{-1} DTPA extractable.

Solubility and availability Fe, Mn, Zn and Cu in soil increased with organic acid concentration covering a range of 10^{-6} to 10^{-2} M, and citrate proved to be a stronger chelating agent than fumarate, oxalate or malate (Msaky and Msanya 1986). The rate of zinc diffusion and the extractability of Zn varied among the soils and were lowest in soil with the highest clay content, organic matter, and CEC (Modalish 1990). Lorenz *et al* 1997 reported great variability among soils in solubility of Zn and hence rate of release and Zn uptake by crop. Applications of organic and mineral amendments reduce mobility (Convert 20-60% of water soluble and exchangeable form into fixed state) of Pb and Zn and their uptake by maize and barley plants (Obakhov and Plekhanov 1995). Hydrogen ion of equilibrium soil suspension, decreased with increasing concentration of Zn solutions (Deka and Poonia 1996). It was reported that 11 and 32% of the applied Zn as Zn-EDTA were recovered in the leachate from the Ultisol and Oxisol respectively, where as Zn elution was observed when Zn was applied as $ZnCl_2$ showing high mobility of chelated zinc (Cunha *et al* 1996). Natural chelating agents isolated from various organic materials are more effective in the diffusion of Zn, percentage utilization of applied Zn and crop production than those of inorganic salts. Synthetic chelated Zn was less efficient than natural chelated Zn (Prasad 1997). Application of FYM resulted in significantly higher availability of N, P and Zn over control. In addition, zincated suphala proved to be a good source of available Zn, N, and P (Indulkar and Malewar, 1996). Arambarri *et al* (1994) reported that application of basic salt of Zn and Fe are as effective as the chelates and are more environmentally safe. Mehdi *et al* (1990) reported that chelated zinc was superior to other inorganic zinc carriers. Maftoun and Karimian 1989, reported greater effectiveness of Zn-EDTA the Zn SO_4 as fertilizer due to lower levels of soil Zn fixation and greater mobility of chelated Zn, Organic amendments and chelated zinc compounds were expected to be more effective than inorganic sources in supplying Zn to plants (Prasad *et al* 1993). The supply parameter of Zn through Zn chelates to plant roots was greater than that of $ZnS0_4$ (Prasad and Sarangtham 1992). Application of chelated Zn at an equivalent concentration of Zn was effective as zinc sulfate and sometime even more but high cost of material is a great impediment. The residual effect of three zinc sources were in the order $ZnSO_4 >$ Zn Frits >ZnO. Ferrandon and Chamel (1988) reported that application of Fe, Mn, and Zn on leaves in the form of either the EDTA chelates or sulfate salt resulted in extensive fixation in treated area. The elements were less absorbed as chelates than as inorganic salts. Further translocation within the plant was much greater with chelates. The Zn-EDTA was always more effective than $ZnSO_4$ in maintaining a higher amount of available zinc in soil for a larger period (Chatterjee and Mandal 1985).

Pasricha *et al* (1987) reported that applying P to the soil did not decrease Zn intensity in the soil solution. Zinc buffer power capacity of the soil was in the increasing order in Gangtok acid soil >Gurdaspur neutral soil > Ludhiana alkaline soil > Bhatin eka calcareous soil, the reverse was true for the Zn intensity values. High levels of phosphorus lead to low available zinc and caused rosette disease to apple trees (Naumov *et al* 1984). For soils with marginal Zn availability, application of 10kg Zn ha^{-1} is essential to obtain best yield of rice and wheat in rotation (Chhibba *et al* 1989). Dang *et al* (1988) after conducting a green house experiment concluded that application of all types of zincated P-fertilizers significantly increased grain and straw yield of wheat. The yield obtained were significantly higher with $ZnSO_4$ as compared to ZnO blended P-fertilizers. Zincated DAP produced higher yield than zincated SSP. Single superphosphate zincated with $ZnSO_4$ left the highest amount of residual Zn in the soil. FYM (10t ha^{-1}) increased N, P, and Zn availability significantly and zincated suphala was a good source of Zn, N, and P (Indulkar and Malewar 1990).

Total concentration of Zn, Cu, Mn, and Pb were greater in the upper horizon and decreased considerably with depth (Zhang *et al* 1997). Soils in upper elevation contained more micronutrient cations than those in lower elevation (Chattopadhyay *et al* 1996). Total and available Zn, Fe, and Cu decreased with depth in Lithic Haplustalfs, typic Ustochrepts and typic Chromustersts. (Pramasivam and Gopalaswamy 1994). Castro *et al* (1992) reported that Zn and Mn in soils decreased with depth, their concentration was closely correlated with soil organic matter. Tillage had no effects on Zn and Fe in soils. Anand Swarup *et al* (1994) after conducting a laboratory leaching experiment using undisturbed column of forest soil, reported that most of the applied heavy metals (Zn, Pb and Cd) were retained in the top 10cm of the soil (87 to 96%) and this resulted in lower recovery of heavy metals in the leachates (Zn 12.6%, Pb 6.0% and Cd 8.3%).

2.2.2 Crop Response to Zinc

The response of zinc to different crops were reported by several workers and are summarized below:

a) Zinc on yield and quality of perennial crops

Crop	Rate/ method of application	Effect on Yield and Quality	Responses	Reference
Apple	Zn spray weakly interval	--	Corrected Zn deficiency	Pons (1996), Basso *et al* (1990)
"		--	Zn deficiency depressed protein synthesis and accumulated amino acid.	Quguimin *et al* 1994.
Banana	Foliar application of 0.3% Zn + 0.1% Cu +0.2% B two times	Increased individual fruit weight, size, pulp, TSS and ascorbic acid content	--	Ghanta and Dwivedi 1993
Ber	0.5% foliar $ZnSO_4$	---	Increased total soluble sugar and ascorbic acid content of fruits	Surender Singh and Ahlawat 1995
Ber	2% urea + 0.8% $ZnSO_4$ Foliar	--	Increased fruit weight and quality	Joom *et al* 1984
Betelvine	0.5% foliar $ZnSO_4$ thrice weakly	6.7% increase in leaves yield	--	Arulmozhizan *et al*, 1993
"	Soil Application	Increased yield and quality	--	Balasubramanyam *et al* 1992
Black pepper	0.5% foliar $ZnSO_4$	--	Reduced spike shedding	Geetha and Sivaraman Nair, 1990

Crop	Rate/ method of application	Effect on Yield and Quality	Responses	Reference
Citrus	Zn application	Increase yield	--	Eaorashvili *et al* 1991
"	Zn application @ 500 g/tree	Highest yield and quality	--	Khera *et al* 1985
"	"	--	Wide spread Zn deficiency corrected	Chauhan *et al* 1984
Coffee	Zn applied	Increased tryptophan and total amino acid content	---	Lambot 1990
Guava	Foliar K, Ca and Zn	Increased yield and quality	--	Sharma *et al* 1991
Guava	Foliar Zn with urea and etheral	Increased fruit size	--	Pandey *et al* 1988
Mandarin	--	--	Sub standard quality fruit due to Zn deficiency	Patil and Malewar, 1998
"	0.7% foliar	Increased yield and quality	--	Daulta *et al* 1986
Mango	1% foliar $ZnSO_4$	--	Maintained critical leaf zinc level	Little more *et al* 1991
Papaya	Foliar $ZnSO_4$ with B or Fe	Increased in yield	--	Veena Pate and Lavania, 1998.
Pine apple	Zn+NPK application	Increased yield fruit size and ascorbic acid content	--	Torreschinea *et al* 1986
Sugar Cane	Zn, Fe and Press mud application	Increased yield and quality		Kumaresan *et al* 1985

b) Zinc on yield of other crops

Crop	Rate / Method of application	Effect on Yield	Reference
Barley	Zn @ 4 kg ha^{-1}	Increased yield	Choudhary and Mali, 1988
"	Application of highest dose of Zn-EDTA	Highest yield	Mac Naeidhe and Fleming 1988.
Bush beans	Increased Zn concentration under hydroponic	Decreased DM yield	Ruano *et al* 1987
Chick Pea	Responded to Zn and S application	--	Tripathi *et al* 1997

Crop	Rate / Method of application	Effect on Yield	Reference
Chilly	20 to 40kg $ZnSO_4$ ha^{-1} or 0.5% foliar $ZnSO_4$	Increased yield	Singh *et al* 1989
Cotton	Zn@ 5 to 10 kg ha^{-1} or 0.5% foliar	Increased yield	Sharma *et al* 1988, Shrivastava and Singh, 1988.
"	25 to 50 kg $ZnSO_4$ ha^{-1} or 0.5% foliar spray	Increased yield by 15 and 7% respectively	Basilious *et al*, 1991, Kumar and Gupta 1989, Sharma and Gupta 1987.
Corn	2.5 mg kg^{-1} Zn	Increased yield	Gupta *et al*, 1986.
Fodder Oats	$ZnSO_4$ @ 50 kg ha^{-1}	Increased yield	Singh *et al* 1989
Ground nut	$ZnSO_4$ with Rhizobium and Gypsum	Increased yield	Ram *et al* 1993
"	Zn @ 20 kg ha^{-1}	Increased yield	Bahl *et al* 1986
"	Resudual effect of 6.3 kg Zn applied to previous crop	Increased DM yield	Grewal *et al* 1989
Jasmine	Foliar spray of 0.5% and 0.25% Zn	Increased growth and flower production	Bhattachare, 1990
Lentil	$ZnSO_4$ @ 25 kg ha^{-1}	Increased yield	Sharma *et al* 1992
"	Zn applied	Not altered yield	Islam *et al* 1989
"	Zn applied @ 12.5 kg $ZnSO_4$ ha^{-1}	Produced highest yield	Azad *et al* 1993
Lemon grass	Responded to Zn	--	Rao and Sukmal Chand, 1996
Maize	Soil application @ 1.2 kg ha^{-1} or 1% foliar application or seed treatment @ 1 kg Zn/20kg seed	Increased yield	Galrao 1996
"	Zinc enrichment in soil with more sand and less organic matter	Reduced yield	Singh and Ram 1996
"	Zn @ 5.1 kg ha^{-1}	Increased yield	Ramon and Villemin 1989
"	In a red lateritic soil $ZnSO_4$ @ 30 kg ha^{-1}	Increased yield by 42%	Srinivasan 1992
"	Zn @ 7.1 kg ha^{-1}	Increased yield by 6%	Abdul Halim *et al* 1990
Mint	Zn @ 5 $mgkg^{-1}$	Increased yield	Subramanian *et al* 1991

Crop	Rate / Method of application	Effect on Yield	Reference
Mint	0.25% $ZnSO_4$ foliar	Increased yield	Duraisamy *et al* 1990
Okra	Zn+Mo application	Increased yield	Srihari *et al* 1987
Peanut	5 ppm Zinc in pot	Increased yield and tissue concentration	Gupta and Potalia 1987
Potato	Zn @ 10 kg ha^{-1}	No effect on growth and tuber yield	Rashid Ahamed *et al* 1989
"	Zn @ 20 kg ha^{-1}	Increased yield	Sharma and Grewak 1988
"	1% foliar $ZnSO_4$ in heavily limed sandy loam soil	Increased yield by 200%	Tiwari and Dwivedi 1991, Aasen 1987
Pearl millet	10kg Zn ha^{-1}	Yield in increase by 93%	Yadav *et al* 1989
"	Zn rate	Increased yield	Manohar *et al* 1992, Maliwal *et al* 1985
Rice	Basal Zn application at 0.5 kg ha^{-1} followed by topdressing @ 2 kg ha^{-1} and foliar spray 0.1% as Zn-EDTA	Reduced Pest infestation Increased Yield	Padhee and Mishra 1995
"	Zn and S application	Significantly increased yield. Residual effect increased yield of mustard crop	Islam *et al* 1997
"	Response to Zn	-	Sahu *et al* 1994
"	Zinc application	Increased grain yield	Trivedi *et al* 1998
"	Zn applied @ 25.8 to 45.8 kg $ZnSO_4$ ha^{-1}	Increased grain yield	Nagarajan and Manickam 1986
"	Zn applied @ 20-25 kg $ZnSO_4$ ha^{-1}	Increased gram and stress yield	Prasad and Umar 1993, Sachedev and Deb 1991, Singh *et al* 1988, Shamin *et al* 1991, Rajan 1995, Salam and Subramanian 1988.
"	Zincated Urea @ 5 kg Zn ha^{-1} gave highest utilization of fertilizer zinc (3.6%)	Increased yield	Sarkar and Deb 1990,
"	Chelated Zn @ 1 kg ha^{-1} gave higher yield compared to $ZnSO_4$ @ 20 kg ha^{-1}	Increased yield	Srivastava *et al* 1992
"	Zinc application	Increased yield by 64%. Decreased sterility from 20 to 15%	Jayarama and Ramiah 1989

Crop	Rate / Method of application	Effect on Yield	Reference
Rice	Zincated super and $ZnSO_4$	Higher yield than Zn frits	Bansal & Patel 1986.
"	4 kg ha^{-1}	Increased chlorophyll content and carbonic anhydrase activity in leaves	Indulkar and Malewar 1989
Sorghum	Increase in soil available Zn	Significantly increased Bray's percentage yield and zinc concentration in index leaf	Chibba *et al* 1997
Soybean	P+Zn+Rhizobium	Increased DM yield	Tomar *et al* 1991
"	P+Zn	Increased DM yield	Devarajan and Palaniappan, 1995. Ma *et al* 1989
"	Zn application	Increased yield reduced foot- rot disease	Deb and Dutta 1992
Sugar cane	Foliar or soil application	Increased yield and sugar content	Stratieva *et al* 1990
Tomato	Zn @ 10 kg ha^{-1}	Optimum plant growth and highest yield and income	Singh and Verma 1991
Tomato	Zn application	Negative effect on fruit dry weight	Niazi and Chohan 1986
"	Zn @ 0.15 kg ha^{-1} or 0.5% foliar	Increased yield by 35%	Balashanmugum *et al* 1990
"	Zn application soil or foliar	Increased DM	El-sherif *et al* 1993
"	Foliar application of 0.3% Zn	Increased yield by 68%	Gezerel 1988
Turmeric	Application as $ZnSO_4$	Increased Rhizome concentration and yield	Tiwari *et al* 1995.
Wheat	Application of zincated superphosphate	Increased DM production and reduced Fe content	Yaduvanshi 1995, Singh and Rakipov 1990
"	Zn @ 25-50 kg $ZnSO_4$ ha^{-1}	Increased paddy and wheat yield	Parik *et al* 1992, Rajan 1995, Pradhan *et al* 1990, Kumar and Gupta 1989
"	In a limed acid silty clay soil application of Zn upto 20 $mgkg^{-1}$	Increased shoot and root weight concentration	Verma and Bhagat 1990
"	Zn application	No effect on yield without P, but effect with P application	Germa and Minha 1987
"	Foliar spray of Zn-EDTA $ZnSO_4$	Increased yield but Zn-EDTA, 1.4 to 1.7 times more effective than $ZnSO_4$	Brennan 1991

c). Effect of Zinc on quality of other crops

Crop	Zn rate/method of application	Influence on quality	Reference
Bean	Zinc application	Increased protein content	Ahamed *et al* 1986
Brinjal	Zn and Cu application	Increased yield, titratable acidity TS and crude protein content	Dhakshinamoorthy and Krishnamoorthy 1989
Barley	Zn and S application	Increased total protein, N and S concentration	Ragubbir Singh *et al* 1995
Cauliflower	Zn application	Increased yield, protein carbohydrate and ascorbic acid content	Singh *et al* 1991
Cotton	Zn up to 15 mgkg^{-1}	Increased seed oil content	Kashyap *et al* 1988
Chickpea	S and Zn application	Increased protein and amino acid content	Tripathi *et al* 1997
Onion	Foliar application of 0.5% Zn + 0.2% B	Increased yield, bulb diameter, FW percentage, TSS and DM	Baghel and Sarnik 1988
Pearl millet	Zn @ 10 kg ha^{-1}	Increased protein content and yield	Keshawa and Jat 1992
Pepper mint	Zn application	Increased essential oil	Kocourkova and Vralova 1992
Soybean	Foliar Zn	Increased protein, oil content and yield	Thalooth *et al* 1989
Sorghum	Zn @ 5 ppm mgkg^{-1}	Increased protein N concentration	Sharma *et al* 1994
Tobacco	Zn deficiency	Depressed protein content of plant cells	Obata and Umebayashi 1988
Wheat	Application of Zn enriched fertilizer	Increased protein content	Zhamurko and Kudryavtseva 1996
"	7.5 mg Fe+7.5 mg Zn in potted condition	Increased yield and total carbohydrate and starch content	Hementaranjan and Garg 1988

2.2.3 Zinc Adsorption-Desorption

Zn adsorption also could reduce solution Zn^{2+}. Adsorption of Zn^{2+} by clay minerals, Al, and Fe oxides, OM, and $CaCO_3$ increases with increasing pH. Correlation analysis showed that Cation Exchange Capacity (CEC) and organic carbon were the dominant soil variables contributing towards sorption or desorption of Zn (Singh *et al* 1997). The concentrations and pattern of desorption of both native and added Zn varied between different soils. Greater concentrations of native Zn were desorbed from surface soils than from subsoils, and greater concentrations of added zinc were desorbed from sub soil than from their corresponding surface horizons (Singh *et al* 1998). The binding of trace metals by humic acids depends not only on ion strength and pH, but also on the competition of ions for reaction centres of humic acids (Ladonin and Margoline 1997). Environmental change and management practices which alter soil properties (pH and O.C status) may effect the capacity of soils to sorb trace metals such as Cu, Zn and Cd thus influence the bioavailability and leachability of the metals (Yuan and Lavkulich 1997). Experiments on adsorption of Cu and Zn showed that trioctachedral montmorillonite, vermiculite, chlorite, and biotite showed highest affinity for Cu and Zn (Ladonin 1997). Kand (1989) reported that Zn^{2+} adsorption decreased by the presence of NH^{4+}, but converse not true. Zinc and cadmium accumulation is mainly due to passive processes such as surface adsorption/or diffusion in to the periplasm and adsorption is pH dependent (Dominik *et al* 1996). Adsorption of Zn^{2+} by bentonite, illite, and kaolinite clay minerals is directly related to the CEC of clays. Zn reversibly bound by clay minerals is exchangeable and, thus can be desorbed to solution. Zn^{2+} forms stable complexes with soil organic matter-components. The humic and fulvic acid fractions are prominent in Zn adsorption. Three classes of reactions of organic matter have been distinguished viz., immobilization by high molecular weight organic substances such as lignin, solubilization and mobilization by short-chain organic acids and bases, complexation by initially soluble organic substances that then form insoluble salts. Other metal cations, Cu^{2+}, Fe^{2+}, and Mn^{2+}, inhibit Zn^{2+} uptake, because of competition for the same carrier site. Adsorption of Zn was inversely correlated to soil P content (r=-0.65** Krishnasamy 1993). The diffusion coefficient of Zn increased with increasing temperature and with addition of crop residues and FYM. This may be due to presence of chelating agents converting solid phase Zn to soluble complexes and thereby increasing the concentration of total diffusible Zn (Prasad and Sinha 1995). Adsorption studies in entisol, oxisol, and inceptisol in India showed that adsorption of Zn increased with increase in rates in all the soils. Application of Mg or P decreased adsorption of Zn in acid soils, but increased in alkaline soil (Paul *et al* 1996). Rimmer and Luo Yong (1996) reported that addition of Cu salt reduced Zn adsorption and increased the amount of $CaCl_2$ extractable Zn. Zn adsorption is closely related to pH and CEC of soil (Cunha *et al* 1994). Other cations like Cd compete with Zn for adsorption sites (Rajendra Prasad and Shukla 1996). Sandy soils and soils low in organic matter had low Zn adsorption capacities and therefore Zn would be readily available to plants for uptake but would also be lost rapidly through leaching. Clay rich soils and soils with high organic matter content had high Zn adsorption capacities but Zn fertilizer would be needed to provide available Zn at concentrations sufficient to plant growth (Muneera Siddiqui *et al* 1993). Application of MOP and DAP had significant effects on the Zn adsorption pattern by soil. MOP decreased where as DAP increased Zn adsorption (Li and Dang 1991). At low pH value, where Zn adsorbed did not exceed 50% of Zn applied, specific adsorption was the dominant mechanism, free Zn^{2+}ion being the species of Zn specifically adsorbed (Sun 1993). Desorption of adsorbed Zn decreased with an increase in pH (Anjana Srivastava and Srivastava 1990). The higher values of adsorption maxima in Alfisols and vertisols accounted for the precipitation of $Zn(OH)_2$ (Borah *et al* 1990). Sorption of Cu, Zn, and Cd by soil and clay minerals increased exponentially with pH between pH 4 and pH 7. The effect was greater with organic matter content, oxides, and a lesser extent with the type of clay minerals. Hazra and Biswapati Mandal (1996) after conducting desorption studies in Alfisol and inceptisol concluded that added Zn desorbed from Alfisols was low, indicating their greater fixing ability than inceptisol. There was significant relationship between soil properties and amount of desorbed Zn (Joshi and Sharma 1986). Borah *et al* (1992) reported that all the soils in general showed a decrease in the adsorption maximum and selectivity coefficient values for the trace elements after removal of organic matter. Basta and Tabata bai (1992) after conducting adsorption studies on Cd, Cu, N, Pb and Zn, concluded that differences in metal adsorption were dependent on the initial heavy metal concentration. At low concentration, all the added metals were adsorbed regardless of solution pH. At high concentration, however, metal adsorption by soils correlated positively with soil pH. Adsorption of Zn and Cu was greater in Vertisols, followed by inceptisols and Alfisols and adsorption was mainly influenced by clay content, CEC, and organic carbon. Further DTPA extracted relatively higher amount of adsorbed Zn and Cu as compared to $CaCl_2$ and $Mg(NO_3)_2$ (Rupa and Shukla, 1998). With addition of increased amount of zinc, there was a simultaneous increase in the equilibrium concentration, adsorption, percentage saturation of adsorption capacity, and supply parameter of zinc in all soils (Diatta and Kuclakowski, 1998). Deopal and Sastry (1985) after conducting adsorption study in Alfisols of Kerala reported that zinc was preferentially sorbed throughout the range of surface coverage on both sodium and magnesium clays. The selectivity coefficient was between 100 and 700 in sodium clays, but less than 5.5 in magnesium clays. Sorption of Zn increased with increasing pH, and retention increased abruptly at pH >6.0. Desorption decreased continuously with rising pH and became a trace at pH>6.0. An increase in the ionic strength of the background electrolyte decreased Zn sorption and enhanced the amount of sorbed metal that could be subsequently released (Prado and Guadalix 1996).

Effect of zinc fertilizer on rice yield was positively correlated with Zn uptake, utilization of zinc fertilizer and Langmuir adsorption maxima (Quian and Xie 1992). Dhane and Shukla (1996) reported that zinc adsorption data on soil clays conformed to the linear form of Langmuir adsorption isotherm. The clay separated from vertisols adsorbed zinc more strongly (25.44 mg kg^{-1}) than clay separated form inceptisol (21.7 mg kg^{-1}) and Entisols (18.6 mg kg^{-1}). Krishnasamy and Krishnamoorthy (1991) reported that Zn adsorption in vertisol and inceptisol fitted the Langmuir and Freundlich equation, but zinc adsorption and relative bonding energy of zinc in soil is reduced by organic matter removed. They also reported (1991 b) that the interference of four bivalent cations of Zn adsorption was in the order Cu^{2+}>Mn^{2+} Fe^{2+}>Mg^{2+}. Further variation in soil properties particularly soil texture also influence Zinc adsorption in vertisols and Inceptisols. Zinc adsorption fitted Langmuir adsorption isotherm (Manjunathaiah *et al* 1992). The solubility of zinc in soils decreased linearly with increasing soil pH and data fitted the Langmuir isotherm. The maximum adsorption capacity and bonding energy increase with increase in pH (Machado and Pavan 1987). Zinc adsorption increase with pH and follows Langmuir adsorption isotherm and adsorption maxima decreased as loam >Sandy loam > Sand and adsorption maxima were related to the clay content, free $CaCO_3$ and CEC of soil (Prasad and Kusum Agarwal 1991). Zinc (11) adsorption followed Langmuir behavior only at small adsorption densities, while at higher adsorption densities the availability of strong binding sites decreased. Zinc adsorption was higher in alluvial (1.23μg g^{-1}) than in lateritic soils (0.67μg g^{-1}) and the data were fitted well to the Langmuir adsorption isotherm equation. The adsorption maxima and bonding energy values computed from the equation were higher for the former (1.61μg g^{-1} and 0.25μg g^{-1}

Zn) than the latter 0.97 µg g^{-1} and 0.03 µg g^{-1} Zn. The higher values were due to higher contents of clay, organic carbon, $CaCO_3$ and amorphous Fe-oxide and higher CEC and pH of the alluvial soil. Significant positive correlations of adsorption maxima and bonding energy of Zn with clay (0.84** and 0.57**), CEC (0.78 **and 0.77**), organic carbon (0.85** and 0.62**) and amorphous Fe oxide (0.83** and 0.78 **) contents of the soils supported these adsorptions (Hazra and Mandal 1995). Cunha *et al* (1994) after conducting adsorption studies in four oxisol, two ultisols and an alfisol of Brazil concluded that Freundlich model is the most suitable fit, followed by Langmuir equation. Temkin isotherm did not present a good fit and least suitable for Zn adsorption data. Adsorption of Zn was linear in the Langmuir equation in untreated soils where as in Ca- saturated soils, the Ca- Zn exchange equation proved a better method for Zn adsorption. Application of lime, decreased Zn desorption, in loam and sandy soils (Gaszezyk *et al* 1995). Soils with higher amounts of clay and $CaCO_3$ had higher capacities to adsorb Zn and Cu than soils with lower amounts. Van Huay, Langmuir and Van Bemmelen Freundlich equations were well fitted for Cu and Zn adsorption in soils at all concentrations except Langmuir, which failed at higher Zn and Cu concentrations (Abbas *et al* 1996). Mandal and Mandal (1987) reported a higher Zn retention capacity for inceptisol compared with Alfisols due to higher content of clay, organic carbon, $CaCO_3$ amorphous Fe-oxides and higher cation exchange capacity and pH values for the Inceptisols. Increasing concentration of Mg decreased adsorption of zinc (Krishnasamy 1996). Adsorption of Zn and Cu in acid tropical soils can be explained by Freundlich equation rather the Langmuir equation and adsorption is influenced by CEC ($r = 0.888^{**}$), total Al content ($r = 0.675^{**}$) and extractable Al ($r = 0.875^{**}$) (Hanafi and Sjiaola 1998). P treatment changed the Zn sorption isotherm from L-curve isotherm to an H-curve isotherm indicating strong affinity of P treated soil for Zn, as a result of Zn-phosphate complex on the soil surface and precipitation at sufficiently large concentration of P and Zn. In other words fertilizer P placement around a growing crop plant can potentially limit Zn solubility and availability (Agbenia 1998).

2.2.4 Correlations of Zinc with Soil Properties

The DTPA-extractable Zn, Cu, Fe, Mn showed high correlation with their total amounts indicating a genetic relationship among them (Khan *et al* 1997). DTPA extractable zinc correlated with labile zinc fractions. Arriechi and Ramirez (1997) by using 5 extractant *viz.*, DTPA, DTPA-HCl, Na-EDTA, 0.1 N HCl and Mehlich 1 to predict Zn availability in 14 acid soils with maize as test crop reported significant positive correlations between Zn extracted among five extractants. They also stated that Zn extracted was related with soil pH and organic matter content not with CEC and clay content. DTPA extractable Zn positively and significantly correlated with soil pH, EC, O.C, and calcium carbonate (Sharma *et al* 1992). DTPA extractable Zn positively correlated with amount of added zinc and that Zn extractability was higher in coarse textured soils than in clay soil. Kuldeep Singh and Gupta (1986) reported that DTPA extractable zinc negatively correlated with pH (r = -0.81**) and positively with organic carbon (r=0.79**), Olsen's P (r=0.63**), and yield (r = 0.86**). Soil zinc extracted by DTPA significantly correlated with percentage grain yield of rice (Bansal and Patel 1986). Zn uptake positively correlated with soil organic matter and negatively with soil 'P'. VAM colonization, soil respiration, and DTPA extractable Zn were most important variable affecting Zn uptake (Hamilton *et al* 1993). DTPA extractable Zn positively correlated with organic carbon and pH in valleys of Himachal Pradesh (Kanwar *et al* 1984). Extractable Zn positively correlated with organic carbon in red laterite soils of West Bengal (Karan *et al* 1993). Zn extracted with DTPA correlated with previously applied Zn fertilizers (Brennan 1996). Available phosphorus content of the soil showed positive correlation with available Zn and Cu (Saha *et al* 1996). Ion exchange resin extracted soil Zn, correlated better with plant Zn concentration and uptake throughout the growing season than DTPA extracted soil Zn (Hamilton and Westernmann, 1991). Available Zn, Cu, and B levels in the soils significantly and positively correlated with their respective concentrations in rice plants (Saha *et al* 1996). Available Zn significantly and negatively correlated with $CaCO_3$, EC, and pH (r= -0.70**, -0.52** -0.70**) respectively (Chattopadhyay *et al* 1996). For soil with high organic matter content, the amount of Zn extracted by HCl, EDTA or DTPA were positively correlated with soil CEC, where as the correlations were negative or insignificant for soil with low organic matter content (Jahiruddin *et al* 1992). Benhi and Brar (1992) reported significant positive correlation between soil organic carbon and DTPA extractable micronutrients. The content of DTPA extractable micronutrients directly related to soil texture. The finer, the texture, the higher the content of these micronutrients. Results of the study conducted by Daug *et al* (1992) indicated that Zn extracted with NH_4OAC, DTPA, and 0.1 or HCl were significantly correlated with soil pH. Dhane and Shukla (1995) reported that DTPA extractable Zn and Mn were positively and significantly correlated with organic carbon, clay, and CEC. Soil available Zn correlated positively with Zn concentration in index leaf (Chibba *et al* 1997). Judicious application of N result in increased plant growth, which can dilute the zinc concentration and can cause Zn deficiency. Further Zn-P interactions are antagonistic at higher level of P or low level of zinc (Hemantaranjan, 1996).

Correlations between Zn, Mn, Fe and humus content and soil acidity were found in gray forest soils (Kiteva 1990). The effect of Zn on the concentration of P and K in all plant parts of pearlmillet was *antagonistic,* while it had *synergic* effect on concentration of Fe and Mn (Kumar *et al* 1986). Uptake of Cd and Zn into leaves correlated with the mass flow of Cd and Zn (Lorenz *et al* 1994). Values of maximum adsorption of Langmuir equation were negatively correlated with Zn uptake and positively with $CaCO_3$ and organic matter content (Abbas *et al* 1996). Data on distribution of available trace elements in acid alluvial soils (Entisols and inceptisols) in West Bengal showed that soil pH and base saturation were positively correlated with available Zn (Mukopodhayay and Halder 1992). The Zn fixing capacities are higher in clayey soils and lower in sandy loam soils (Nagarajan and Manickam 1985). Zn absorption by maize correlated with exchangeable Zn and Zn associated with soil organic matter. A negative correlation observed between Zn availability and content of amorphous Fe oxides (Rodriguez and Adams 1997). Leaf Zn decreased with increasing P and this was attributed to a possible P-Zn interaction within the plant (Raju and Desphande 1986). Rice yield positively correlated with soil Zn content at the tillering and panicle initiation stage (Saravanan and Ramanathan, 1988). Kuldeep Singh and Karwasra (1988) reported that Bray's percentage yield of pearl millet positively and significantly correlated with both soil Zn (r=0.88) and plant Zn (r=0.72). Negative correlation between soil Fe and Zn were reported (Sen *et al* 1997). Zinc availability in soil is affected by soil properties like pH, $CaCO_3$, P, O.C, and total zinc. Available zinc was positively correlated with organic carbon and clay content and negatively with pH, and $CaCO_3$ content (Mazumdar and Singh, 1989).

2.2.5. Fractions of Zinc

Significant and positive correlations were reported among different fractions of soil Zn, indicating the existence of a dynamic equilibrium among them, and the amount of Zn in water soluble, exchangeable, MnO_2 occluded and organic matter occluded fractions were significantly and positively correlated with clay content (Rupa and Shukla 1996). Sharma *et al* 1992 reported that complexed occluded and residual Zn correlated significantly with Bray's percent yield, concentration and uptake of zinc by wheat. Organically bound Zn extracted by Sodium pyrophosphate constituted higher proportion of total Zn and was significantly correlated (r=0.726) with organic carbon (Sinha and Prasad 1996). The water soluble plus exchangeable, DTPA extractable and amorphous sesquioxide bound zinc content showed significant negative correlation (r=-0.60**-0.40*, and -39*) with pH. The organic complexed and crystalline sequioxide bound zinc showed significant positive correlations with organic C content and most of the different fractions of Zn had positive and significant correlations among themselves (Mandal *et al* 1986). Prasad and Sakal (1988, 1992) and Paul *et al* (1992) reported significant and positive correlations among different pools of soil Zn, suggesting existence of a dynamic equilibrium among various forms of soil zinc. They also reported that most of the Zn fractions were correlated negatively with pH, and free $CaCO_3$ and positively with organic carbon and clay content of the soil. Most of the zinc fractions were correlated positively and significantly with DTPA extractable Zn and negatively with soil pH (Prasad *et al* 1990). CEC was positively correlated with non-exchangeable but not with exchangeable Zn forms. (Stahl and James 1991). Halen *et al* 1991 reported that 0.5 M $MgCl_2$ and 0.1 N HCl extractable Zn is negatively correlated with organic matter. $MgCl_2$, HCl, DTPA, and NaOAc extractable Zn negatively correlated with $CaCO_3$. Strong correlation was reported between extractable Zn with clay and silt percentage. Water soluble and exchangeable Zn showed positive relationship with coarse sand (r= 0.370*). Organically bound Zn correlated positively with fine sand (r= 0.430**) and coarse sand (r=0.512**) and negatively with clay (r = -0.520**) pH (r = -0.432**) and free $CaC0_3$ (r = -0.372*). The residual zinc was positively correlated with clay (r = 0.470**), EC (r =3.77*), CEC (r = 0.444*), $CaCO_3$ (r = 0.457**), Org. C (r = 0.437*) and total Zn and negatively with coarse Sand (r = -0.455**) (Gowrisankar and Murugappan 1998). Exchangeable weakly adsorbed, moderately adsorbed zinc fractions, DTPA extractable Zn was correlated with dry matter yield, Zn content, and uptake by maize (Randhawa and Singh 1995). Significant correlations and dynamic equilibrium among different fractions of zinc in red and lateritic soils of West Bengal was reported by Mete *et al* 1996. They also reported that about half (52.5%) of the total soil Zn remains in relatively inactive fractions. Soluble, exchangeable, Iron, manganese oxide bound, chelated and insoluble organic forms of zinc had a different distribution in andosol, inceptisol, and vertisol. The exchangeable form predominated in the andosol, followed by Fe-Mn oxide bound Zn, Where as Fe-Mn oxide Zn was abundant in inceptisol and vertisol. Phosphate pre treatment of the inceptisol and vertisol did not alter the distribution of the different forms of Zn, where as in the andosol the exchangeable, as well as Fe-Mn oxide bound Zn increased markedly (Ahumada *et al* 1997). Compared with field moisture soils, the exchangeable forms of Zn in the air-dried soils increased 1.4- 1.7 times (Makino *et al* 1997). The proportions of zinc in individual fractions varied between soils- on average 3% occurred as exchangeable Zn, 5% as organic bound Zn, 9,18 and 24% were associated with Mn, amorphous iron and crystalline iron oxides respectively and 40% as residual fractions of total zinc (Chowdhury *et al* 1997). Concentrations of the exchangeable Zn and organic matter associated Zn were affected by lime, irrespective of soil type, where as Zn associated with amorphous iron oxides unaffected (Rodriguez and Adams 1997). Higher levels of Zn (5 mg kg^{-1}) and its enrichment with organic manures increased amounts of Zn present in water soluble and exchangeable complex, organically bound, occluded form of zinc and crop yield (Chitdeshwari and Krishnasamy 1997). Studies on controlled release of zinc through chelating or coating showed that added zinc by coating or chelating remained in the soils in more favorable forms for uptake by plants (Alvarez *et al* 1997). Increasing P levels resulted in lower Zn and Cd in crystalline Fe oxide, organic bound are carbonate fraction, with a concomitant increase in the amorphous Fe oxide and water soluble plus exchangeable fractions (Kaushik *et al* 1993). Most of the applied Zn was recovered in OH-Zn and Mn-Zn fractions showing that applied Zn was preferentially associated with hydrous oxides, functional group of soil organic matter and bound to Mn oxides (Liang *et al* 1991). The Zn content in the residual fraction of soil was 60-90% of the total Zn where as the percentage of Zn in exchangeable fractions was less than 3%. The percentage of Zn in organic matter fractions was in the order upland> grassland>forest (Yamamoto and Watanabe 1996). Most Cu, Zn, Mn, and Ce in soil occurred in residual mineral forms and bound to iron oxide (amorphous and crystalline). Exchangeable form and the form loosely bound to organic matter were the most available forms of Cu, Zn, Mn, and Fe for plants (Shao Yuting *et al* 1995). Li and Shuman (1996) after conducting incubation experiment in eight agricultural soils of Georgia -USA reported that, increasing the amounts of sodium EDTA significantly increase zinc concentration in exchangeable fractions and decrease in organic matter fraction. This is due to solubilisation of metal from organic matter fraction by EDTA and converting to exchangeable fraction. By conducting a profile study, Li and Shuman (1996) reported that large portion of zinc in the subsoil was in the exchangeable fraction, suggesting movement of Zn in this profile. Rupa and Shukla (1996) reported that soil Zn was primarily in the residual fraction. Zinc predominantly present in the organically bound form in spodosols, where as organically bound, associated with FYM oxide and amorphous form represent the dominant form in alfisol and entisols (Zhang *et al* 1997). Application of poultry litter to metal contaminated soil might cause Zn and Cd redistribution from exchangeable to the water-soluble fractions and enhance metal mobility (Lizhenbin and Shuman 1997). Total extractable concentrations of Cu and Zn in the fine particles were higher than their total concentrations in the original bulk soil. The concentrations of Cu and Zn in the various extractable fractions were significantly affected by the application of lime and lime stabilized sewage sludge cake or inorganic metal salts. Crop residues and organic manure added to soil, modify the form of Zn and their availability in soil. Further water soluble + exchangeable and HCl extractable Zn fractions decrease with increasing NPK fertilizers (probably due to enhanced biomass production) and increase with organic manure and crop residues application (Sinha and Prasad 1996). Most of the total Zn (85-91%) remained in residual fraction, having little significance during growing period of crops and need proper management to bring it in plant available forms (Anonymous 1998). Soil zinc fraction studies conducted by Mandal and Mandal (1986) revealed that more than 90% of total zinc occurred in the relatively inactive clay lattice bound form and that a small fractions, viz., 0.26, 0.74, 0.58 and 0.71% of the total, occurred as water soluble + exchangeable, organic complexed, amorphous sesquioxide and crystalline sequioxide bound forms. Applied Zinc was transformed to the later four forms and constituted on an average 3.68, 12.18, 19.85, and 5.33% respectively. Mandal and Mandal (1987) reported that greater amount of applied Zn distributed to $(NH_4)_2C_2O_4$ and CBD-extractable fractions, may be due to lower CEC, higher sesquioxide and lower organic matter content in the Ultisols. The table zinc pool, chelated and complexed and occluded fractions were proportional to silt, carbonate content and soil pH but inversely related to sand content. The specifically bound fraction increased with soil organic carbon but both specifically and weakly bound fractions decreased with soil pH. For zinc uptake by rice, the specifically bound fractions were the most important. (Srivastava and Singh 1988). Jiang *et al* (1993) after conducting sequential extraction studies concluded that >90% of total zinc in soils occurred in mineral and iron oxides (amorphous and crystalline). Exchangeable zinc, bound to manganese oxide and soil organic matter increased with decreasing pH and/or increasing soil organic matter. The distribution of various pools of zinc in an oxisol of Karnataka was in the order - Water soluble < exchangeable < organically bound< complex< occluded<residual. Most of the total zinc in soil existed in the residual form, the amount of water soluble, exchangeable and complexed forms of zinc diminished due to crop removal while addition of zinc to the soil increased these three forms considerably (Chandrasekaran and Kedlaya 1988). Organically bound Zn (1.2-8.3 $\mu g\ g^{-1}$) did not vary as much as the organic matter content in the soils, where as reserve Zn (8-44 $\mu g\ g^{-1}$) was found to be a function of the type and proportion of clay minerals in the soils. Fine clay and very fine sand fractions contain maximum amount of Zn (Choudhari 1988). El-Sabour and Soliman (1990) reported that when zinc was added to soil, about 2.4 to 33.9% of retained Zn was readily available (extracted by KNO_3) and about 1.6 to 16.35 (of retained Zn) was considered potentially available (NaOH extractable). The sparingly soluble form (extracted by Na_2 EDTA and HNO_3) ranged from 50.4% to 92% of retained Zn. Fine textured soil retains more zinc than coarse soil. The order of retention was alluvial>calcareous >Sandy loam>Sandy soil. Experiment conducted by Dahiya *et al* (1991) showed that >80% of total soil Zn occurred in residual from; where as 5.8, 4.33, 2.68, 0.55 and 0.35% total soil Zn occurred in crystalline Fe-oxide bound, amorphous Fe- oxide bound, Mn-oxide bound, water soluble plus exchangeable or organically bound form respectively. The different zinc forms except the residual fraction had positive significant correlation among each other and with Zn uptake by rice. Bogaez,1993,reported that acid soils contained greater share of water-soluble and non-specifically adsorbed, exchangeable Zn, while those with neutral pH contain greater share of specifically adsorbed; Zn, Mn and Fe bound and residual Zn.

Dhane and Shukla (1995) reported that water soluble exchangeable, specifically adsorbed, acid soluble, Mn occluded, organic matter occluded, amorphous Fe occluded, crystalline Fe occluded fractions of Zn contributed very little, where as residual fraction was a dominant constituent (95.9%) in bench mark and other soils of Maharashtra. The positive relationship amongst these fractions suggest the existence of a dynamic equilibrium of Zn fractions in soil, while the positive and significant relationship of solution and exchangeable fractions of Zn with organic carbon suggested the dependence of zinc availability on organic matter content of soil. Water soluble plus exchangeable pools of zinc constituted the most readily available form of soil Zn and pH is the dominant soil properties that influence this fraction. Depletion in the concentration of readily available zinc is replenished by other pools of soil zinc. The occluded zinc was the major fraction next to residual zinc constituting 69 to 94% of total zinc (Rajendra Prasad and Shukla 1996). Different zinc fractions of soil found to be correlated among themselves (Randhawa and Singh 1995).

MATERIALS AND METHODS

Hamza Srambikkal “Studies on Zinc and Molybdenum nutrition of black pepper in relation to yield and quality” Thesis. Department of Chemistry, University of Calicut, 2000

MATERIALS AND METHODS

3. MATERIALS AND METHODS

The details of the soil survey made out, laboratory, pot and field experiments conducted using Zn and Mo, and the methods employed for soil and plant nutrient analysis, oil, oleoresin and piperine determinations in black pepper are presented in this chapter

3.1 SURVEY

3.1.1 Soil and Leaf Nutritional Survey

Soil and leaf nutrient surveys were conducted in major black pepper growing tracts viz., Idukki, Wynad, Calicut, and Cannanore districts of Kerala and Coorg district of Karnataka states. The survey was done during 1995-96 particularly January to March. The yield of the vine was estimated as per procedure adopted by Balakrishnan and Jose Abraham (1986). The variety grown, farmers' practices of manuring, plant protection measures etc., were also recorded. Soil samples were collected 30cm away from the base of pepper vine to a depth of 20cm. A total number of 130 soil samples were collected. The soil collected was air dried and sieved through 2mm sieve. The soil was analyzed for pH (Jackson 1967), lime requirement (Wood Ruff 1977, Hesse 1971), organic carbon (Walkley and Black method), exchangeable potassium, calcium and magnesium by neutral normal ammonium acetate extraction followed by flame photometry (CSTPA 1974). Available sulphur by sodium acetate extraction followed by turbidimetric method (Jackson 1967). Available Fe, Mn, Zn, and Cu were estimated by DTPA extraction (Lindsay and Norwell 1978), boron by hot water extraction (Berger and Truog 1939) and molybdenum by ammonium oxalate (Tamma's reagent) extraction (Grigg 1953) followed by atomic absorption spectrophotometer using graphite furnace. The total Zn and Mo in soil were also estimated by di acid digestion (Hesse 1971) using atomic absorption spectrophotometry.

Leaf samples were collected from each garden. Youngest mature leaves from fruit bearing lateral with petiole from middle portion of vine were collected

(Sadanandan and Rajagopal 1989) in paper bags. The samples were washed with tap water, 0.1% detergent, 0.1 N HCl, distilled water, and double distilled water and dried at 70^0 C in hot air oven. The samples were powdered in cyclotec mill, weighed and digested using 9:4 nitric acid: perchloric acid mixture and made up to 100 ml. From this, aliquots were taken and analyzed for P as per vanadomolybdate method, sulphur by turbidimetry method (Jackson 1967). K, Ca, Mg, Fe, Mn, Zn, Cu, B, and Mo were analyzed after proper dilution using atomic absorption spectrophotometer (Black 1965).

From analytical and yield data, ranges of nutrients, simple and multiple correlations of zinc and molybdenum with other nutrients in soil, leaf and yield were worked out separately for Coorg, Idukki, Wynad (Higher altitude) and Calicut (Lower altitude) and altogether

3.1.2 Soil Suitability for Black Pepper

After soil leaf nutritional survey, in order to evaluate the soil suitability for growing black pepper, four districts of Kerala, viz., Idukki, Wynad, Calicut and Cannanore were selected. Each district was further divided in to three groups viz., high, moderate and low yielding areas. Soil profile samples were taken from the above 12 locations during February-March 1996 at four depths viz., 0-20, 20-40, 40-60 and 60-80cm, where pepper roots are normally covered. Samples were processed and analyzed for various physico-chemical properties as per standard procedures. (Jackson 1967, Black 1965). The data obtained were grouped based on location (higher and low altitude) and yield performance (high, moderate and low yielders). An yield level up to 3kg green pepper was considered as low, 3 to 5 as moderate and more than 5 kg as high. Similarly samples from more than 750 m above MSL as taken as higher and below as lower altitude. Statistical analysis carried out using standard procedures to work out the ranges of nutrients and correlations of Zn and Mo, yield and elevation with different soil chemical properties. Multiple regression analysis also carried out.

3.2 LABORATORY EXPERIMENTS

3.2.1. Extractability of Zn and Incubation

To study the extractability of applied zinc in pepper growing soils, Zn deficient soils from 5 locations *viz.*, Thamarassery, Ambalawayal, Peruvannamuzhi, Coorg and Idukki were collected, sieved in 2 mm sieve, weighed 100 gm each in to 12 cm petriplates. The physico chemical characteristics of the soil are given in Table.1, 2 and 3. Above soils were treated with zinc sulphate solution to get a final concentration of 0, 5, 10, 25, 50, 100, 200, 300, 400 and 500 mg kg^{-1} Zn and incubated at 25± 2^0 C after moistening with distilled water to keep 50% field capacity by weighing and adjusting daily.

Table 1. Physical characteristics of Soils used for experiment

Location	Order	Great Group	Colour	Texture	Particle size distribution (%)			B.D gm/cc
					Sand	Silt	Clay	
Coorg	Ultisols	Haplustult	10 YR 4/4	Sl	79.0	8.0	13.0	1.50
Ambalawayal	Mollisols	Argiustoll	7.5 YR 4/6	Scl	47.2	22.6	30.2	1.30
Peruvannamuzhi	Inceptisols	Humitropept	7.5 YR 4/4	C	27.0	15.0	58.0	1.41
Thamarassery	Inceptisols	Humitropept	10YR 2/2	Scl	65.5	11.6	22.9	1.26
Pulpalli	Mollisols	Argiustoll	10YR 2/2	Scl	49.5	17.1	33.4	1.28
Idukki	Ultisols	Halplohumult	10Y 2.5/2	Scl	49.1	16.2	34.7	1.49

Table 2. Major and Secondary nutrient status of soils used for experiment

Location	PH	CEC	Lime R	Org. C	Bray P	Available			
						K	Ca	Mg	S
		Cmol $(p^+) kg^{-1}$	t/ha	%	(......................mg kg^{-1}	................)			
Coorg	5.35	12.6	4.4	2.3	3.0	212	996	156	66
A.Wayal	5.30	10.2	4.1	1.6	6.0	185	545	88	31
P.Muzhi	5.26	9.8	3.6	1.4	2.5	78	237	46	61
Thamarassery	6.14	13.8	2.5	1.8	8.0	397	425	44	25
Pulpalli	5.92	15.2	3.2	1.1	13	110	792	140	21
Idukki	5.03	14.4	4.4	1.6	7.0	360	638	165	23

Table 3. Micro nutrient status of soils used for experiment (mg kg^{-1})

Location	Available					Total	
	Fe	Mn	Zn	Cu	Mo	Mo	Zn
Coorg	28	29	0.88	5.8	0.51	11.7	52
A.Wayal	37	44	0.98	7.8	0.73	21.0	38
P.Muzhi	18	14	0.64	1.3	0.93	33.0	52
Thamarassery	21	11	0.94	2.5	1.20	17.0	48
Pulpalli	46	33	1.40	2.6	0.17	12.3	26
Idukki	61	41	1.40	4.8	0.48	10.9	39

After one week of incubation, samples were drawn and extracted with DTPA and 0.01 M $CaCl_2$ solution, and amount of zinc extracted in different soils was analyzed in AAS Varian AA 20.

3.2.2 Adsorption-Desorption Studies on Zn

To study the adsorption-desorption pattern, five soils from traditional pepper growing areas having physico-chemical characteristics as described in Table. 1, 2 and 3 were selected. Two gram each of dry, 2 mm sieved soil, equilibrated with 40 ml 0.01 M $CaCl_2$ solution containing 0, 2.5, 5, 10, 25, 50, 100, 200 and 400 mg kg^{-1} zinc for 24 hours at 180 oscillation per minute in duplicate. After 24 hours centrifuged at 10,000 rpm filtered through Whatman No.41 filter paper, collected the extract and analyzed for zinc in AAS. The difference in initial applied zinc (C) concentration and that of leachate (Ce) after the extraction and from this Zn adsorbed (µg g^{-1}) was calculated for each soil. The soil in the centrifuge tube was washed with 60% alcohol to free from floated zinc, centrifuged and one set extracted with 20 ml each of 0.01 M $CaCl_2$ solution for 24 hours centrifuged and zinc concentration was measured using AAS. From this Zn desorption by 0.01 M $CaCl_2$ was calculated. To another set 20 ml DTPA was added and extracted for two hours centrifuged and analyzed using AAS. From this Zn desorbed by DTPA was also calculated. Percentage of applied zinc adsorbed, percentage of adsorbed zinc desorbed by 0.01M $CaCl_2$ and DTPA were also worked out. From the data obtained above, taking Ce in X-axis and Ce/ x/m in Y-axis plotted Langmuir adsorption curve. From the slope and intercept of the curve Ce/ x/m = 1/ kb+ c/b adsorption maxima (b) and bonding energy (k) were calculated.

Freundlich isotherms were also plotted taking log Ce in X axis and log x/m in Y-axis. From the slope and intercept of Freundlich equation log x/m= logk+1/nlogC_e 1/n and distribution coefficient (k) were calculated for each soils. Desorption isotherms for zinc extraction with 0.01M $CaCl_2$ and 0.005 M DTPA were also plotted as above in both Freundlich and Langmuir equation. From the slope and intercept desorption maxima (Dm), bonding energy constant and distribution coefficients were worked out (Murali 1991, Manjunathaiah 1992, Rupa and Shukla 1998, Pareek *et al* 1998).

Zn adsorbed (mg g^{-1}) = A - RS/g, where

A = Amount of Zn added to soil (mg kg^{-1}), R = Zn remaining in solution (mg l^{-1}), S = Volume of equilibrium solution (ml), g = Amount of soil taken (g) (Manjunathaiah 1992, Murali 1991, Rupa and Shukla 1998).

3.2.3 Adsorption-Desorption Studies on Molybdenum

To study the adsorption desorption nature of Mo in pepper growing soils, 5 gm (2mm sieved) dry soils of Thamarassery, Ambalawayal, Peruvannamuzhi and Coorg were equilibrated with 25 ml solution of 0, 10, 15, 20 and 25 mg kg^{-1} Mo for 24 hrs at 180 oscillation per minute, filtered through Whatman No.41 filter paper and molybdenum was estimated in the filtrate using graphite furnace of Atomic Absorption Spectrophotometer Varian AA20. Mo adsorption was calculated. Freundlich and Langmuir isotherm plotted and constants worked out as for zinc.

3.2.4 Fractionation Study

To study the transformation of applied Zn in pepper growing soils, a fractionation experiment was done (Mandal and Mandal 1986, and modified by Edward Raja and Iyengar 1986). The soil samples from five major black pepper growing tracts viz., Ambalawayal, Thamarassery, Peruvannamuzhi, Idukki, and Coorg were collected and sieved 2mm. One set was treated with zinc sulphate solution to get 10 mg kg^{-1} Zn and another set with distilled water as check. From both sets, samples were taken after 1 month and air-dried. Five gram of soil each weighed into 50 ml polypropylene centrifuge tube. Then extracted by shaking for one hour with 20 ml each of 1M neutral ammonium acetate, 0.01 M cupric acetate, 1% sodium pyrophosphate, 0.1M HCl and sodium bicarbonate (1M) + sodium citrate (0.3 M)

+sodium dithionite (CBD) reagents as described in flow chart below, to get fractions of water soluble +exchangeable, complexed, organically bound, bound to carbonate and amorphous oxide, bound to crystalline oxide respectively. Zinc was analyzed using Atomic Absorption Spectrometer. Correlations were worked out among different fractions of zinc in soils.

Flow chart showing the scheme adopted for fractionation of soil zinc.

Dry soil (5 g)		
↓		
NH_4OAc, 1.M pH7.0 (20 ml)	Supernatant solution →	Water soluble+ exchangeable Zn
↓ Soil ↓		
Cu $(OAc)_2$ 0.05 M	Supernatant solution →	Complexed Zn
↓ Soil ↓		
Sodium pyrophosphate (1%) (20 ml)	Supernatant solution →	Organically bound Zn
↓ Soil ↓		
HCl (0.1 M) (20 ml)	Supernatant solution →	Zinc bound to carbonates and amorphous oxides
↓ Soil ↓		
Citrate bicarbonate dithionite (CBD) (20 ml 0.3 M Sod. citrate +2.5 ml 1 M Sod. bicarbonate +0.5 gm Sod. dithionite)	Supernatant solution →	Zinc bound by crystalline oxides

3.3. POT EXPERIMENTS

3.3.1 Studies on Nutrient Deficiency (Zn and Mo)

To produce artificial zinc and molybdenum deficiency symptoms in black pepper, a pot experiment was conducted. For the purpose quartz sand (2mm) soaked overnight in 0.1 N HCl, washed with distilled water until free of chloride ions to remove any element adhered to it, filled in plastic container holding two kg each. Three months old bush pepper plants and rooted pepper cuttings (after removing soil adhered to the root and washing with distill water) were planted in these containers separately. The plants were irrigated daily with fixed quantity of Hoagland's solution (details given below) devoid of zinc, to produce artificial zinc deficiency symptoms, and devoid of molybdenum to produce artificial molybdenum deficiency symptoms. After getting clear deficiency symptoms the plants were photographed and documented.

Hoagland solution

i. Molar stock solution of each of the following four salts was prepared separately. From each molar stock solution indicated quantity of aliquot (per liter) was taken and diluted to get solution (A)

1)	1 M KH_2FO_4 :	1 ml/liter
2)	1MKN O_3 :	5 ml/liter
3)	1M $Ca\{NO_3\}_2$:	5 ml/liter
4)	1 M $MgSO_4$:	2 ml/liter

ii. To each liters of nutrient solution prepared in (A) added 1 ml of a solution of following trace element salts

5) 2.86g boric acid/liter
6) 0.08g $CuSO_4$. $5H_2O$/liter
7) 0.020g molybdic acid/liter
8) 0.22 g $ZnSO_4$. $7H_2O$/liter
9) 2.81g$MnCl_2$.$4H_2O$ /litre

iii. To each liter of a nutrient solution, prepared in (A), added 1 ml of iron solution (0.5% $FeSO_4$. $5H_2O$ + 0.4% citric acid) was added once in a week.

3.3.2 Effect of application of zinc as soil/ foliar (zinc sulphate, zinc chelates) on zinc availability, uptake, yield, and quality of pepper

For the purpose, zinc deficient pepper growing soils from Peruvannamuzhi (Calicut) having pH 5.26, Organic Carbon 1.4%, Bray-P 2.5 mg kg^{-1}, exchangeable K, Ca, Mg of 78, 237, 46 mg kg^{-1} respectively and available S of 61 mg kg^{-1} and DTPA

Fe, Mn, Zn and Cu status of 18, 14, 0.64 and 1.3 mg kg^{-1} respectively with available molybdenum of 0.93 mg kg^{-1} was collected. The soils were sieved and weighed 10kg each filled in 30cm diameter earthen pots lined with polyethylene sheet. Three months old bush pepper sapling cv Karimunda were planted in the containers. After three months of establishment (Plate 1), treatments were super imposed as given below.

To study the response of applied zinc, zinc was applied @ 0, 1.25, 2.5, 5, 7.5 and 10 mg kg^{-1} zinc in pots.

To study the effect of amendments and use efficiency of zinc to bush black pepper, the following treatments were given. They are (i) Check, (ii) 1.25 mg kg^{-1} zinc, (iii) 2.5 mg kg^{-1} zinc, (iv) 2.5 mg kg^{-1} EDTA, (v) 2.5 mg kg^{-1} EDTA+1.25 mg kg^{-1} Zn, (vi) 2.5 mg kg^{-1} EDTA+2.5 mg kg^{-1} Zn, (vii) 2.5 mg kg^{-1} Zn as Zn EDTA chelate, (viii) 0.25 % $ZnSO_4$ foliar, (ix) 0.5% $ZnSO_4$ foliar, and (x) 0.1% Zn EDTA chelate as foliar (Plate 2.). Foliar spray was given one in June and another in September.

The CRD design with three replications was adopted. NPK were applied @ 1, 0.5, 2g pot^{-1} at bimonthly intervals (Sadanandan and Hamza 1998) to all pots. The Zn availability in soil, leaf, and berry concentrations of Zn was analyzed as per standard procedures (Jackson 1967). Spiking intensity and yield were recorded. Black pepper quality (Oleoresin and piperine content) was analyzed as per standard procedure (ASTA 1968) as detailed below.

Pepper Oleoresin: 10g powdered pepper (0.5 mm mesh) was taken in a chromatographic column plugged with cotton. Forty ml acetone was added and kept overnight. The extractant was drained in to pre weighed beaker. Again, 20 ml acetone was added and kept for 30mts, drained into above beaker and evaporated in water bath. The mass is then kept in oven at 105^{0}C for constant weight. From the weight obtained oleoresin, percentage was calculated (ASTA 1968).

Piperine: Hundred milligram-powdered pepper taken in to 100ml volumetric flask, made up to volume with acetone. From this 1ml again diluted to 10ml in acetone and taken the absorbance in spectrophotometer at 337nm using piperine

Plate 1 Bearing bush black pepper

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42A

standard curve (5, 10, 15 and 20 μg). From this percentage piperine was computed (Genest *et al* 1963).

3.3.3 Effect of application of Molybdenum on soil availability and uptake of Mo yield and quality of pepper

For this, Mo deficient pepper growing soil from Pulpalli area of Wynad (having pH 5.9, Lime requirement 3.0 t/ha, Org.C 1.1%, Bray P of 11 mg kg^{-1}, exchangeable K, Ca and Mg of 110, 792, 140 mg kg^{-1} respectively, available sulphur 21 mg kg^{-1}, DTPA extractable Fe, Mn, Zn and Cu of 46, 33, 1.4, 2.6 mg kg^{-1} respectively) was used. The available Molybdenum was 0.17 mg kg^{-1}. The soil was collected, sieved using 2 mm mesh, weighed 10kg each and filled in 30cm earthen pots lined with polyethylene sheet. Three-month-old bush black pepper sapling cv Karimunda were planted in these pots. After three months treatment were imposed as follows (Plate 3).

To study the response of applied molybdenum, Mo was applied @ 0, 0.25, 0.5, 1, 1.5 and 3 mg kg^{-1} into the pots.

To study the effect of soil amendments on the use efficiency of Mo to bush black pepper the following treatments were used. They are (i) Check (ii) 100g FYM, (3) 0.25 mg kg^{-1} Mo (iv) 0.5 mg kg^{-1} Mo (v) 20 g Lime (vi) 0.25 mg kg^{-1} Mo +20g lime (vii) 0.1% foliar sodium molybdate, and (viii) 0.2% foliar sodium molybdate. Foliar spray was given one in June and another in September. Lime alone was given during May and all other treatments in June.

The plants were given NPK @ 1, 0.5, 2g (per pot) at bimonthly intervals for proper establishment (Sadanandan and Hamza 1998).

Observations on soil availability, leaf, and berry composition of molybdenum, morphological growth, and yield were recorded during 1996 to 1999. Pepper was analyzed for piperine and oleoresin (ASTA 1968) and data subjected to statistical analysis (Anonymous 1985).

Plate 2. Green house study on zinc response

Plate 3. Green house study on Mo response

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FIELD EXPERIMENTS

3.4.1 Effect of application of zinc as soil/foliar (zinc sulphate, zinc chelates) on zinc availability, uptake, yield and quality of black pepper

For studying the response of zinc and the effect of amendments to black pepper, a field experiment was laid out during June1996 in zinc deficient soil at the Ashoka plantation (Pvt.) Ltd, Boikeri, Coorg district of Karnataka having elevation 1000m above MSL, rainfall 2500 to 3000mm and temperature ranging from 14 to 32^0C. The physico-chemical properties of the soil were pH 5.35, Org.C 2.3%, Bray P 3 mg kg^{-1}, exchangeable K, Ca, Mg and S were 212, 996, 156 and 66 mg kg^{-1} respectively. Soil available Fe, Mn, Zn, Cu, and Mo were 28, 29, 0.88, 5.8 and 0.51 mg kg^{-1} respectively. The soil is acidic, medium in P and K status, and low in zinc. Five-year-old uniform black pepper vines trailed on *Erythrina indica* were used (Plate 4 and 5). Six vines were used for each treatment and there were three replications. The design was RBD.

To study the response of applied zinc, zinc was given at @ 0, 2.5, 5, 7.5 and 10kg ha^{-1} as zinc sulphate as soil application at the onset of monsoon during June.

To study the effect of soil amendments and Zn use efficiency the following treatments were given. They are (i) Check, (ii) 2.5 kg Zn as Zn-EDTA,(iii) 2.5 kg EDTA, (iv) 2.5 kg EDTA+ 2.5 kg Zn as $ZnSO_4$, (v) 2.5 kg Zn as Zn-EDTA chelate, (vi) 0.25 % $ZnSO_4$ foliar, (vii) 0.5% $ZnSO_4$ foliar, and (viii) 0.1% Zn EDTA chelate as foliar.

Soil and plant samples (index leaf and berry) were drawn before the harvest during March every year and analyzed for zinc concentrations and quality of the produce as per standard procedures.

The yield data was recorded and the response function was worked out as $Y = b_o+b_1x + b_2 x^2$ from where physical and economic optimum and net profit were worked out.

Plate 4. Bearing black pepper vine

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$$\text{Physical optimum} = \frac{-b_1}{2b_2}$$

$$\text{Economic optimum} = \frac{1\ [q/p-b_1]}{2b_2}$$

Where q= cost/unit output

P =price/unit output

The maximum net profit was worked out as $P(b_1x + b_2x^2) - qx$

Where x = economic optimum of input factor (Rangaswamy 1995)

3.4.2 Effect of Molybdenum application as soil or foliar on availability, uptake, yield, and quality of black pepper

A field experiment was laid out during 1996 June in a traditional pepper growing tracts at Ashoka Plantation Pvt. Ltd. Boikeri, Coorg district of Karnataka having elevation 1000m above MSL receiving rainfall 2500-3000 mm in 132 rainy day and mean temperature varying from 14 to 32^0 C.

The soil was acidic, high in organic matter, medium in P status and high in K status, deficient in Zn and molybdenum status. The soil characteristics of experimental field are given in Table .3. Lime requirement 3.4t ha^{-1}, pH 5.35, Org.C 2.3%, Bray-P 3 mg kg^{-1}, exchangeable K, Ca, Mg of 212, 996, 156 mg kg^{-1}, available S of 66 mg kg^{-1}, DTPA extractable Fe, Mn, Zn Cu was 28, 29, 0.88 and 5.8 mg kg^{-1}, available Mo was 0.51 mg kg^{-1}. For the purpose five year old, black pepper vine (Panniyur-1) having uniform growth, trailed on *Erythrina indica* was selected. Six vines were used per treatment. The design was RBD with three replications. NPK @ 100, 40,140 g were given $vine^{-1}$. Treatments were imposed at the onset of monsoon during June.

To study the response of black pepper to molybdenum, sodium molybdate was applied at a dose of 0, 0.5, 1.0, 1.5, and 2.0 kg Mo ha^{-1}

To study the effect of amendments and Mo use efficiency the following treatments were applied. They are (i) Check (ii) 10 t FYM ha^{-1} (iii) 0.5 kg Mo ha^{-1}

Plate 5. Field view of experimental plantation

(iv) 0.5 t lime ha^{-1} (v) 0.25 kg Mo+0.5 t lime ha^{-1} (vi) 0.5 kg Mo+0.5 t lime ha^{-1} (vii) 0.1%foliar sodium molybdate, and (viii) 0.2% foliar sodium molybdate. Foliar spray was given one during June and another September. Lime treatment given during May and all others in June every year.

Soil, leaf, and berry were sampled during March before the harvest and analyzed for soil availability, leaf and berry content of molybdenum as per standard procedure (Black 1965). The quality parameters (oleoresin and piperine) were also analyzed (ASTA 1968). The yield was recorded and data were subjected to statistical analysis and response function, physical and economic optimum and maximum net profit was worked out as per Rangaswamy (1995) as described for zinc.

RESULTS

RESULTS

4. RESULTS

4.1 SURVEY

4.1.1 Status of soil nutrients in major black pepper growing areas

Ranges of soil nutrients, in major black pepper growing areas viz., Coorg, Idukki, Wynad (high altitude) and Calicut (low altitude) with minimum, maximum, mean and standard deviations are given in Table 4. Soil pH varied from a minimum of 4.4 to a maximum of 6.7 with a mean of 5.7 for Coorg, 5.3 for Idukki, 5.7 for Wynad and 5.4 for Calicut. The Calicut soil is slightly acidic compared to other locations (high altitude). Lime requirement varied from traces to 7.1 tha^{-1} with a mean of 1.8 for Coorg, 3.0 for Idukki, 1.3 for Wynad (lowest, may be due to farmers application) and 3.2 for Calicut. Organic carbon varied from 5.1 to 37 with mean of 22 g kg^{-1} for Coorg, 25 g kg^{-1} for Idukki and Wynad and 21 g kg^{-1} (lowest) for Calicut. Bray extractable P varied from 1.6 to 154 mg kg^{-1} with mean of 37 for Coorg, 35 for Idukki, 63 for Wynad and 24 (lowest) for Calicut. Exchangeable K varied from 61 to 1194 mg kg^{-1} with a mean of 528 for Coorg, 397 for Idukki, 445 for Wynad and 308 (lowest) for Calicut. Exchangeable Ca varied from 244 to 3310 mg kg^{-1} with a mean of 1258 for Coorg, 1036 for Idukki, 1584 for Wynad and 888 (lowest) for Calicut. Exchangeable Mg varied from 24 to 455 mg kg^{-1} with a mean of 167 for Coorg, 202 for Idukki, 231 for Wynad and 128 (lowest) for Calicut. Available sulphur varied from 14 to 193 mg kg^{-1} with a mean of 64 for Coorg, 58 for Idukki, 50 (lower) for Wynad and 60 for Calicut. Available Fe varied from 26 to 60 mg kg^{-1} with a mean of 49, 49, 48 and 44 mg kg^{-1} respectively for Coorg, Idukki, Wynad and Calicut locations. Available Mn varies from 5.8 to 31 mg kg^{-1} with a mean of 27, 25, 27 and 20 mg kg^{-1} respectively for Coorg, Idukki, Wynad and Calicut.

Available zinc varied from 0.62 to 14 mg kg^{-1} with a mean of 2.7 for Coorg, 2.4 for Idukki, 2.8 for Wynad and 1.9 (lowest) for Calicut. Available Cu varied from 1.5 to 55 mg kg^{-1} with a mean of 16.2 for Coorg, 6.1 for Idukki 13.4 for Wynad and 16.7 for Calicut. This is due to heavy drenching of copper fungicides against disease for pepper. Available Mo varies from 0.02 to 0.66 mg kg^{-1} with mean of 0.35 for Coorg, 0.34 for Idukki, 0.22 for Wynad and 0.45 for Calicut. Total zinc varied from 15 to 132 mg kg^{-1} with a mean of 57, 54, 44 and 62 mg kg^{-1} respectively for Coorg, Idukki, Wynad and Calicut. Total Mo varied from 0.9 to 4.2 mg kg^{-1} with a mean of 2.5, 3.4, 1.7 and 2.4 respectively for Coorg, Idukki, Wynad and Calicut respectively.

The survey showed that 67, 60, 58 and 38% soil samples of Coorg, Idukki, Wynad and Calicut, respectively were either deficient or low in Zn status. Similarly, 13, 31, 61 and 5% soil samples of Coorg, Idukki, Wynad and Calicut respectively were having available Mo status less than 0.5 mg kg^{-1}.

4.1.2 Leaf nutrient status and yield of black pepper in major growing areas

The ranges of leaf nutrient composition of black pepper, from major growing locations viz., Coorg, Idukki, Wynad (high altitude) and Calicut (lower altitude) are given in Table 5. Leaf N varied from 19 to 27 g kg^{-1} with a mean of 24 g kg^{-1} for Coorg, 23 g kg^{-1} for Idukki, Wynad and Calicut locations. Leaf P varied from 0.6 to 5 g kg^{-1} with a mean of 2.4, 1.8, 1.7 and 1.7 g kg^{-1} for Coorg, Idukki, Wynad and Calicut. Leaf K varied from 9 to 47 g kg^{-1} with a mean of 24, 33, 18 and 36 g kg^{-1} respectively for Coorg, Idukki, Wynad and Calicut. Leaf Ca varied from 11 to 49 g kg^{-1} with a mean of 33, 37, 35 and 34 g kg^{-1} respectively for Coorg, Idukki, Wynad and Calicut. Leaf Mg varied from 1.2 to 16 g kg^{-1} with a mean of 4.7, 6.4, 8.4 and 3.7 g kg^{-1} respectively for Coorg, Idukki, Wynad and Calicut. Sulphur status varied from 0.8 to 5.3 g kg^{-1} with a mean of 1.5, 1.7, 1.1 and 1.8 g kg^{-1} for Coorg, Idukki, Wynad and Calicut respectively. Leaf Fe varied from 110 to 537 mg kg^{-1} with a mean of 177, 223, 180 and 225 mg kg^{-1} respectively for Coorg, Idukki, Wynad and Calicut. Leaf Mn varied from 33 to 810 mg kg^{-1} with a mean of 279, 406, 276 and 385 mg kg^{-1} respectively, leaf Zn varied from 18 to 46 mg kg^{-1} with a mean of 30, 43, 31 and 27 mg kg^{-1} respectively for Coorg, Idukki, Wynad and Calicut. Leaf Cu varied from 7.6 to 750 mg kg^{-1} with a mean of 84, 43, 13 and 127 mg kg^{-1}respectively. Leaf Mo varied from 0.23 to 2.6 mg kg^{-1} with a mean of 0.69, 1.5, 1.4 and 1.6 respectively for Coorg, Idukki, Wynad and Calicut. The yield of pepper varied from minimum of 0.10 kg to 8.0 kg per vine with a mean of 4.0 kg for Coorg, 1.5 kg each for Idukki and Wynad and 1.1kg per vine for Calicut. In brief, there is not much difference among leaf nutrient concentration of various locations as that of soil nutrients but there was marked difference in yield and was highest in Coorg (high altitude).

Table 4. Ranges of Soil nutrients in major black pepper growing areas

Nutrients/ Location	Minimum				Maximum				Mean				SE			
	Coorg	Idukki	Wynad	Calicut	Coorg	Idukki	Wynad	Calicut	Coorg	Idukki	Wynad	Calicut	Coorg	Idukki	Wynad	Calicut
pH	4.7	4.6	4.4	4.8	6.7	6.6	6.7	5.9	5.7	5.3	5.7	5.4	0.24	0.07	0.10	0.08
Lime req. t ha^{-1}	trace	trace	Trace	1.0	4.7	7.1	4.7	7.1	1.8	3.0	1.3	3.2	0.45	0.30	0.26	0.41
Org. C gkg^{-1}	6.8	5.1	4.6	8.0	37	27	20	30	22	25	25	21	2.0	0.8	0.7	1.5
Bray P. mg kg^{-1}	2.5	1.6	2.4	4.8	158	137	154	151	37	35	63	64	13	6.8	9.0	9.9
Exch. K "	114	92	61	83	1194	1108	1011	737	528	397	445	308	122	40	97	43
" Ca „	248	320	663	244	2709	3310	2703	1808	1258	1036	1548	888	202	101	105	134
" Mg „	24	61	93	34	305	559	455	309	167	202	231	128	23	20	18	21
Av. S „	48	17	14	25	193	174	170	133	64	58	50	60	11	6.2	13	6.9
" Fe „	41	32	37	26	60	56	55	57	49	49	48	44	1.4	0.80	0.83	1.8
" Mn „	12	9	18	5.8	31	29	31	29	27	25	27	20	1.6	0.87	0.61	1.9
" Zn „	0.66	0.62	1.0	0.90	12	11	13	14	2.7	2.4	2.8	3.9	0.98	0.40	0.46	1.0
" Cu „	2.2	1.8	1.5	3.8	46	29	55	52	16.2	6.1	13.4	26.7	3.8	0.92	2.8	4.9
" Mo „	0.04	0.02	0.02	0.07	0.25	0.66	0.42	0.83	0.35	0.34	0.22	0.45	0.15	0.12	0.11	0.25
Total Zn „	16	24	15	22	120	86	90	132	57	54	44	62	6.8	2.4	3.1	6.4
" Mo „	1.2	2.2	1.2	0.9	3.8	4.2	2.1	3.9	2.5	3.4	1.7	2.4	0.23	0.18	0.10	0.27

Table 5. Range of leaf nutrients and yield of black pepper in major growing areas*

Leaf nutrients/ Location	Minimum				Maximum				Mean				SE			
	Coorg	Idukki	Wynad	Calicut	Coorg	Idukki	Wynad	Calicut	Coorg	Idukki	Wynad	Calicut	Coorg	Idukki	Wynad	Calicut
N g kg^{-1}	20	19	20	20	27	27	26	27	24	23	23	23	0.5	0.4	0.3	0.5
P ”	1.1	0.6	0.5	0.3	4.3	4.8	4.5	5.0	2.4	1.8	1.7	1.7	0.2	0.2	0.2	0.3
K ”	13	9.0	16	19	40	42	47	42	24	33	18	36	2.0	1.6	2.0	1.8
Ca ”	21	26	22	11	48	49	47	49	33	37	35	34	2.1	1.1	1.2	2.4
Mg ”	1.7	2.0	2.1	2.0	7.7	13	16	8.0	4.7	6.4	8.4	3.7	0.5	0.4	0.9	0.4
S ”	0.8	0.9	0.8	1.0	3.7	5.3	1.7	2.6	1.5	1.7	1.1	1.8	0.2	0.2	0.1	0.1
Fe mg kg^{-1}	110	121	134	120	377	516	226	537	177	223	180	225	20	13	44	24
Mn ”	118	86	33	163	502	779	810	706	279	406	276	385	36	33	46	45
Zn ”	21	20	23	18	46	35	41	46	30	43	31	27	2.1	9.1	0.91	1.8
Cu ”	17	11	8.9	7.6	747	395	20	750	84	43	13	127	118	13	0.55	48
Mo ”	0.39	0.78	0.60	0.23	1.0	2.5	2.6	2.3	0.69	1.5	1.4	1.6	0.54	0.74	0.94	0.12
Yield kgvine^{-1}	0.100	0.100	0.200	0.15	8.0	5.6	5.0	3.5	4.0	1.5	1.5	1.1	0.68	0.20	0.20	0.22

- Calicut 21 locations, Wynad 59 locations, Idukki 35 locations, Coorg 15 locations

The survey showed that 13, 17, 10 and 14% leaf samples of Coorg, Idukki, Wynad and Calicut were either deficient or low in zinc status. Further 13, 26, 15 and 38% garden surveyed in Coorg, Idukki, Wynad and Calicut were having pepper yield status, less than one kilogram per vine.

4.1.3 Physical properties of black pepper growing soils grouped on altitude basis

The results obtained from the soil survey of black pepper gardens in major growing districts of Kerala viz., Idukki and Wynad of higher altitude, Calicut and Cannanore of lower altitude are given in Table. 6 & 7. It was found that pH of Wynad soil was the highest (5.82) and that of Calicut the lowest (5.36). Sand fraction was highest in Wynad (49%) and least in Cannanore (35%). Silt fraction was lowest in Calicut (12%) followed by Wynad (13%) and highest for Idukki and Cannanore (16%). Clay fraction was highest for Cannanore (49%) and least for Wynad (high elevation 37%). Base saturation was lowest for Calicut (14.1%) and highest for Wynad (62.8%). Cation exchange capacity was highest in Wynad (12.7) followed by Idukki (11.3), Cannanore (10.9) and least for Calicut (9.8 C mol (p+) kg^{-1}). Regarding organic carbon status, there was not much difference among locations. Bray extractable P was highest for Wynad (8.5), followed by Idukki (4.9), Calicut (3.8) and least for Cannanore (2.8 mg kg^{-1}). Exchangeable K was highest in Wynad 254 mg kg^{-1}, followed by Idukki (142), Cannanore (134) and least for Calicut (12.7 mg kg^{-1}). Exchangeable Ca was highest in Wynad (1850) followed by Idukki (553), Cannanore (278) and least for Calicut (226 mg kg^{-1}). Exchangeable Mg was highest for Wynad (516 mg kg^{-1}), and least for Calicut (49 mg kg^{-1}). Available S was highest for Cannanore (60) and lowest for Wynad (37 mg kg^{-1}). DTPA extractable Fe was highest for Wynad (47 mg kg^{-1}), followed by Idukki (42 mg kg^{-1}), Calicut (28 mg kg^{-1}) and lowest for Cannanore (23 mg kg^{-1}). DTPA extractable Mn was highest for Wynad (39.8 mg kg^{-1}), followed by Idukki (16.9) Cannanore (5.8) and least for Calicut (3.8 mg kg^{-1}). DTPA extractable Zn was highest for Wynad (1.5 mg kg^{-1}), followed by Idukki (0.64), Cannanore (0.6) and lowest for Calicut (0.51 mg kg^{-1}).

DTPA Cu was maximum in Idukki (3.4), followed by Wynad (3.3), Cannanore (2.9) and least for Calicut (1.7 mg kg^{-1}). Available Mo was maximum in Calicut (0.94 mg kg^{-1}), followed by Idukki (0.81 mg kg^{-1}), and least for Wynad (0.27 mg kg^{-1}).

In short, physicochemical characteristics like-lower clay fractions, higher sand and silt fractions, organic carbon, CEC, BS, major, secondary and micronutrient which favors good growth and high yield of pepper were higher in high altitude areas, where as clay fractions and sulfur and manganese status were higher in low altitude areas.

Table 6. Physico-chemical properties of black pepper growing soils- grouped on altitude basis

Locations	PH	Sand	Silt	Clay	BS	CEC
		(..............g/100g		..............)	C mol (p+) kg^{-1}	
Wynad*	5.82	49	13	38	63	12.7
Idukki*	5.37	43	16	41	29	11.3
Calicut**	5.36	45	12	43	14	9.8
Cannanore**	5.43	35	16	49	28	10.9
CD 5%	0.08	1.4	0.94	1.2	1.4	0.49

* High altitude ** Low altitude

Table 7. Nutrient status of black pepper growing soils grouped on altitude basis

Locations	O.C	Bray P	Exchangeable K	Exchangeable Ca	Exchangeable Mg	Avail. S	DTPA Fe	DTPA Mn	DTPA Zn	Cu	Avail. Mo
	%	(........................				........mg kg^{-1}........					........................)
Wynad*	1.27	8.5	254	1850	516	41	48	40	1.5	3.3	0.27
Idukki*	1.32	4.9	142	553	123	48	42	17	0.77	3.4	0.81
Calicut**	1.24	3.8	126	226	49	72	28	3.8	0.51	1.7	0.94
Cannanore*	1.26	2.1	134	278	139	60	23	5.8	0.60	2.9	0.42
CD 5%	0.12	1.9	24	73	29	6.7	3.0	2.6	0.21	0.5	0.33

* High altitude ** Low altitude

4.1.4 Physico-chemical properties of black pepper growing soils grouped on yield basis

Physico-chemical properties of black pepper growing soils, grouped as high, moderate and low yielding in four major pepper growing districts of Kerala viz., Idukki, Wynad, Calicut and Cannanore are depicted in Table 8. In general, acidity was low in high yielding gardens and high in low yielding gardens in all the four locations. Soil mean pH varies from 5.8 in high yielding gardens to 5.5 in moderate to 5.2 in low yielding gardens with an over all mean of 5.5. Sand fraction was found to decrease from 51% for high yielding garden to 40% for low yielding garden with a mean value of 43.1%. Clay fractions found to increase from high yielding garden (34.2%) to low yielding gardens (45.3%). Base saturation was found to decrease from high yielding location (52.3%) to low yielding locations (21.5%) with a mean of 33.7%. The CEC decreased from high yielding gardens (12.2) to low yielding gardens [10.6 C mol (p+) kg^{-1}]. Organic carbon was found to decrease from high yielding gardens (1.3%) to moderate and low yielding gardens (1.1%) with mean of 1.2%, Bray P decreased from high yielding garden (9.3) to moderate (3.7) and low yielding gardens (1.5) with a mean of 4.8 mg kg^{-1}. Similar to other nutrients, exchangeable K also decreased from high yielding gardens (225 mg kg^{-1}) to low yielding gardens (114 mg kg^{-1}) with a mean of 164 mg kg^{-1}. Exchangeable Ca decreased from high yielding gardens (1177 mg kg^{-1}) to low yielding garden (370 mg kg^{-1}) with a mean of 726 mg kg^{-1}. Exchangeable Mg decreased from high yielding gardens (326 mg/kg) to moderate yielding (161 mg kg^{-1}) to low yielding gardens (132 mg kg^{-1}) with a mean of 207 mg kg^{-1}. Unlike other nutrients, S was found to increase from high yielding gardens (28 mg kg^{-1}) to low yielding gardens (88 mg kg^{-1}) with a mean of 55 mg kg^{-1}. There was not much difference between high yielding and low yielding gardens with regard to iron. Similar to sulfur, manganese was also found to increase from high yielding gardens (12 mg kg^{-1}) to low yielding gardens (19 mg kg^{-1}) with an average value of 17 mg kg^{-1}. Zn status was found to decrease from high yielding gardens (1.2 mg kg^{-1}) to low yielding gardens (0.65 mg kg^{-1}) with a mean value of 0.85 mg kg^{-1}. There was no clear trend in copper availability between high and low yielding gardens. Mo availability increased from 0.38 mg kg^{-1} in high yielding to 0.91 mg kg^{-1} in low yielding garden (Table. 9).

Table 8. Physico-chemical properties of black pepper growing soils grouped on yield performance

Yield performance	pH	Sand	Silt	Clay	Base Saturation	CEC
	(...................	........g	100g^{-1}	....	..............)	C mol (p+) kg^{-1}
High	5.79	51	15	34	52	12.2
Moderate	5.53	39	14	47	27	10.7
Low	5.16	40	15	45	22	10.6
CD 5%	0.07	1.2	0.8	1.1	1.3	0.4

Table 9. Nutrient status of black pepper growing soils grouped on yield performance

Yield performance	O.C	Bray P	Exchangeable K	Ca	Mg	Av. S	Fe	DTPA Mn	Zn	Cu	Av. Mo
	%	(..........	....	....	....	mg kg^{-1}	....	....	....	....	..........)
High	1.32	9.3	225	1177	326	28	35	12	1.2	2.6	0.38
Moderate	1.21	3.7	154	633	161	51	34	19	0.67	3.7	0.80
Low	1.14	1.5	114	370	132	88	36	19	0.65	2.1	0.91
CD 5%	0.10	1.6	21	63	25	5.8	2.6	2.3	0.18	0.5	0.15

Overall, soils of pepper gardens, from high yielding locations were found to have higher pH, sand, silt fractions and low clay fractions. Further, chemical constituents like extractable bases, base saturation, CEC, organic carbon, major, secondary and micronutrients with exception of S, Cu and Mo were also found to be high in high yielding locations compared to moderate and low yielding locations. In other words, by increasing the soil pH and availability of above nutrients the low yielding gardens can be upgraded to high yielding gardens.

4.1.5 Soil physico-chemical characteristics at different depths of soil

The physico-chemical characteristics of major black pepper growing areas (Wynad, Idukki, Calicut and Cannanore) in four depth (0-20, 20-40, 40-60 and 60-80 cm) where the pepper roots mainly concentrate are given in Table 10. It was found that from surface to bottom the sand fractions decreased from 45.3% to 40.8% with a mean of 43.1%. The silt fraction also decreased from 15 to 14.4% with a mean of

14.8%. From top to bottom, clay fraction increased from 39.9 to 44.7% with a mean 42.5%, probably due to settling of clay fractions to the bottom layers. Base saturation decreased from 35.7 to 31.7% with a mean 33.7%. Exchangeable base decreases from 5.0 to 3.9 C mol (P+) kg^{-1}, CEC from 12.2 to 10.5 C mol (p+) kg^{-1} and organic carbon from 1.6 to 0.88%. Bray-extractable P decreased from 7.4 to 2.1 mg kg^{-1}, exchangeable K from 227 to 136 mg kg^{-1}, Ca from 852 to 585 mg kg^{-1} while going from top to bottom layers. With regard to exchangeable Mg, there was a decrease from the top to bottom layers up to 40cm, and there after an increase up to 80 cm with a mean value of 207 mg kg^{-1}. Available sulphur increased from top to bottom layer with a mean value of 55 mg kg^{-1}. This may be due to accumulation of sulphate ions due to leaching. The decrease in pH from 5.6 to 5.4, from top to bottom, supports the above reasoning.

Table 10. Assessment of various physico chemical properties of soil at root zone (0-80 cm) of major black pepper growing areas *

Property	0-20 cm	20-40 cm	40-60 cm	60-80 cm	Pooled
Sand %	45.3 (3.3)	44.9 (3.4)	41.3 (3.1)	40.8 (3.5)	43.1 (1.6)
Silt %	15.0 (0.91)	13.2 (1.1)	14.8 (1.1)	14.4 (1.2)	14.3 (0.54)
Clay %	39.7 (3.0)	41.9 (2.8)	43.9 (3.4)	44.8 (3.3)	42.5 (1.5)
Base Saturation %	35.7 (7.9)	34.3 (7.3)	31.7 (7.4)	33.1 (7.4)	33.7 (3.7)
Exch. Base {Cmol (P$^{\prime}$) kg^{-1}}	5.0 (1.5)	4.7 (1.5)	4.1 (1.3)	3.9 (1.2)	4.4 (0.67)
CEC "	12.2 (0.67)	11.0 (0.67)	10.9 (0.65)	10.5 (0.41)	11.2 (0.31)
pH	5.5 (0.15)	5.6 (0.13)	5.4 (0.13)	5.4 (0.11)	5.5 (0.06)
B.Density (gm cc^{-1})	1.3 (0.02)	1.3 (0.02)	1.3 (0.02)	1.3 (0.02)	1.3 (0.01)
Org.C %	1.6 (0.10)	1.4 (0.12)	1.0 (0.13)	0.88 (0.08)	1.2 (0.07)
Bray P mg kg^{-1}	7.4 (2.9)	7.3 (2.6)	2.6 (1.60)	2.1 (0.52)	4.8 (1.1)
Exch. K "	227 (42)	154 (30)	137 (23)	136 932)	164 916.7)
" Ca "	852 (293)	825 (293)	643 (207)	585 (194)	926 (123)
" Mg "	206 (57)	175 (56)	198 (67)	248 (90)	207 (33)
Avail S "	43 (4.3)	52 (11)	62 (11)	65 (13)	55 (5.1)
" Fe "	38 (3.2)	37 (3.9)	36 (4.6)	30 (4.9)	35 (2.1)
" Mn "	20 (5.1)	15 (4.6)	14 (5.4)	17 (7.3)	17 (2.8)
" Zn "	1.1 (0.26)	1.2 (0.45)	1.0 (0.09)	0.64 (0.09)	0.97 (0.18)
" Cu "	4.0 (0.91)	2.8 (0.43)	2.3 (0.38)	2.1 (0.40)	2.8 (0.29)
" Mo "	0.16 (0.04)	0.16 (0.03)	0.15 (0.03)	0.11 (0.02)	0.14 (0.02)

*Mean value of properties with SE in parenthesis

With regard to DTPA extractable Fe, there was not much difference where as Mn decreased from 20 to 14 mg kg^{-1} up to 60 cm, and then increased to 17 mg kg^{-1}. The zinc availability was almost same (1.2 mg kg^{-1}) up to 40 cm, and then decreased to 0.64 mg kg^{-1} with a mean of 0.97 mg kg^{-1}. DTPA extractable Cu was higher, but decreased from 4.0 to 2.1 mg kg^{-1}, probably due to high drenching of copper fungicide in topsoil against *Phytophthora* diseases. The availability Mo also decreased from 0.16 to 0.11 mg kg^{-1} from top to bottom.

4.1.6 Correlations of soil physico-chemical properties with black pepper yield

The correlations obtained between various physico-chemical properties with black pepper yield are depicted in Table 11. Black pepper yield was significantly and positively correlated with soil sand fractions (r = 0.401**), pH (r = 0.594**) with exchangeable base (r = 0.475**) with base saturation (r = 0.502*) with CEC (r = 0.301*), with organic carbon (r = 0.287*), with Bray P (r = 0.322*) with exchangeable K (r = 0.397**), with exchangeable Ca (r = 0.392**), with exchangeable Mg (r = 0.345*) and with DTPA Zn (r = 0.355*). Pepper yield was negatively correlated with clay fraction (r = -0.441**) and the correlations were not significant with soil silt fraction, soil S, DTPA Fe, Mn, Cu and Mo status. In brief soil physico-chemical properties except clay, S, Fe, Mn, Cu and Mo significantly and positively correlated with pepper yield.

Table 11. Correlations of soil physico-chemical properties with black pepper yield

Properties	r value	Properties	r value
Sand	0.401**	Ex.K	0.397**
Silt	NS	Ex.Ca	0.392**
Clay	-0.441**	Ex.Mg	0.345*
PH	0.594**	Av. S	NS
Exe. Base	0.475**	DTPA Fe	NS
Base saturation	0.502**	" Mn	NS
CEC	0.301*	" Zn	0.355*
Organic Carbon	0.287*	" Cu	NS
Bray P	0.322*	Av.Mo	NS

*Significant at 5%, ** Significant at 1%

4.1.7 Correlations of soil physico-chemical properties with elevation of black pepper growing gardens

The correlations obtained between altitudes of black pepper growing gardens with soil physico-chemical properties are depicted in Table 12. Altitudes of gardens were significantly positively correlated soil exchangeable base (r = 0.471**), with base saturation (r = 0.493**), with exchangeable K (r = 0.296*), with Ca (r = 0.564**), with Mg (r = 0.491**), with DTPA Fe (r = 0.673**), with Mn (r =0.651**), with Zn (r= 0.361*). Altitude of gardens negatively correlated with clay fraction (r= -.335*), with available S (r= -.314), with Mo (r = -890**).

Table 12. Correlations of soil physico-chemical properties with altitude of black pepper growing areas

Properties	r values	Properties	r values
Sand	NS	Ex. K	0.296*
Silt	NS	Ca	0.564**
Clay	-335*	Mg	0.491**
PH	NS	Av.S	-0.314*
E.B	0.471**	DTPA Fe	0.673**
BS	0.493**	Mn	0.651**
CEC	NS	Zn	0.316*
O.C	NS	Cu	NS
Bray P	NS	Av.Mo	-890**

*Significant at 5%, ** Significant at 1%

4.1.8 Correlations of soil available Zn vs soil physico chemical properties in major black pepper growing soils(Grouped on yield performance)

Correlations of soil Zn with major soil physico-chemical properties of black pepper growing soils grouped as high, moderate and low yielding basis are given in Table. 13. Soil zinc was positively correlated with exchangeable base in high (r = .0.780**) and moderate (r = 0.538*) yielding gardens. Soil Zn correlated positively with Base saturation, r-values being 0.639*, 0.493* and 0.569* in high, moderate and low yielding areas, with CEC, r = 548*, 0.604* in high and moderate yielding locations; with organic carbon r = 0.462*, 0.537* in high and moderate yielding locations; with Bray P, r = 0.856** in high yielding locations; with extractable K, r =

0.667**, 0.519*, 0.821** in high, moderate and low yielding locations; with exchangeable Ca, r = 0.812**, 0.525* in high and moderate yielding location; with available Cu, r = 0.652**, 0.630** in moderate and low yielding locations respectively Soil Zinc was negatively correlated with available S, r = -0.787**, -0.485* in moderate and low yielding locations; with available Mo, r = -0.467*, -0.439** in high and low yielding locations respectively.

Table 13. Correlation of Soil available Zn vs Soil chemical properties in major black pepper growing soils grouped on yield performance

Property	r value			
	High Yield	Moderate Yield	Low Yield	Pooled Location
EB	0.780**	0.538*	NS	0.755**
BS	0.639*	0.493*	0.569*	0.629**
CEC	0.548*	0.604**	NS	NS
PH	0.612*	NS	NS	0.452*
Org.C	0.462	0.537*	NS	0.313*
Bray P	0.856**	NS	NS	0.807**
Ex.K	0.667**	0.519*	0.821**	0.632**
Ex.Ca	0.812**	0.525*	NS	0.737**
Ex. Mg	NS	NS	NS	0.404*
Av.S	NS	-0.787**	-0.485*	NS
Av.Fe	NS	NS	0.606**	NS
Av.Cu	NS	0.652**	0.630**	NS
Av.Mo	-0.467*	NS	-0.439**	-0.317*

*Significant at 5% ** Significant at 1%

4.1.9 Correlations between soil available Zn with other nutrients in major black pepper growing areas (Grouped on altitude basis)

Correlations among soil Zn and other soil chemical properties and leaf zinc in major black pepper growing areas, viz., Coorg, Idukki, Wynad (higher altitude), Calicut (lower altitude) are given in Table. 14. Soil zinc was positively correlated with organic carbon (r = 0.404*) in Idukki; with Bray P, r = 0.851*, 0.492** in Coorg and Idukki respectively. With exchangeable Ca, r = 0.502**, 0.436* in Coorg and Idukki; with exchangeable Mg, r = 0.550**, 0.471** in Coorg and Idukki; with available Fe (r = 0.479*) in all locations pooled together; with available Mn (r = 0.472*); with available Cu (r = 0.590**) in Calicut; with total zinc, r =

0.473**, 0.582**, 0.890** in Idukki, Wynad and Calicut respectively. Available zinc was correlated with pepper yield (r =0.827**) only in Coorg region.

Table 14. Correlation between soil available Zn with other nutrients and yield in major black pepper growing areas (Grouped on altitude basis)

			r Value		
Nutrient	Coorg	Idukki	Wynad	Calicut	Pooled
Org.C	NS	0.404*	NS	NS	NS
Bray P	0.851**	0.492**	NS	NS	NS
Ex.K	NS	NS	NS	NS	NS
Ex.Ca	0.502**	0.436**	NS	NS	NS
Ex.Mg	0.550**	0.471**	NS	NS	NS
Av.Fe	NS	NS	NS	NS	0.479*
Av.Mn	NS	NS	NS	0.472*	NS
Av.Cu	Ns	NS	NS	0.590**	NS
Tot. Zn	NS	0.473**	0.582**	0.890**	0.475*
Yield	0.827**	NS	NS	NS	NS

*Significant at 5% ** Significant at 1%

4.1.10 Correlations of leaf zinc with other nutrients in major black pepper growing areas

Correlation of leaf zinc with other nutrients in black pepper leaves from major black pepper growing areas, viz., Coorg, Idukki, Wynad (higher altitude) and Calicut (low altitude) are given in Table. 15. Leaf zinc was negatively correlated with leaf N (r = -0.725**), soil pH (r= 0.511*), leaf N (r = -0.725**), and with soil Mg (r= -0.494*) and leaf Zn positively correlated with leaf Mn (r = 0.334*), leaf Cu (r =.761**), available soil S (r=0.526*) and with Soil Zn (r = 0.760**).

Table 15. Correlation coefficient of leaf Zn with soil and leaf nutrients in major black pepper growing areas

Nutrient	r value
Soil pH	-0.511*
Soil ex Mg	-0.494*
Soil Av. S	0.526*
Soil Av. Zn	0.760**
Leaf N	-0.725**
Leaf Mn	0.334*
Leaf Cu	0.761**

*Significant at 5% ** Significant at 1%

4.1.11Correlations of soil molybdenum with soil physico-chemical properties in major black pepper growing soils (grouped on yield performance).

Correlations of soil Mo with soil physico -chemical properties of black pepper grown at high, moderate and low yielding gardens are given in Table 16. It was found that soil available Mo correlated positively with organic carbon (r = 0.604* and 0.467*) in moderate and low yielding locations and also with Ex. K (r = 0.331*) when all locations were considered together. Soil Mo was found to be negatively correlated with exchangeable base in high (r = -0.736**) moderate (r = -0.626**) and low yielding (r = -0.715**) locations; with base saturation in high (r = -0.730**), moderate (r = -0.652**) and low yielding (r = -0.772**) locations; with exchangeable Ca in high (r = -0. 802**), moderate (r = -0.613*) and low yielding (r = -0.731**) locations; with exchangeable Mg, in high (r = -0.601*), moderate (r = -0.657**) and low yielding (r = -0.731**) locations, with available Fe in moderate (r = -0.667**) and low yielding (r = -0.687**) locations, with available Mn in high (r = -0.508*), moderate (r = -0.725**) and low yielding (r = -0.682**) locations and with available Zn (r = 439*) and with available Cu (r = -0.740**) in low yielding gardens.

Table 16. Correlation coefficient of soil Mo vs. Soil chemical properties in major black pepper growing soils grouped based on yield performance

Properties/yield performance	r value High	Moderate	Low	Pooled
EB	-0.736**	-0.626**	-0.715**	-0.542**
BS	-0.730**	-0.652**	-0.772**	-0.595**
CEC	NS	-0.334	NS	NS
Org.C	NS	0.604**	0.467*	0.424*
E-k	NS	NS	NS	0.331*
E-Ca	-0.802**	-0.613*	-0.731**	-0.637**
E-Mg	-0.601**	-0.657**	-0.731**	-0.589**
Av. Fe	NS	-0.667**	-0.687**	-0.586**
Av. Mn	-0.508*	-0.725**	-0.682**	-0.604**
Av. Zn	NS	NS	-0.439*	-0.317*
Av. Cu	NS	NS	-0.740**	NS

*Significant at 5% ** Significant at 1%

4.1.12 Correlation of soil Mo with soil chemical properties at different depths of black pepper growing soils

Correlations obtained between soil Mo with soil physico-chemical properties in different depths (0-20, 20-40, 40-60 and 60-80) are given in Table 17. Soil Mo was significantly negatively correlated with exchangeable base in 0-20 cm (r= -0.660*); 20-40 cm (r = -0.583*) and 40-60 cm (r = -0.598*) depths; with base saturation in 0-20 cm (r = -0.690*), 20-40 cm (r = -0.583*) and in 40-60 cm (r = - 598*) depth; with CEC (r= -590*), with exchangeable K (r =-0.598*), with available Zn (r = -.585*) in top soil of 0-20 cm. With exchangeable Ca in 0-20cm (r = -0.718**), 20-40 cm (r = -0.678*), 40-60 cm (r = -644*) and 60 –80 cm (r = -0.633*), with exchangeable Mg in 0-20 cm (r = -0.797**), 20-40 cm (r = -0.704**) and 40-60 cm (r = - 627*) with available Fe in 0-20 cm (r = 0.661*), 20-40 cm (r = -647*) and 40-60 cm (r = -0.767**) and with available Mn in 0-20 cm (r = -0.738**) in 20-40 cm (r = -0.802**) and in 40-60 cm (r = -0.671*).

Table 17. Correlation of soil Mo vs soil chemical properties in different depths of black pepper growing areas

Property/depth Cm	r value 0-20	20-40	40-60	60-80	Pooled
E.B	-0.660*	-0.583*	-0.598*	NS	NS
B.S	-0.690*	-0.583*	-.598*	NS	NS
CEC	-0.590	NS	NS	NS	-0.396**
E. K	-0.598*	NS	NS	NS	NS
E. Ca	-0.718**	-0.678*	-0.664*	-0.633*	NS
E. Mg	-0.797**	-0.704**	-0.627*	NS	NS
A. Fe	-0.661*	-0.647*	-0.767**	NS	NS
A.Mn	-0.738**	-0.802**	-0.671*	NS	NS
A.Zn	-0.585*	NS	NS	NS	NS

*Significant at 5% ** Significant at 1%

4.1.13 Correlation between total soil Mo and other soil nutrients, leaf Zn and Mo in major black pepper growing areas

Correlations between total soil Mo and other soil nutrients, leaf Zn and leaf Mo grouped on elevation basis in major black pepper growing areas viz., Coorg, Idukki, Wynad (High altitude) and Calicut (low altitude) are given in Table 18. Total soil Mo was significantly negatively correlated with soil pH in Idukki (r = -507**) and Wynad (r = -0.453*), with Bray P in Wynad (r = -0.442*), with leaf Zn in Wynad (r = -0.498*) and Calicut (r = -0.552**). Total soil Mo was positively correlated with lime requirement in Idukki (r = 0.451*), with organic carbon in Coorg (r = 0.556**) and Idukki (r = 0.495*), with exchangeable K (r = 0.607*), available S (r = 0.589**) and available Fe in Calicut (r = 0.594*), with available Mo in Coorg (r = 0.660**), Idukki (r = 0.995**) Wynad (r = 0.541**), with leaf Mo in Coorg (r = 0.683**) Calicut (r = 490*) and with total zinc in Calicut (r = 636 **) regions.

Table 18. Correlation between total soil Mo and other soil nutrients and leaf Zn and leaf Mo in major black pepper growing areas

Nutrient	r value			
	Coorg	Idukki	Wynad	Calicut
PH	NS	-0.507**	-0.453*	NS
Lime R	NS	0.451**	NS	NS
Org.C	0.556*	0.495*	NS	NS
Bray P	NS	NS	-0.442*	NS
Ex-K	NS	NS	NS	0.607**
Av-S	NS	NS	NS	0.589*
Av-Fe	NS	NS	NS	0.594*
Av-Mn	NS	NS	0.552**	0.713**
Av-Zn	NS	NS	NS	0.516*
Av-Mo	0.660**	0.995**	0.541**	NS
Leaf Zn	NS	NS	0.498**	-0.552**
Leaf Mo	0.683**	NS	NS	-0.490*
Total Zn	NS	NS	NS	0.636**

*Significant at 5% ** Significant at 1%

4.1.14 Correlation of leaf Mo with leaf nutrients in major black pepper growing areas

Correlations obtained between leaf Mo with other nutrients in major black pepper growing areas are given in Table. 19. It was found that leaf Mo negatively correlated with leaf Fe (r = -0.435*) and with leaf Zn (r= -0.479*). Leaf Mo positively and significantly correlated with leaf N (r = 0.528*) with leaf P (r=0.460*), with leaf Ca (0.673**) and with leaf Mg (r = 0.537*).

Table 19. Correlation of leaf Mo with soil and leaf nutrients in major black pepper growing areas

Nutrient	r value
Leaf N	0.528*
Leaf P	0.468*
Leaf Cu	0.673**
Leaf Mg	0.557*
Leaf Fe	-0.435*
Leaf Zn	-0.479*

4.1.15 Multiple Regression Analysis

Results of multiple regression worked out by taking black pepper yield as dependant variable and other soil properties as independent variables is depicted in Table 20. Results showed that regression of black pepper yield with soil pH was significant.

The results of regression obtained by taking soil available zinc as dependant, black pepper yield and other soil properties as independent variables is depicted in Table 21. It was found that regression of soil available zinc with extractable base, CEC, base saturation, available P and Cu status of soils were significant.

The results of regression obtained by taking soil available Mo as dependant variable, yield and other soil chemical properties as independent variables are depicted in Table 22. It was found that regression of soil available Mo with organic carbon is significantly positive and that with soil available Mg and Cu were significantly negative.

Table 20. Regression of black pepper yield with soil properties

Variable	Regression Coefficient	Standard Error	Student t Value	Probability	Correlation Coefficient
pH	1.0541e+000	3.7485e-001	2.812	0.007	0.603
O.C	-2.3331e+001	3.7507e+001	-0.622	0.537	0.176
Bray P	2.9292e-002	2.9487e-002	0.993	0.326	0.320
K	-4.0349e-004	1.4857e-003	-0.272	0.787	0.415
Ca	-8.5843e-005	5.9041e-004	-0.145	0.885	0.401
Mg	-1.4176e-003	1.5407e-003	-0.920	0.362	0.346
S	7.5944e-004	3.9101e-003	0.194	0.847	-0.212
Fe	2.4197e-002	1.1821e-002	2.047	0.046	0.027
Mn	-2.9258e-002	1.4175e-002	-2.064	0.045	-0.114
Zn	-3.8804e-001	2.8277e-001	-1.372	0.176	0.255
Cu	1.0567e-001	6.8266e-002	1.548	0.128	0.116
Mo	1.3550e-001	2.1581e-001	0.628	0.533	-0.021
EB	-1.5643e-002	2.0004e-001	-0.078	0.938	0.475
CEC	4.1156e-002	7.4098e-002	0.555	0.581	0.301
BS	3.0856e-002	2.3187e-002	1.331	0.190	0.502

Table 21. Regressions of soil available zinc with black pepper yield and soil properties

Variable	Regression Coefficient	Standard Error	Student t Value	Probability	Correlation Coefficient
Yield	-1.4323e-001	1.0437e-001	-1.372	0.176	0.255
pH	2.6460e-001	2.4998e-001	1.058	0.295	0.447
OC	2.5856e-001	2.2464e-001	1.151	0.256	0.320
P	5.2739e-002	1.5617e-002	3.377	0.001	0.810
K	2.1554e-004	9.0286e-004	0.239	0.812	0.624
Ca	1.4355e-004	3.5791e-004	0.401	0.690	0.734
Mg	-3.3552e-004	9.4649e-004	-0.354	0.725	0.404
S	-1.2275e-003	2.3670e-003	-0.519	0.606	-0.224
Fe	-9.7544e-003	7.4401e-003	-1.311	0.196	0.093
Mn	-2.4805e-003	9.1566e-003	-0.271	0.788	0.045
Cu	1.0713e-001	3.8603e-002	2.775	0.008	0.103
Mo	-1.6671e-001	1.2858e-001	-1.297	0.201	-0.316
EB	2.7468e-001	1.1142e-001	2.465	0.017	0.755
CEC	-1.2486e-001	3.9483e-002	-3.162	0.003	0.261
BS	-3.5910e-002	1.3005e-002	-2.761	0.008	0.629

Table 22. Regression of soil available molybdenum with black pepper yield and soil properties

Variable	Regression Coefficient	Standard Error	Student t Value	Probability	Correlation Coefficient
Yield	1.1927e-001	1.5252e-001	0.782	0.438	-0.021
pH	3.4539e-001	3.4116e-001	1.012	0.317	-0.252
OC	1.1519e+000	2.7395e-001	4.205	0.000	0.430
P	4.9903e-002	2.2990e-002	2.171	0.035	-0.228
K	-1.5468e-003	1.2653e-003	-1.222	0.228	-0.345
Ca	-2.8239e-004	4.8900e-004	-0.577	0.566	-0.629
Mg	3.1880e-003	1.2667e-003	2.517	0.015	-0.595
S	1.3250e-003	3.4036e-003	0.389	0.699	0.139
Fe	-2.6309e-002	1.0122e-002	-2.599	0.012	-0.558
Mn	-1.8766e-002	1.1973e-002	-1.567	0.124	-0.652
Zn	-2.9473e-001	2.3336e-001	-1.263	0.213	-0.316
Cu	6.4032e-002	5.7104e-002	1.121	0.268	-0.098
EB	-3.7172e-002	1.6446e-001	-0.226	0.822	-0.545
CEC	-6.7781e-002	6.1540e-002	-1.101	0.276	-0.278
BS	-2.6971e-002	1.9567e-002	-1.378	0.175	-0.584

4.2 LABORATORY EXPERIMENTS

4.2.1 Incubation experiment on extractability of zinc

Effect of incubation of zinc at different concentrations in major black pepper growing soils on DTPA extractable zinc is depicted in Table 23. The physico-chemical properties of soil used are given in Table 1, 2 and 3. Zinc incubation increased DTPA extractable zinc in all the soils. At lower levels (0 to 100 mg kg^{-1}) extraction was maximum in Idukki soil, followed by Ambalawayal, Thamarassery, Coorg and Peruvannamuzhi soils. At higher levels (100 to 500 mg kg^{-1}); Coorg, Thamarassery, Ambalawayal and Idukki soils behaved similarly and showed maximum value, whereas Peruvannamuzhi soil showed the least.

Effect of incubation of soils with different levels of zinc on 0.01M $CaCl_2$ extractable zinc, is depicted in Table 24. At lower incubated levels, Idukki soil showed highest value, followed by Ambalawayal, Peruvannamuzhi, Thamarassery and Coorg soils. At higher levels, Peruvannamuzhi soil showed highest value followed by Thamarassery, Idukki, Ambalawayal and Coorg soil showed the least value. This points to the weak buffering mechanism in Peruvannamuzhi soil. At lower levels, applied zinc will undergo fixation the magnitude of which depend upon the nature and properties of applied soil including type of clay minerals present. At higher applied levels fixation points will gets saturated and applied zinc will remain in soil solution independent of soil properties and all soils behaves in similar manner.

Table 23. Effect of incubation on different levels of zinc on extractability of Zn by DTPA solution in major black pepper growing soils

Incubated zinc level (mg kg^{-1})	DTPA extractable zinc (mg kg^{-1})				
	Thamarassery	Ambalawayal	Peruvannamuzhi	Coorg	Idukki
0	0.86	0.96	0.60	0.82	1.3
5	1.4	2.4	0.96	1.3	3.3
10	3.0	4.5	2.8	2.9	6.2
25	7.2	11.4	6.8	6.6	14.6
50	17.2	19.4	17.5	15.0	30.5
100	40.0	51	38	41	60
200	125	124	113	93	136
300	175	188	138	175	175
400	213	288	200	213	238
500	300	350	238	338	300
Mean	88	104	76	89	96

CD 5% for levels 1.64, for soils 0.52

Table 24. Effect of incubation on different levels of zinc on extractability of Zn by 0.01MCaCl$_2$ solution in major black pepper growing soils

Incubated zinc level (mg kg^{-1})	0.01 M CaCl$_2$ Extractable Zinc (mg kg^{-1}) Thamarassery	Ambalawayal	Peruvanna-muzhi	Coorg	Idukki
0	0.16	0.18	0.16	0.14	0.26
5	0.18	0.20	0.24	0.16	0.50
10	0.18	0.44	0.42	0.18	0.78
25	0.68	1.5	1.5	0.28	2.1
50	2.4	4.8	6.0	0.90	4.8
100	7.6	9.6	14.4	3.4	9.8
200	22.6	22.0	32.0	9.4	24.0
300	38.0	34.0	44.0	18.4	32.0
400	48.0	48.0	52.0	28.0	46.0
500	56.0	50.0	62.0	38.0	54.0
Mean	17.6	17.1	21.3	9.9	17.4

CD 5% for levels 0.73, for soils 0.23.

4.2.2 Adsorption Desorption Studies

Adsorption of applied zinc (0 to 400 mg kg^{-1}) in major black pepper growing soils and its desorption by 0.01M CaCl$_2$ and 0.005 M DTPA are depicted in Table. 25. The adsorption was found to vary from 12 mg kg^{-1} (in Idukki soil) to a maximum of 820 mg kg^{-1} in Thamarassery soil. The percentage of adsorption over applied level was found to decrease with increase in levels of application. That is when applied level increased from 2.5 to 400 mg kg^{-1}, percentage of adsorption decreased from 24 to 1.6%. Maximum percentage of applied zinc (24%) was adsorbed in Thamarassery soil at 2.5 mg kg^{-1} applied level, where as minimum percentage of adsorption was recorded by Idukki soil (1.6%) at 400 mg kg^{-1} applied level.

Desorption of adsorbed zinc by 0.01 M $CaCl_2$ was found to vary from 0.5 (Thamarassery soil) to 57 µg g^{-1} (in Idukki soil). Desorption of zinc by 0.01M $CaCl_2$ was found to decrease with increase in amount of adsorption. For examples desorption of adsorbed zinc decreased from 10.8 to 3.4%. When amount of adsorption increased from 24 to 820 µg g^{-1} in Thamarassery soil. Percentage desorption of adsorbed zinc decreased form 10 to 4.4% when amount of adsorption increased from 20 to 700 µg g^{-1} in Ambalawayal soil. Similar trend was observed for other soils also. Among soils, Idukki scored maximum desorption both by $CaCl_2$ and DTPA at all applied levels.

In brief, though adsorption increased with increase in level of application of zinc in all the soils, percentage of adsorption over applied zinc reduced drastically with increase in levels of applications. Desorption by both 0.01M $CaCl_2$ and DTPA though increased with increase in level of application, the percentage of desorption (over adsorption) decreased with increase in adsorption. Further DTPA desorbed more zinc compared to 0.01M $CaCl_2$.

Table 25. Adsorption-desorption zinc in major black pepper growing soils

Applied levels $\mu g g^{-1}$	Adsorbed zinc ($\mu g\ g^{-1}$)					Desorbed zinc by 0.01M $CaCl_2$ ($\mu g\ g^{-1}$)					Desorbed zinc by 0.005 M DTPA ($\mu g\ g^{-1}$)				
40 ml/2g soil	Thama-rassery	Ambala-vayal	P. Muzhi	Coorg	Idukki	Thamara-ssery	Ambala-vayal	P. Muzhi	Coorg	Idukki	Thama rassery	Ambal-avayal	P. Muzhi	Coorg	Idukki
0	0	0	0	0	0	0.5	0.7	0.8	1.1	0.9	1.1	1.1	1.5	0.98	1.6
2.5	24	20	18	22	12	2.6	2.0	2.7	2.8	3.1	3.0	3.3	3.9	4.5	4.8
5.0	42	32	24	36	22	3.8	3.6	3.7	4.3	4.8	7.4	6.4	6.1	7.9	8.6
10	66	54	42	58	26	4.0	3.8	4.6	5.4	5.1	8.0	6.9	7.9	10.1	9.1
25	88	94	98	118	58	4.4	4.6	4.9	6.5	6.8	9.0	7.8	8.4	11.7	10.7
50	172	170	144	144	98	4.7	4.8	5.1	7.0	10.2	9.4	8.2	8.7	12.9	14.5
100	320	260	282	174	158	11.8	16.7	16.6	16.2	21.3	16.8	22.2	22.9	22.7	29.1
200	460	420	460	260	220	12.1	19.8	27.2	37.5	55.0	17.2	26.9	33.7	44.1	63.7
400	820	700	640	300	260	27.6	31.0	50.0	41.0	57.0	36.1	39.7	60.1	49.4	66.3
	CD 5% for levels 8.1					0.2					0.3				
	for soils 0.27					0.1					0.1				
	for interactions NS					NS					NS				

4.2.3 Langmuir and Freundlich isotherms of major black pepper growing soils

The plot of Langmuir isotherms for zinc adsorption in major black pepper growing soils viz., Thamarassery, Ambalawayal, Peruvannamuzhi, Coorg and Idukki are represented in Fig. 1 and Freundlich isotherms in Fig. 2 respectively. The Langmuir and Freundlich isotherm constants for zinc adsorption are depicted in Table 26.

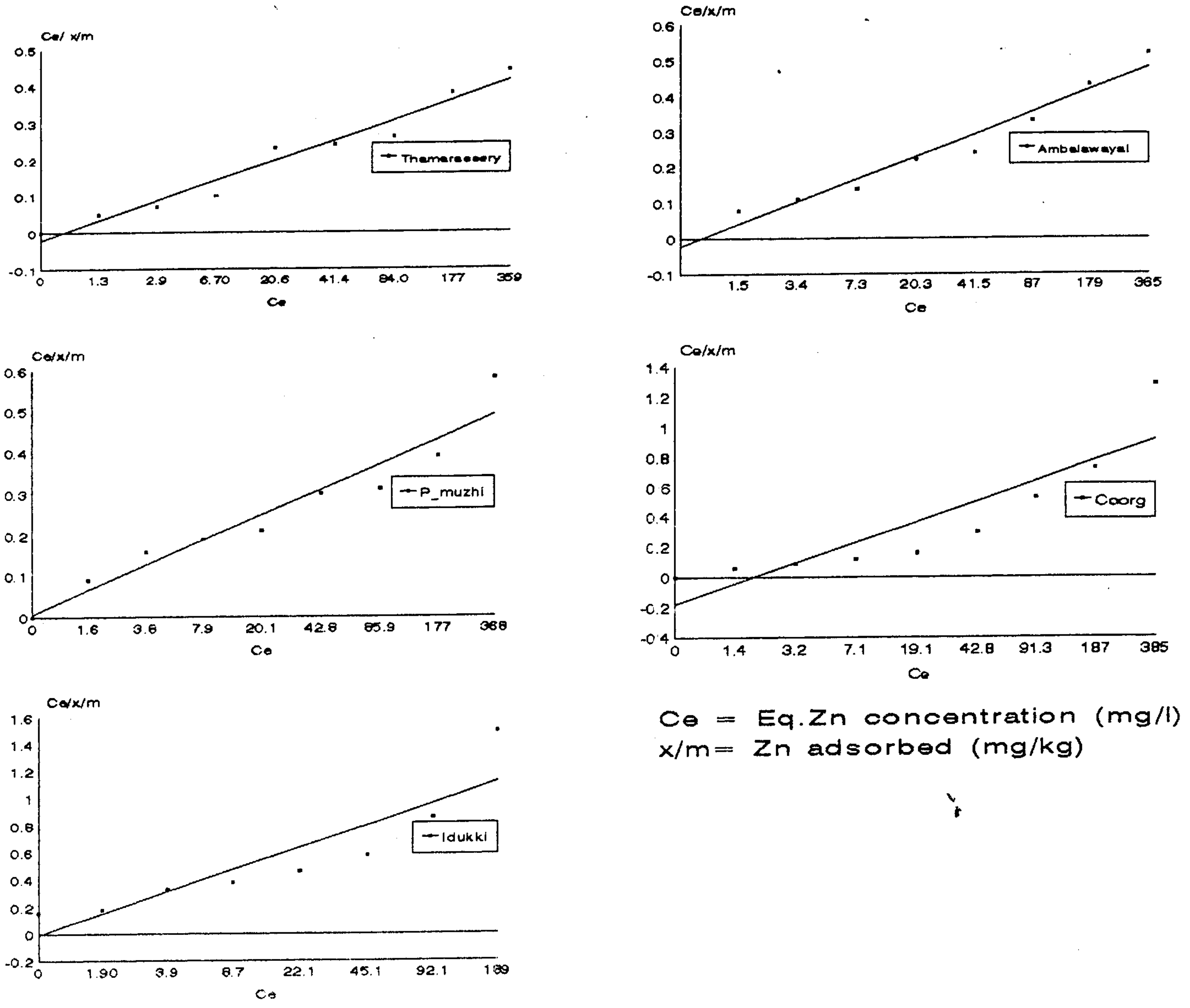
Table 26. Isotherm constant for adsorption of zinc in major black pepper growing soils

Soil	Langmuir constants			Freundlich constants		
	Bonding energy, K (ml μg^{-1})	Adsorption Max. (Am) (mg kg^{-1})	r value	1/n	Dist. Co efficient,C (ml μg^{-1})	r value
Thamarassery	-0.72	18.35	0.980	0.295	0.424	0.928
Ambalawayal	-0.81	16.35	0.983	0.294	0.375	0.937
P.muzhi	-1.11	16.53	0.965	0.302	0.304	0.948
Coorg	-0.43	7.35	0.891	0.245	0.538	0.884
Idukki	-0.95	6.21	0.897	0.262	0.304	0.939

On perusal of Table. 26, it was found that for Thamarassery, Ambalawayal, Peruvannamuzhi and Coorg soils isotherm confined more to Langmuir's equations for which the correlation coefficient varies from 0.980 to 0.891 rather than Freundlich equation for which correlations varies from 0.928 to 0.884. But for Idukki soil Freundlich equation ($r = 0.939$) was found to be more fit than Langmuir equation ($r = 897$). The adsorption maxima (Am) calculated from Langmuir isotherm was found to vary from 18.35 mg kg^{-1} to 6.21 mg kg^{-1} and is highest for Thamarassery and least to Idukki soil. The bonding energy constant (K) was found to vary from –1.11 to –0.43 m l μg^{-1}.

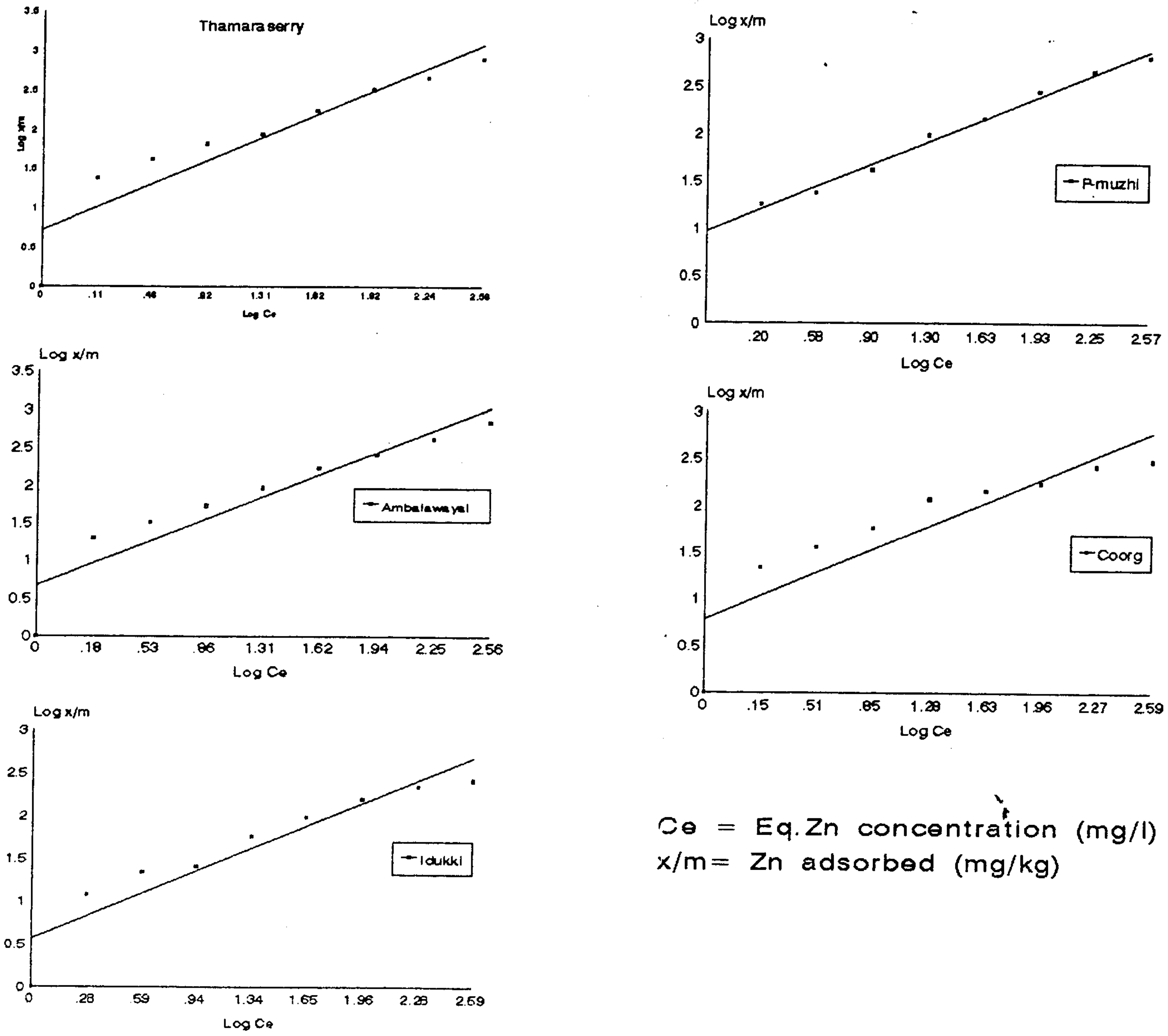
The 1/n value of Freundlich isotherm varied from 0.302 to 0.295 and distribution coefficient (C) from 0.304 to 0.538 ml μg^{-1}.

Fig.1 Langmuir adsorption isotherms of zinc



Ce = Eq.Zn concentration (mg/l)
x/m= Zn adsorbed (mg/kg)

Fig.2 Freundlich adsorption isotherms of zinc



Ce = Eq. Zn concentration (mg/l)
x/m = Zn adsorbed (mg/kg)

In brief adsorption of zinc in major black pepper growing soils through fit to both Langmuir and Freundlich isotherm, it is highly confined to Langmuir equation as indicated by high value correlation coefficients. Also zinc adsorption maximum was highest for Thamarassery and least for Idukki soil.

4.2.4 Langmuir and Freundlich isotherm of zinc desorption by 0.01M $CaCl_2$ in major black pepper growing soils

The plot of Langmuir isotherms for zinc desorption by 0.01M $CaCl_2$ in major black pepper growing soils viz., Thamarassery, Ambalawayal, Peruvannamuzhi, Coorg and Idukki soils are represented in Fig. 3 and that of Freundlich isotherms in Fig. 4 respectively. The Langmuir and Freundlich isotherm constants for zinc desorption by 0.01M $CaCl_2$ and depicted in Table. 27.

Table 27. Isotherm constant for desorption of zinc by 0.01M $CaCl_2$ in major black pepper growing soils

Soil	Langmuir constants			Freundlich constants		
	Bonding energy, K (ml μg^{-1}.)	Desorption Max. , Dm (mg kg^{-1})	r value	1/n	Dist. Co efficient, C (ml μg^{-1})	r value
Thamarassery	-0.53	0.391	0.839	0.167	-0.14	0.927
Ambalawayal	-0.49	0.302	0.879	0.175	-0.12	0.945
P.muzhi	-0.40	0.176	0.796	0.197	-0.17	0.955
Coorg	-0.47	0.210	0.864	0.170	0.05	0.961
Idukki	-0.43	0.146	0.851	0.190	0.03	0.954

On perusal of Table 27, it was found that for zinc desorption by 0.01M $CaCl_2$ confined more to the Freundlich equation for which correlation coefficient varies from 0.961 to 0.927 rather than Langmuir equation for which correlation coefficient varies from 0.864 to 0.796 only. The desorption maxima (Dm) calculated from Langmuir isotherm varies from 0.391 to 0.146 mg kg^{-1} and is highest in Thamarassery and least in Idukki soil. The bonding energy for desorption (K) varied from –0.40 to –0.53 ml μg^{-1}.

Fig. 3 Langmuir desorption isotherms of zinc by calcium chloride

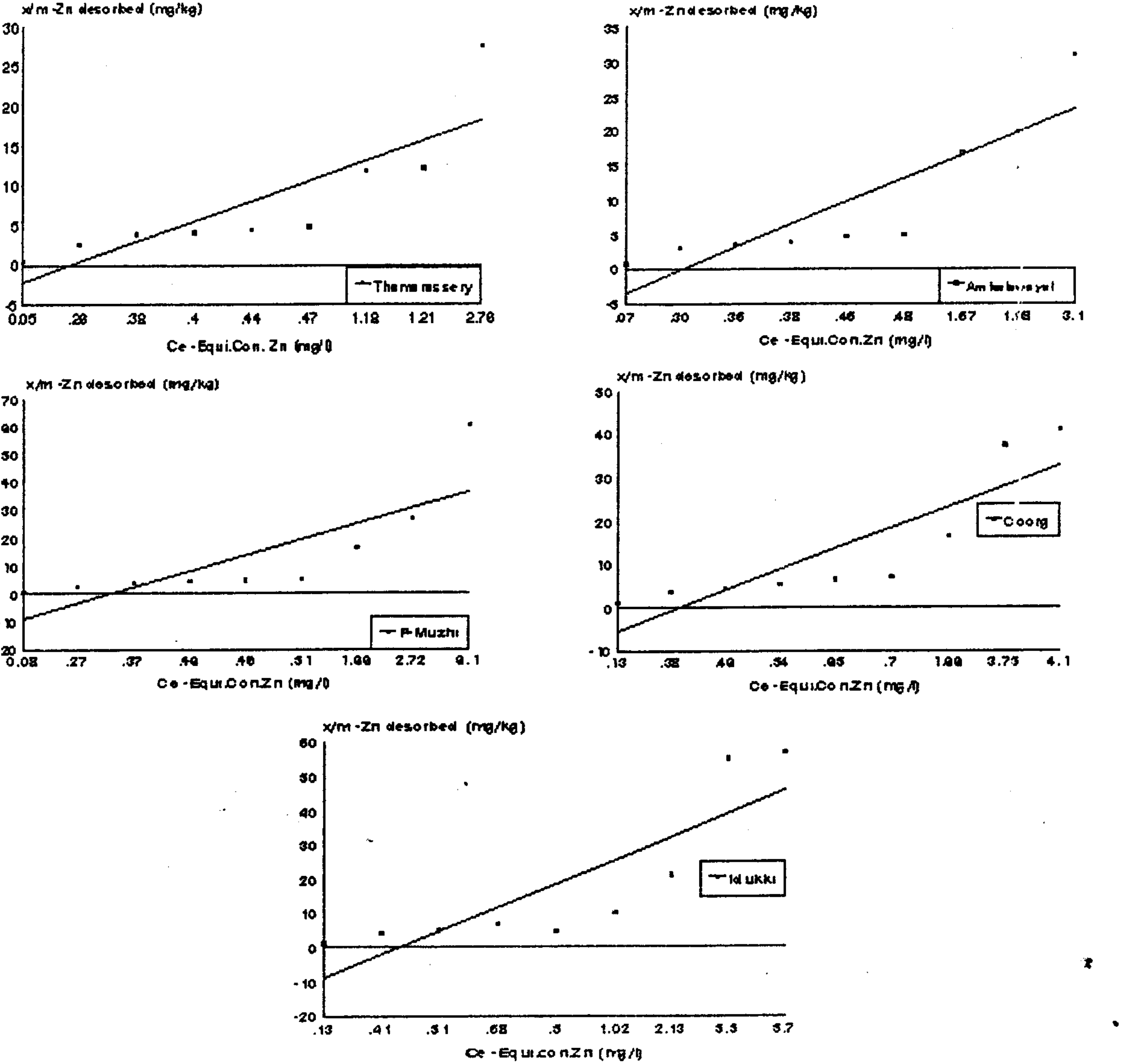
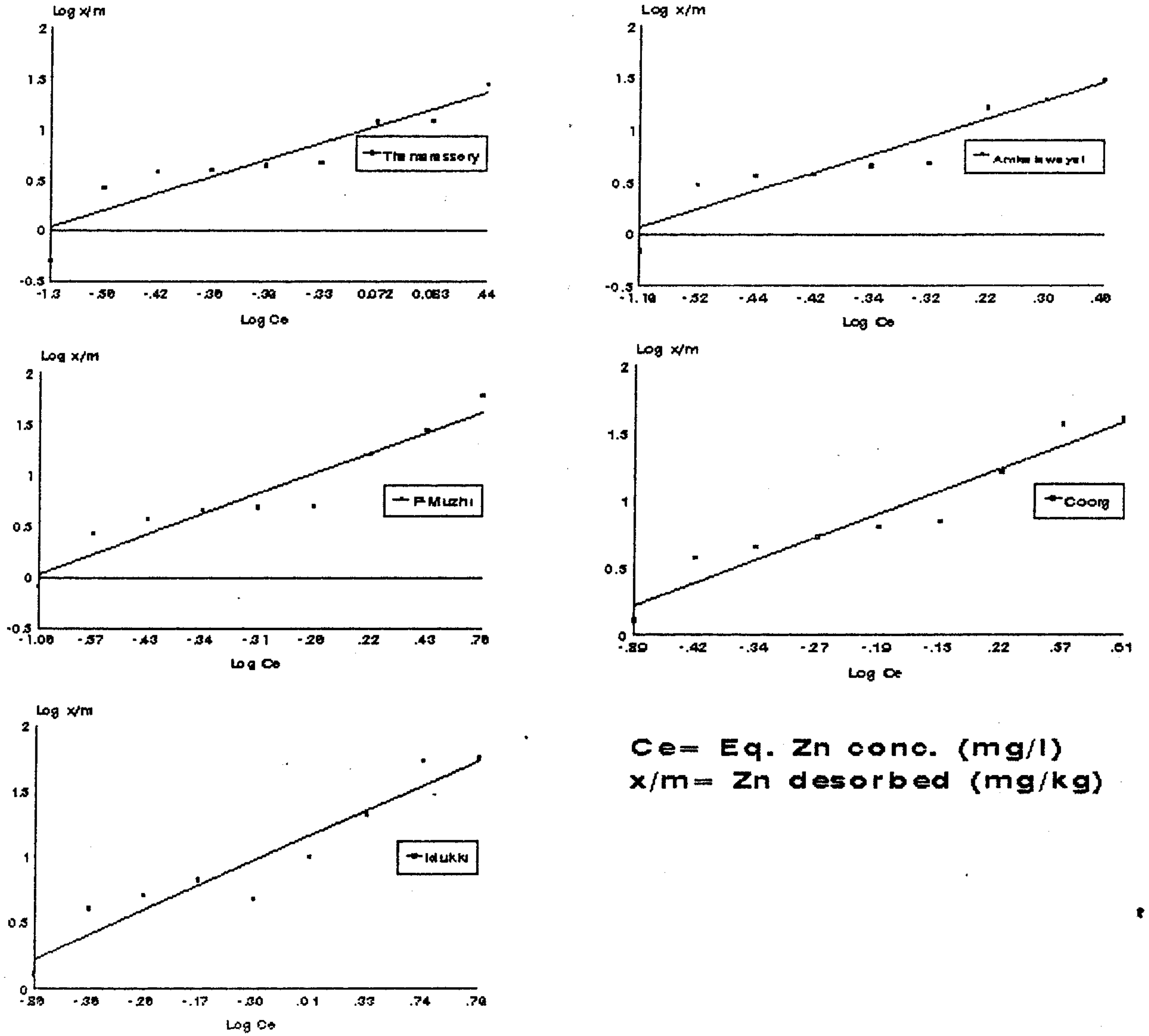


Fig. 4 Freundlich desorption isotherms of zinc by calcium chloride



Ce= Eq. Zn conc. (mg/l)
x/m= Zn desorbed (mg/kg)

The 1/n value calculated from Freundlich isotherm varies from 0.167 to 0.190. The distribution coefficient (C) varies from 0.05 to –0.14 ml μg^{-1}.

In brief, desorption of zinc by 0.01M $CaCl_2$ through fit to both Langmuir and Freundlich isotherm, it is highly confirmed to Freundlich equation as indicated by high value of correlation coefficient.

4.2.5 Langmuir and Freundlich isotherm of zinc desorption by 0.005 M DTPA in major black pepper growing soils

The plot of Langmuir isotherm for zinc desorption by 0.005M DTPA in major black pepper growing soils *viz.*, Thamarassery, Ambalawayal, Peruvannamuzhi, Coorg and Idukki soils and represented in Fig. 5 and of Freundlich isotherms in Fig. 6 respectively. The Langmuir and Freundlich isotherms constants for zinc desorption are depicted in Table. 28.

On perusal of Table 28, it was found that zinc desorption by DTPA also confirmed more to the Freundlich equation as the correlation coefficients varies from 0.966 to 0.931 where as those for Langmuir varies from 0.90 to 0.828 only. The desorption maxima (Dm) calculated from Langmuir isotherm varies from 0.127 to 0.307 mg kg^{-1} and is maximum for Thamarassery and least for Idukki. The bonding energy constant (K) for DTPA desorption of zinc varies from –0.81 to –0.45 ml μg^{-1}.

The 1/n value calculated from Freundlich isotherm for DTPA desorption of zinc varies from 0.135 to 0.172. The distribution coefficient (C) varies from 0.15 to 0.35 ml μg^{-1}.

In brief, zinc adsorption by 0.005M DTPA also more confined to Freundlich equation as that of the desorption by 0.01m $CaCl_2$. Here also desorption maxima was highest for Thamarassery soil and least for Idukki soil.

Fig.5 Langmuir desorption isotherms of zinc by DTPA

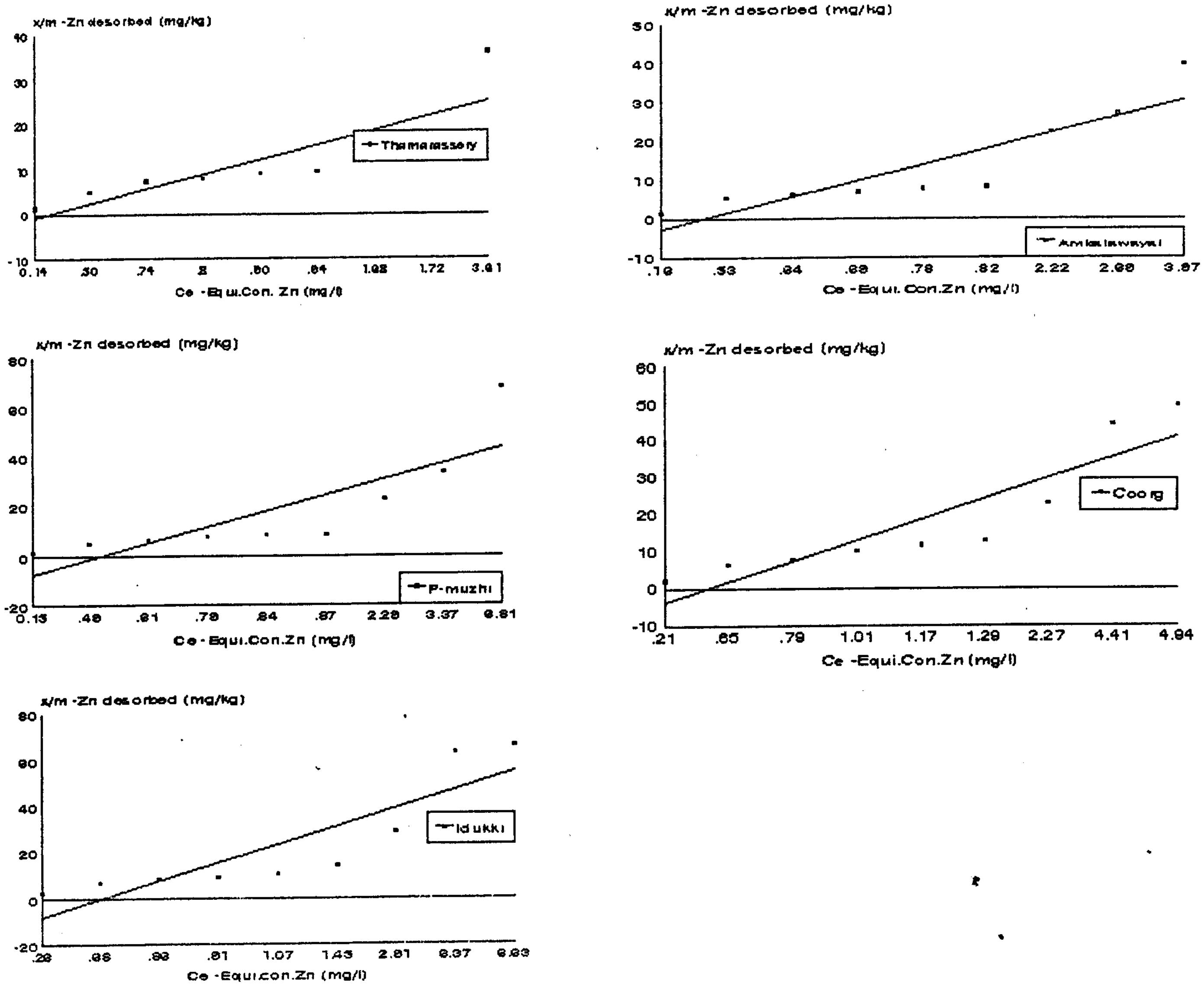
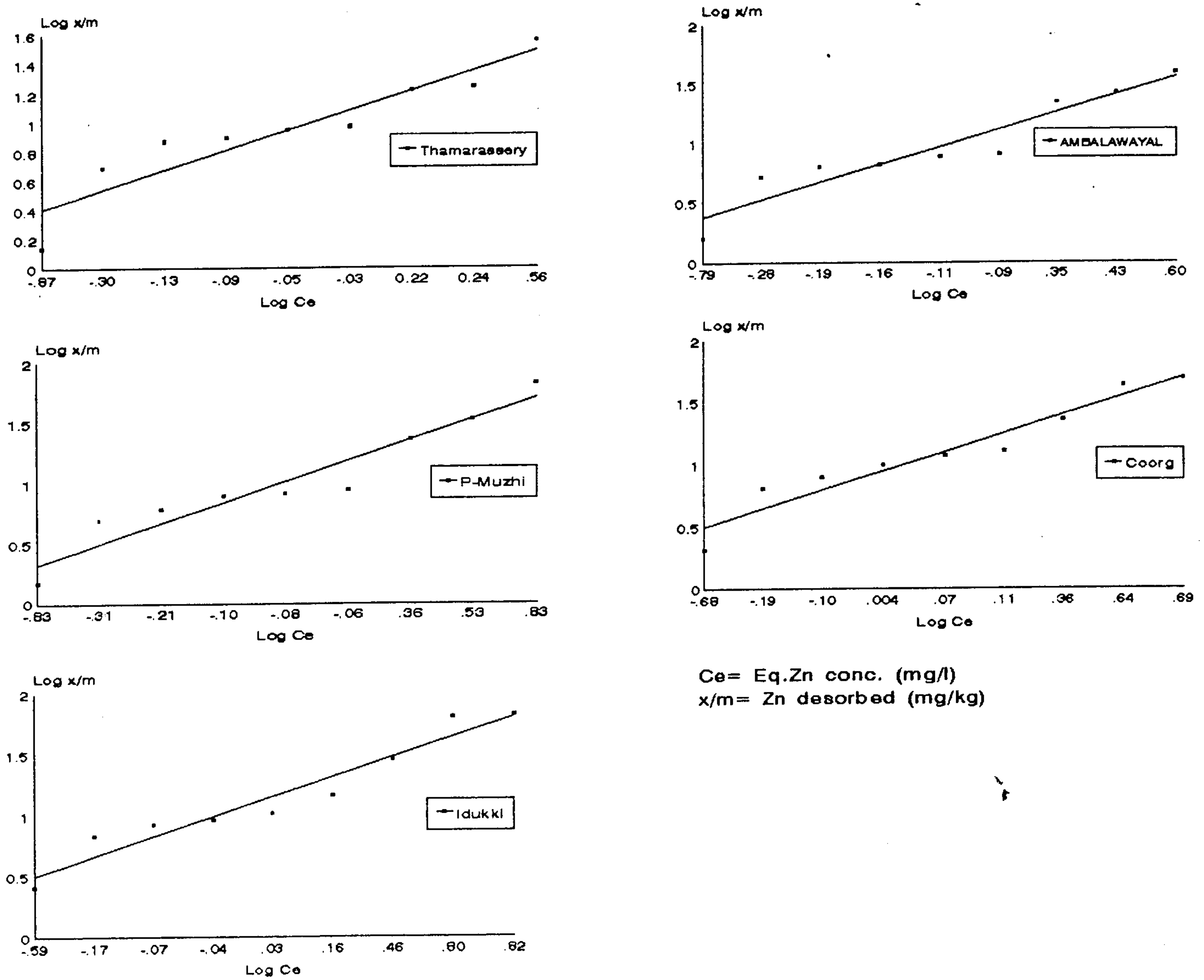


Fig.6 Freundlich desorption isotherms of zinc by DTPA



Ce= Eq.Zn conc. (mg/l)
x/m= Zn desorbed (mg/kg)

Table 28. Isotherm constant for desorption of zinc by DTPA in major black pepper growing soils

Soil	Langmuir constants			Freundlich constants		
	Bonding energy, K (ml μg^{-1})	Desorption Max. (Dm) (mg kg^{-1})	'r' value	1/n	Dist. Co efficient,C (ml μg^{-1})	'r' value
Thamarassery	-0.81	0.307	0.869	0.195	0.27	0.931
Ambalawayal	-0.60	0.239	0.894	0.148	0.23	0.949
P.muzhi	-0.45	0.155	0.828	0.172	0.15	0.957
Coorg	-0.60	0.179	0.900	0.150	0.35	0.965
Idukki	-0.50	0.127	0.873	0.164	0.34	0.966

4.2.6 Langmuir and Freundlich isotherm of molybdenum adsorption in major black pepper growing soils

The plot of Langmuir isotherm for molybdenum adsorption in major black pepper growing soil *viz.*, Thamarassery, Ambalawayal, Peruvannamuzhi and Coorg soils are represented in Fig. 7 and of Freundlich isotherm in Fig. 8 respectively. The Langmuir and Freundlich isotherm constants for Mo adsorption are depicted in Table 29.

On perusal of Table. 29 it was seen that Mo adsorption was more confirmed to the Langmuir equation as the correlation coefficient varies from 0.998 to 0.977 where as those for Freundlich equation varies from 0.958 to 0.878 only. The adsorption maxima (Dm) for molybdenum vary from 1.06 to 63 mg kg^{-1} and are minimum for Peruvannamuzhi and maximum for Ambalawayal soil. The bonding energy constant (K) varies from 1.7 to 23 ml μg^{-1}.

The 1/n value calculated from Freundlich isotherm of Mo adsorption varies from 0.166 to 0.268. The distribution coefficient (C) varies from –2.08 to –0.52.ml μg^{-1}.

In brief, as in the case of zinc adsorption, molybdenum adsorption was also fit to Langmuir equation as indicated by high value of correlation coefficient. Adsorption was highest for Ambalawayal soil and least for Peruvannamuzhi soil.

Fig.7 Langmuir adsorption isotherms of molybdenum

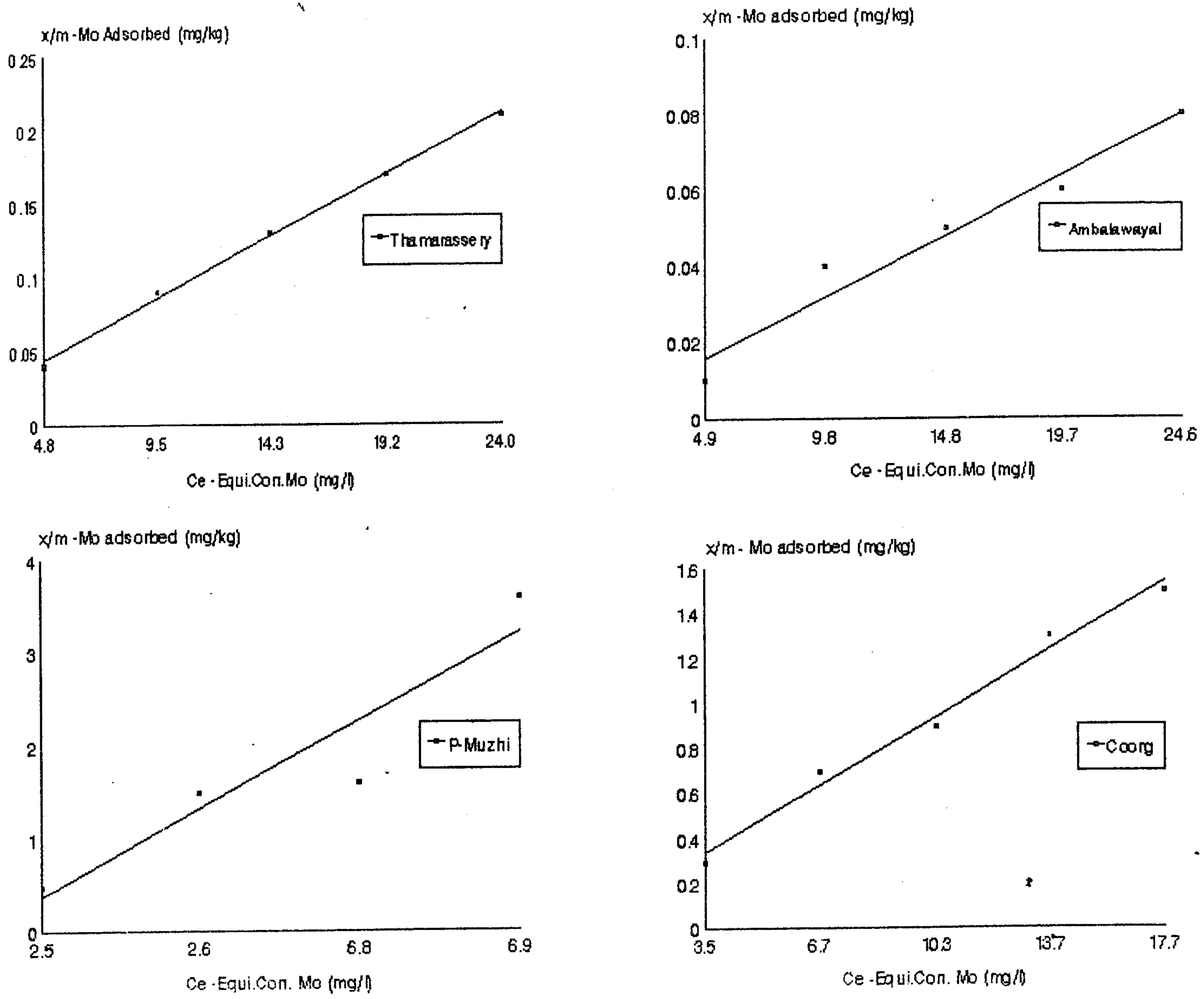
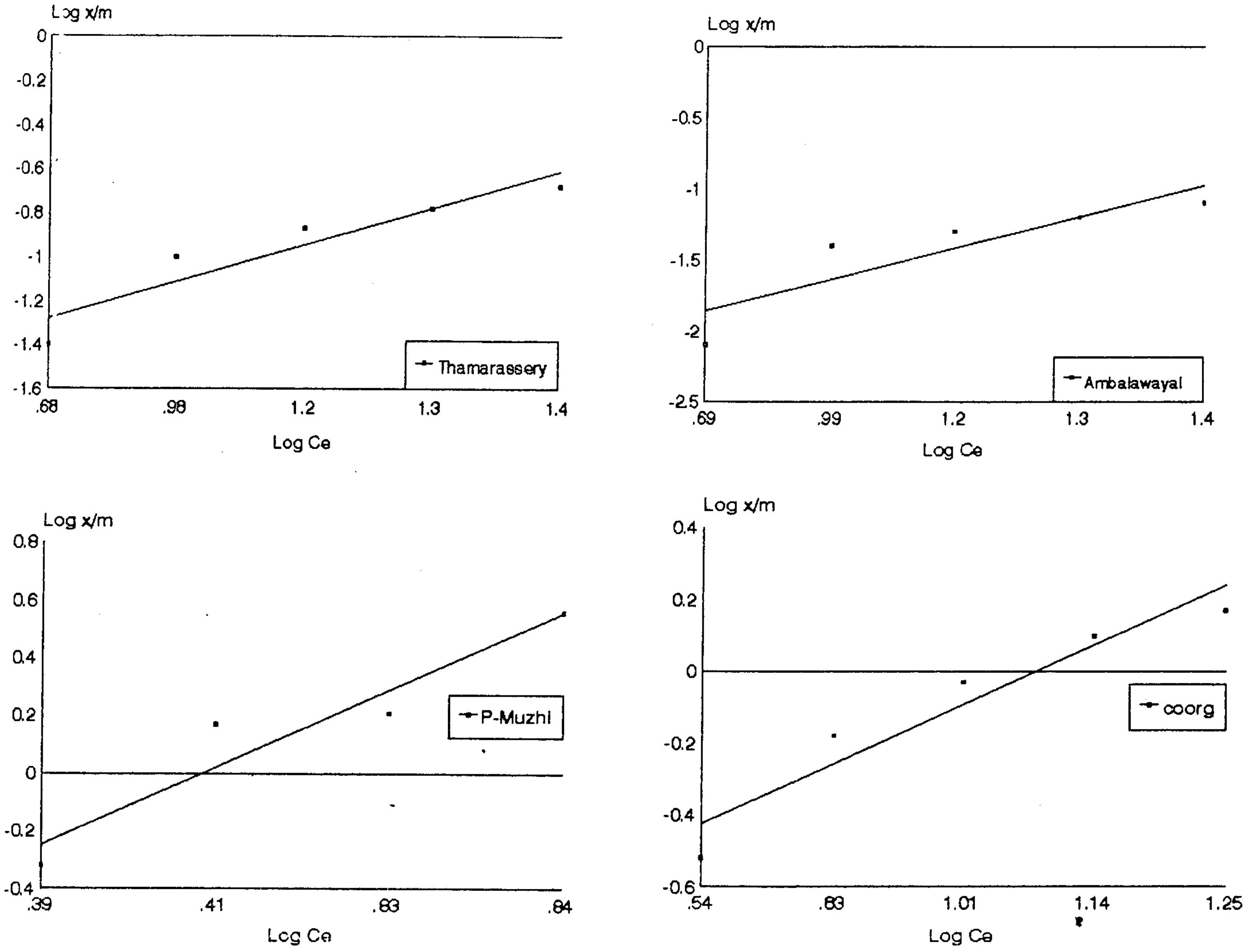


Fig. 8 Freundlich adsorption isotherms of molybdenum



Ce= Eq.Mo conc. (mg/l)
x/m= Mo adsorbed (mg/kg)

Table. 29 Isotherm constant for desorption of molybdenum in major black pepper growing soils

Soil	Langmuir constants			Freundlich constants		
	Bonding energy, K (ml μg^{-1})	Adsorption Max. (Dm) (mg kg^{-1})	'r' value	1/n	Dist. Co efficient,C (ml μg^{-1})	'r' value
Thamarassery	21	50	0.998	0.166	-1.44	0.938
Ambalawayal	23	63	0.977	0.220	-2.08	0.878
P.muzhi	1.66	-1.06	0.986	0.268	-0.52	0.956
Coorg	7.5	3.3	0.993	0.166	-0.59	0.958

4.2.7 Effect of application of zinc on different fractions of zinc in major black pepper growing soils

Different fractions of zinc in major black pepper growing soils are given in Table 30. It was found that water soluble + exchangeable Zn < organically bound < complexed < crystalline oxide bound < carbonate and amorphous oxide bound Zn < residual fractions in all the soils. Among the soils, Idukki soil recorded maximum water soluble + exchangeable Zn (0.26 mg kg^{-1}) followed by Thamarassery soil, and Coorg soil registered the least. Thamarassery soil scored maximum complexed Zn fraction (3.55 mg kg^{-1}), followed by Idukki and Ambalawayal soil. The Peruvannamuzhi soil scored the least. With regard to organically bound zinc fraction, Thamarassery soil recorded maximum (0.31 mg kg^{-1}) followed by Ambalawayal and Peruvannamuzhi soils and were on par. Moreover, the least was in Coorg and was on par with Idukki soil. Carbonate and amorphous oxide bound zinc fractions were maximum in Thamarassery soil (4.84) followed by Coorg and Idukki soils and Peruvannamuzhi soil scored the least. The Crystalline oxide bound zinc fraction was also maximum in Thamarassery soil, but was on par with Coorg soil. Residual zinc fraction was highest (64.2 mg kg^{-1}) in Coorg soil, followed by Idukki, Thamarassery and Ambalawayal soils where as Peruvannamuzhi soil has the least. Due to the application of Zinc (10 mg kg^{-1}), water-soluble + exchangeable Zn fractions increased by 50, 46, 75, 46 and 89% respectively in Thamarassery, Ambalawayal, Peruvannamuzhi, Coorg and Idukki soils. The complexed zinc fractions increased by

81, 214, 126, 173 and 120%, where as organically bound zinc fractions increased by 65, 10, 32, 22 and 41% respectively in Thamarassery, Ambalawayal, Peruvannamuzhi, Coorg and Idukki soils. There was 112, 118, 214, 94 and 103% increase in carbonate and amorphous oxide bound zinc and 32, 59, 29, 44, and 45% increase in crystalline oxide bound zinc due to 10 mg kg^{-1} zinc application in Thamarassery, Ambalawayal and Peruvannamuzhi, Coorg and Idukki soils respectively. In short water-soluble + exchangeable zinc fraction increased maximum in Idukki soil (89%), complexed zinc fraction increased maximum in Ambalawayal soil, organically bound fraction increased maximum in Thamarassery soil (65%), carbonate and amorphous oxide bound zinc fraction increased maximum in Peruvannamuzhi (214%) soil and crystalline oxide bound zinc fraction increased maximum in Idukki soil due to external application of zinc.

Table 30. Effect of application of zinc on different fractions of zinc on major black pepper growing soils (mg kg^{-1})

Soil	Applied Zn levels (mg kg^{-1})	Water soluble +exchange-able	Comple-xed	Organically bound	Carbonate and Amorphous oxide bound	Crystalline oxide bound	Residual
T.ssery	0	0.14	2.53	0.23	3.10	1.82	42.1
	10 mgkg^{-1}	0.21	4.57	0.38	6.57	2.41	47.8
	Mean	0.17	3.55	0.31	4.84	2.12	44.9
A.wayal	0	0.13	1.07	0.21	1.80	1.01	35.7
	10	0.19	3.36	0.23	3.93	1.61	46.9
	Mean	0.16	2.21	0.22	2.86	1.31	41.3
P.muzhi	0	0.12	0.87	0.19	1.33	0.92	31.9
	10	0.21	1.97	0.25	4.17	1.19	42.9
	Mean	0.17	1.42	0.22	2.75	1.05	37.4
Coorg	0	0.13	1.27	0.18	2.62	1.68	58.7
	10	0.19	3.49	0.22	5.09	2.42	69.6
	Mean	0.16	2.38	0.20	3.85	2.05	64.2
Idukki	0	0.18	1.84	0.17	2.29	1.36	45.9
	10	0.34	4.04	0.24	4.66	1.97	50.1
	Mean	0.26	2.94	0.21	3.48	1.67	48.0
CD 5%	Among levels	0.01	0.15	0.05	0.32	0.12	0.70
	Among soils	0.008	0.11	0.04	0.23	0.09	0.49

4.2.8. Correlations among different soil fractions of zinc, DTPA extractable Zn, dry matter production and zinc uptake of pepper

The correlations obtained among different fractions of zinc, among themselves and with DTPA extractable zinc, dry matter production and zinc uptake are given in Table. 31. It was found that availability of zinc with increasing levels of zinc application significantly and positively correlated with DTPA extractable Zn (r = 0.718**), $CaCl_2$ extractable zinc (r = 0.669**), water soluble Zn (r = 0. 870**), organic bound zinc (r =0.661**) and amorphous iron oxide zinc (r = 0.820**). Dry matter production significantly and positively correlated with water soluble zinc (r = 0.511*), crystalline iron oxide bound zinc (r = 0.685**), and zinc uptake (0. 896**). DTPA extractable zinc significantly and positively correlated with water soluble zinc (r = 0.505*), organically bound zinc (r = 470*), and amorphous oxide bound Zn (r = 0.821**). Calcium chloride extractable zinc significantly and positively correlated with water soluble zinc (r= 761**), amorphous oxide bound zinc (r = 0.474*) and crystalline oxide bound Zn (0.576*). Water soluble zinc significantly and positively correlated with organic bound Zn (r =0.727**), amorphous oxide bound Zn (r = 0. 781**), crystalline oxide bound Zn (r = 680**) and zinc uptake (r = 0.757**). Organically bound zinc significantly correlated positively with amorphous oxide Zn (0. 615**) and zinc uptake (r = 0.534*). Amorphous oxide bound zinc correlated positively and significantly with crystalline oxide bound Zn (r = 0.491*) and zinc uptake (0. 535*). Crystalline oxide bound zinc significantly and positively correlated with zinc uptake (r = 0.766**). This clearly indicates the interrelation ship among different forms of zinc in soil and uptake by pepper vines.

Table 31. Correlation of different fractions of zinc with applied zinc level, dry matter production soil DTPA and $CaCl_2$ extractable zinc and zinc uptake

Applied Zinc (A Zn)	A Zn	DM	D Zn	Ca Zn	W Zn	O Zn	A Zn	C Zn
Dry matter (DM)	NS							
DTPA ext. Zn (D Zn)	0.718**	NS						
$CaCl_2$ ext. Zn (Ca Zn)	0.667**	NS	NS					
Water soluble Zn (W Zn)	0.870**	0.511*	0.505*	0.761**				
Organic bound Zn (O Zn)	0.661**	NS	0.470*	NS	0.727**			
Carbonate and amorphous oxide bound zinc (A Zn)	0.820**	NS	0.821**	0.474*	0.781**	0.615**		
Crystalline oxide (C Zn) bound Zinc	NS	0.685**	NS	0.576*	0.680**	NS	0.491*	
Zinc uptake	NS	0.896**	NS	NS	0.757**	0.534*	0.535*	0.766**

4.3 POT EXPERIMENT

4.3.1 Studies on nutrient deficiency (Zn and Mo)

Growing black pepper devoid of Zn, in Hoagland's solution produced reduction in size of petiole, leaf and shoot and chlorosis of younger leaves. First symptom appears as interveinal chlorisis of young leaves restricted to interveinal area only with dark green veins. Terminal growth retarded and internodal length of leaves reduced gradually, producing little leaf disease appearance. There was growth reduction together with short internode and petiole producing a rosetted appearance. Zinc concentration in deficient stem reduced by 42% (from 19 to 11 mg kg^{-1}) in leaves by 60% (from 30 to 12 mg kg^{-1}) and in berries by 53% (from 15 to 7 mg kg^{-1}) compared to healthy ones by starving without zinc (plate 6).

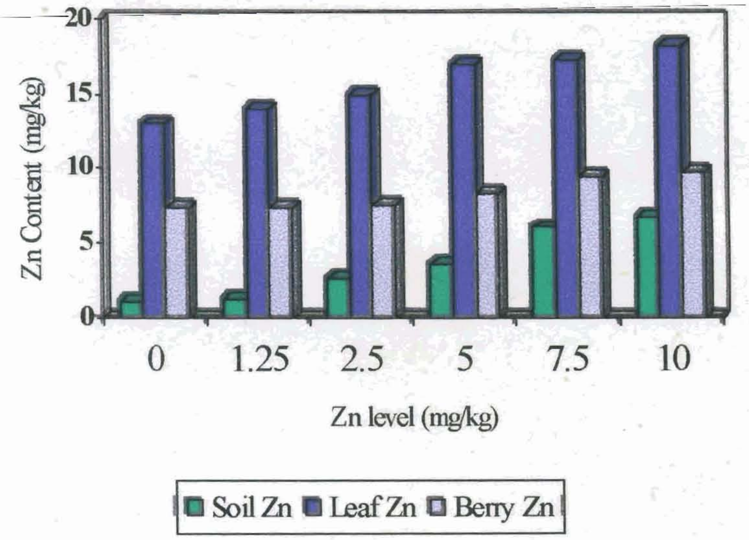
The plants devoid of molybdenum did not produce marked difference with that of normal ones for bush black pepper. The molybdenum deficiency produces chlorosis, which leads to interveinal mottling of the lower leaves, followed by marginal necrosis and unfolding with stunted growth.

4.3.2 Effect of different levels of zinc on soil availability, leaf zinc, yield and quality of pepper (under green house condition)

In green house condition, application of zinc to bush pepper showed that soil, leaf and berry zinc were found to increase significantly with increase in levels of zinc. Soil zinc increased from 1.14 to 6.8 mg kg^{-1}, leaf zinc from 13 to 18.3 mg kg^{-1} and berry zinc from 7.4 to 9.8 mg kg^{-1} (Fig.9). Maximum number of spike was recorded at 5 mg kg^{-1} zinc level (Plate 7&8), but was found to be on par with 2.5, 7.5 and 10 mg kg^{-1} level. There was increase in the number of spikes over control at 5 mg kg^{-1} zinc application. Maximum yield [86.1gm pot^{-1}] was recorded for 5 mg kg^{-1} level but was on par with 2.5 mg kg^{-1} level. There was 18.5 and 31.0% increase in yield over control respectively due to application of zinc at 2.5 and 5 mg kg^{-1} respectively. The oleoresin content (9.99%) was recorded at 7.5 mg kg^{-1}, but it was on par with 5 mg kg^{-1} and 10 mg kg^{-1} level. There was 8.2% increase in oleoresin content over check

Plate 6. Zinc deficiency in bush black pepper

Fig. 9 Effect of zinc on soil, leaf and berry content of zinc in bush black pepper



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due to 5 mg kg^{-1} Zn application. Maximum piperine content (7.27%) was recorded for 5 mg kg^{-1} Zn applied level, but was on par with 2.5 and 1.25 mg kg^{-1} level. Zn @ 5 mg kg^{-1} showed maximum B/C ratio followed by 2.5 mg kg^{-1} (Table. 32).

In brief for economic production of quality bush pepper soil application of, Zn @ 5 mg kg^{-1} is optimum.

Table 32. Effect of zinc on soil and leaf zinc concentration, number of spikes, yield, Oleoresin and Piperine content of bush black pepper

Zinc levels	Soil Zn	Leaf Zn	Berry Zn	Yield	Oleoresin	Piperine	B/C ratio
(------------------mg kg^{-1}------------------)				g vine^{-1}	(----------------%---------------)		
0	1.14	13.0	7.4	65.6	8.93	6.10	1.05
1.25	1.33	14	7.4	71.1	9.26	7.03	1.14
2.5	2.73	15	7.6	77.8	9.33	7.10	1.25
5.0	3.68	17	8.4	86.1	9.67	7.27	1.38
7.5	6.08	17.3	9.4	77.2	9.97	6.80	1.24
10.0	6.81	18.3	9.8	76.7	9.87	6.87	1.23
CD 5%	0.10	0.91	0.62	4.5	0.32	0.24	---

4.3.3 Comparison of different methods and sources of zinc application to pepper on Zn availability, uptake, yield and quality of pepper under green house condition

For bush pepper under potted condition application of 2.5 mg kg^{-1} Zn as Zn EDTA chelate produced maximum soil availability of zinc (2.89 mg kg^{-1}), followed by 2.5 mg kg^{-1} ZnSO4 +EDTA application and 2.5 mg kg^{-1} ZnSO4 application. Leaf content of zinc was maximum due to 0.5% foliar ZnSO$_4$ application followed by 0.1% foliar Zn-EDTA chelate application and 0.25% foliar ZnSO$_4$ application. Berry zinc also was maximum (11.1 mg kg^{-1}) due to 0.5% foliar ZnSO$_4$ followed by 0.25 % foliar ZnSO$_4$, and 0.1% foliar Zn-EDTA chelate (Fig. 10) application. With regard to number of spikes, foliar application of 0.5% ZnSO$_4$, 0.25% ZnSO$_4$, 0.1% Zn-EDTA were all on par. The yield was maximum (92 gpot^{-1}) due to 0.5% foliar ZnSO$_4$

Plate 7. Bush Pepper (Panniyur –1)
A. 0 mg Zn kg^{-1} soil
B. 5 mg Zn kg^{-1} soil

Plate 8. Bush Pepper (Karimunda)
A. 5 mg Zn kg^{-1} soil
B. 0 mg Zn kg^{-1} soil

application (Plate 9&10) followed by 0.1% Zn-EDTA chelate (Plate11), 0.25% $ZnSO_4$ and were on par, followed by soil application of 2.5 mg kg^{-1} Zn+EDTA or 2.5 mg kg^{-1} Zn-EDTA (Plate12). There was 39, 35, 26, 18% increase in yield over check due to 0.5% foliar $ZnSO_4$, 0.1% foliar Zn EDTA chelate,soil application of 2.5 kg Zn-EDTA and 2.5 kg $ZnSO_4$ respectively. The oleoresin content was maximum (11.83%) due to 2.5 mg kg^{-1} Zn-EDTA as soil application but was on par with 0.5% foliar $ZnSO_4$, 0.25% foliar $ZnSO_4$, 0.1% Zn-EDTA foliar application. The piperine content was maximum (7.83%) due to 0.5% foliar Zn application but was on par with soil application of 2.5 mg kg^{-1} Zn as $ZnSO_4$ or $ZnSO_4$+ EDTA or Zn EDTA chelate (Fig.11). Application of 0.5% $ZnSO_4$ as foliar showed maximum B/C ratio followed by 0.25% $ZnSO_4$ spray and 0.1% Zn-EDTA chelate spray (Table. 33)

In summing up application of zinc as soil or foliar either as $ZnSO_4$ or Zn-EDTA chelate increased soil leaf, and berry Zn status. The yield and quality (oleoresin and piperine content) of bush pepper also increased due to zinc application in Zn deficient soil.

Table 33. Comparison of different methods and sources of zinc application on soil, leaf and berry Zn, number of spikes, yield, oleoresin and piperine content of bush black pepper.

Treatment	Soil Zn	Leaf Zn	Berry Zn	No. of spikes	Yield	Oleoresin	Piperine	B/C ratio
	(............mg kg^{-1}			............)	g/bush	(..........%	.........)	
Check	1.14	13.0	7.4	24	66	8.93	6.10	1.1
1.25 mg kg^{-1} Zn as $ZnSO_4$	1.33	14.0	7.4	26	71	9.27	7.13	1.1
2.5 mg kg^{-1} Zn as $ZnSO_4$	2.22	15.0	7.6	26	78	9.33	7.60	1.2
2.5 mg kg^{-1} EDTA	1.19	12.6	7.4	24	64	10.06	6.90	1.0
2.5 mg kg^{-1} EDTA + 1.25 mg kg^{-1} Zn	1.50	13.7	8.0	26	70	11.13	7.23	1.1
2.5 mg kg^{-1} EDTA + 2.5 mg kg^{-1} Zn	2.49	16.0	9.2	30	84	11.36	7.67	1.3
2.5 mg kg^{-1} Zn as Zn EDTA	2.89	17.0	8.5	32	85	11.83	7.57	1.3
0.25 % Zn SO_4 as foliar	2.04	19.7	10.4	31	87	11.53	7.17	1.4
0.5% $ZnSO_4$ as foliar	2.22	22.0	11.1	32	92	11.63	7.83	1.5
0.1% Zn EDTA as foliar	2.16	20.3	9.8	30	89	11.37	7.07	1.4
CD 5%	0.10	1.9	0.62	2.0	4.5	0.32	0.24	

Plate 9. Bush Pepper (Karimunda)
A. 0.5% Foliar $ZnSO_4$
B. Check

Plate 10. Bush Pepper (Panniyur-1)
A. 0.5% Foliar $ZnSO_4$
B. Check

Fig. 10 Comparison of different methods and sources of zinc application on soil availability, leaf and berry zinc content (mg kg^{-1}) of bush black pepper.

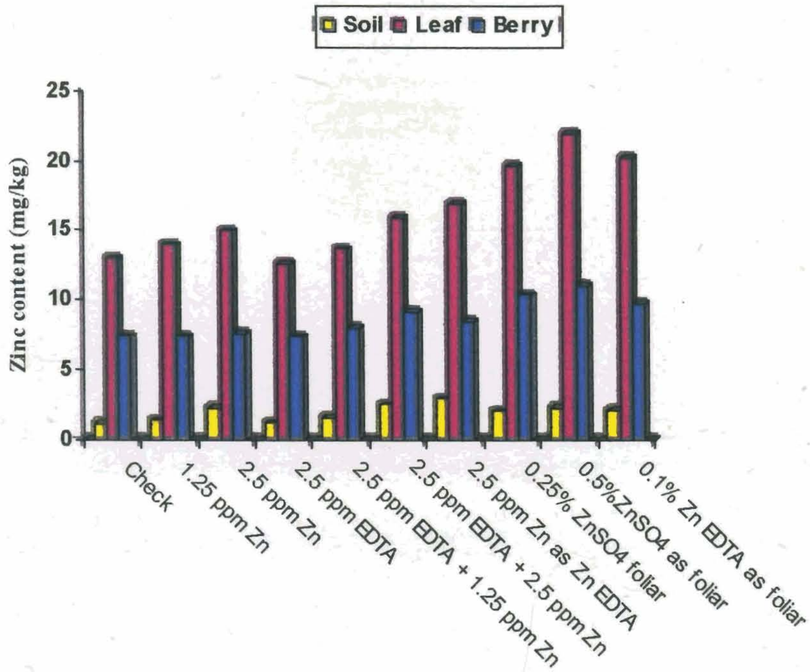
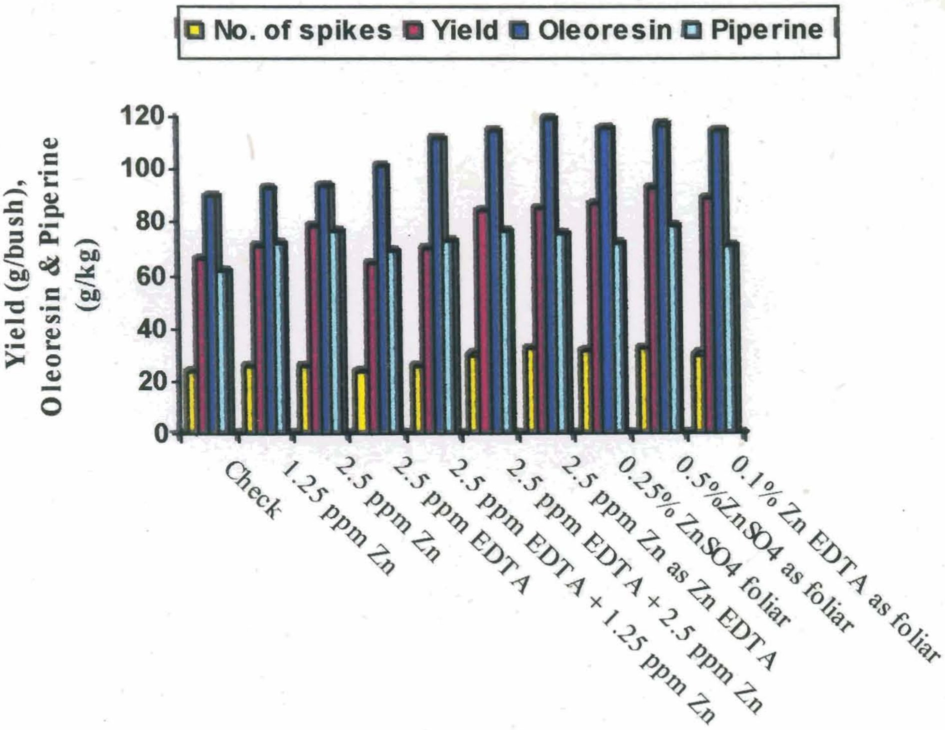


Fig. 11 Comparison of different methods and sources of zinc application on number of spikes, yield, oleoresin and piperine content of bush black pepper



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4.3.4 Effect of different levels of molybdenum on Mo availability, leaf concentration, yield and quality of bush black pepper (green house experiment)

Soil, leaf and berry Mo increased significantly with increase in levels of Mo application from 0 to 3 mg kg^{-1} to bush pepper grown in pots. Soil Mo increased from 0.36 to 1.51 mg kg^{-1}, leaf Mo from 2.1 to 4.8 mg kg^{-1} and berry Mo from 2.5 to 6.4 mg kg^{-1}. The number of spikes and yield were maximum due to 0.25 mg kg^{-1} Mo application and were on par with 0.5 mg kg^{-1} Mo application. There was 21% increase in yield due to 0.25 Mo application over check. The Oleoresin concentration was maximum (9.89%) due to 2 mg kg^{-1} Mo application and was on par with 0.5 mg kg^{-1} Mo application. The piperine concentration was maximum (7.27%) due to 1 mg kg^{-1} Mo application, but was on par with 0.5 mg kg^{-1} Mo application (Table 34). Regarding B/C ratio, application of Mo @ 0.25 or 0.5 mg kg^{-1} were on par followed by Mo @ 1.0 mg kg^{-1}.

In summing up, for bush pepper in a Mo deficient soil, though Mo @ 0.25 mg kg^{-1} is optimum for better yield, 0.5 mg Mo kg^{-1} soil is good for both yield and quality (Plate13 & 14).

Table 34. Effect of different levels of molybdenum on soil, leaf Mo, berry Mo, on production of spikes, oleoresin and piperine content of bush black pepper

Mo level	Soil Mo	Leaf Mo	Berry Mo	No. of spike	Yield	Oleoresin	Piperine	B/C ratio
(……………	mg kg^{-1}	……………	……)		g $bush^{-1}$	(………%…	………)	
0	0.36	2.1	2.5	20	84	9.10	7.09	1.3
0.25	0.38	2.8	2.9	23	102	9.49	7.02	1.6
0.50	0.46	3.0	4.0	23	98	9.84	7.20	1.6
1.0	0.64	3.6	4.4	21	89	9.82	7.27	1.4
1.5	1.08	4.0	4.8	22	84	9.41	7.07	1.3
2.0	1.27	4.2	5.4	19	83	9.89	7.15	1.3
3.0	1.51	4.8	6.4	20	71	9.71	7.14	1.1
CD 5%	0.03	0.16	0.52	1.4	5.7	0.30	0.13	--

Plate. 11 Bush pepper (Panniyur –1)
A. 0.1% Zn-EDTA foliar
B. Check

Plate. 12 Bush pepper (Karimunda)
A. Zn EDTA @ 2.5 mg kg^{-1} soil
B. Check

4.3.5. Comparison of different amendments and method of application molybdenum on soil, leaf and berry Mo content, yield and quality of bush black pepper

For bush pepper growing in pots, soil availability of Mo was maximum (0.46 mg kg^{-1}) due to Mo application @0.5 mg kg^{-1} but was on par with 0.25 mg kg^{-1} Mo application after lime application @20 g pot^{-1}. This was followed by FYM application or lime application alone and was on par. Leaf and berry Mo were maximum (6.5 and 6.4 mg kg^{-1} respectively) due to 0.2 % foliar molybdenum followed by 0.1% foliar application (Fig. 12). The number of spikes was maximum (27) in FYM applied pot followed by 0.25 mg kg^{-1} and 0.5 mg kg^{-1} soil Mo, 0.1% and 0.2% foliar Mo application. The yield was maximum (103g) in FYM applied pot but was on par with 0.25 & 0.5mg kg^{-1} Mo soil application and 0.1% foliar Mo application which in turn was again on par with 0.25 mg kg^{-1} Mo+Lime application and application of lime alone. There was 22.6, 16.7, 9.5% increase in yield respectively over control due to FYM, 0.5 mg kg^{-1} Mo and lime application (Fig. 13). Oleoresin content was maximum (9.93%) in 0.2% foliar Mo treatment, but was on par with 0.1% foliar Mo (9.73%), 0.5 mg kg^{-1} Mo and 0.25 mg kg^{-1} Mo soil application with lime. The piperine content was maximum (7.39%) in lime alone treatment and was on par with 0.2% foliar Mo and 0.25 ppm Mo after lime application (Table. 35). The B/C ratio was same for FYM, 0.25 mg kg^{-1}, Mo, 0.5 mg kg^{-1} Mo+Lime and for 0.1% foliar molybdenum treatment.

In brief, soil, leaf Mo concentration and quality (Oleoresin and piperine) of bush pepper increased with FYM, lime or Mo application in a Mo deficient acidic soil. With regard to economic yield in a Mo deficient soil, application of FYM or 0.5 mg kg^{-1} Mo or 0.25 mg kg^{-1} Mo+lime or 0.1% foliar sodium molybdate are equally effective (Plate 15,16&17).

Plate 13. Bush pepper (Panniyur –1)
A. Check,
B. Mo @ 0.5 mg kg^{-1} soil

Plate 14. Bush pepper (Karimunda)
A. Mo @ 0.5 mg kg^{-1} soil
B. Check

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Fig. 12 Comparison of different amendments and method of application of molybdenum on soil availability, leaf and berry Mo content (mg kg^{-1}) of bush black pepper

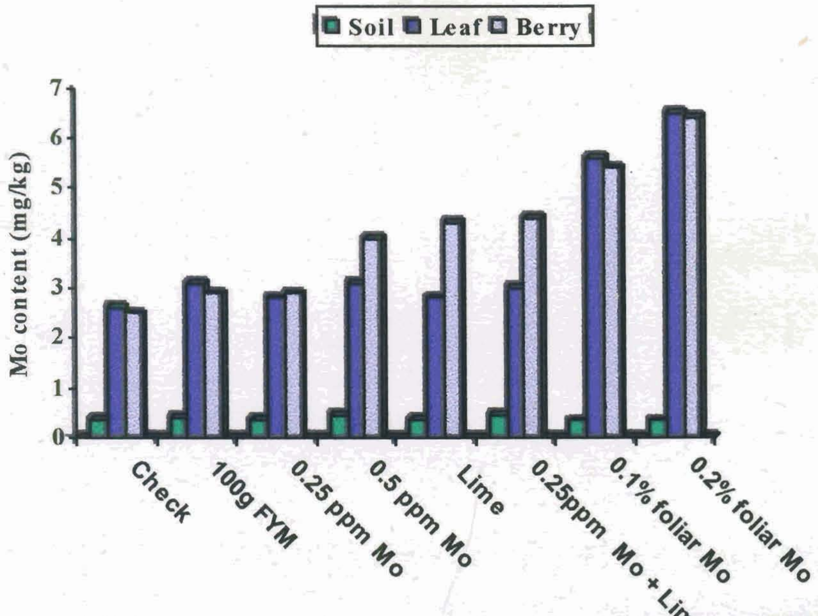

Fig. 13 Comparison of different amendments and method of application of molybdenum on number of spikes, yield, oleoresin and piperine content of bush black pepper

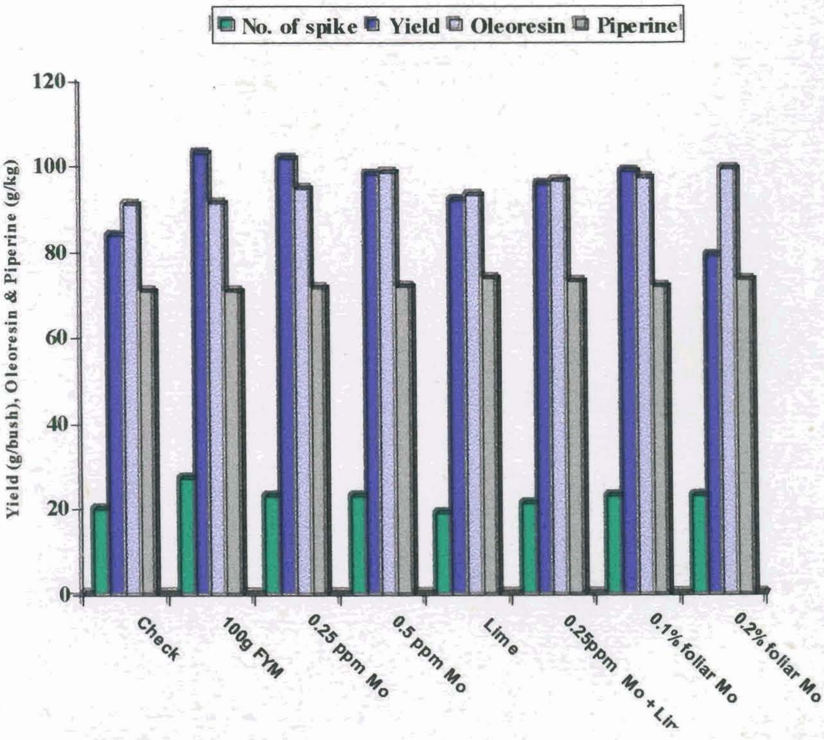

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Table 35. Comparison of different amendments and method of application of molybdenum on soil, leaf and berry Mo content, production of spikes, yield oleoresin and piperine content of bush black pepper

Treatment	Soil Mo	Leaf Mo	Berry Mo	No. of spike	Yield	Oleoresin	Piperine	B/C ratio
	(…….mg/ kg…….)				g/pot	(………..%………)		
Check	0.36	2.6	2.5	20	84	9.10	7.09	1.3
FYM 100g pot^{-1}	0.42	3.1	2.9	27	103	9.13	7.07	1.6
0.25 mg kg^{-1} Mo in soil	0.38	2.8	2.9	23	102	9.49	7.17	1.6
0.5 mg kg^{-1} Mo in soil	0.46	3.1	4.0	23	98	9.84	7.20	1.6
Lime @ 20 g pot^{-1}	0.38	2.8	4.3	19	92	9.34	7.39	1.5
0.25 mg kg^{-1} Mo + Lime	0.45	3.0	4.4	21	96	9.65	7.30	1.5
0.1% Sod. molybdate as foliar	0.35	5.6	5.4	23	99	9.73	7.21	1.6
0.2% sod molybdate as foliar	0.34	6.5	6.4	23	79	9.93	7.36	1.3
CD 5 %	0.03	0.16	0.52	1.4	6	0.30	0.13	

4.4. FIELD EXPERIMENTS

4.4.1 Effect of different levels of zinc application on soil Zn, leaf concentration, yield and quality of black pepper

In a Zn deficient pepper garden, soil, leaf and berry zinc was increased significantly with increasing levels of zinc from 0 to 10 kg ha^{-1}. Soil zinc increased from 0.75 to 5.57 mg kg^{-1} leaf zinc from 19 to 47 mg kg^{-1} and berry zinc content from 6.1 to 9.9 mg kg^{-1}. The yield of pepper was maximum (1.65 kg vine^{-1}) with 5 kg Zn ha^{-1} and was on par with other levels of zinc application. There was 25% increase in yield over control due to soil zinc application @ 5 kg Zn ha^{-1}. The oleoresin content was maximum (8.78%) at 5 kg Zn ha^{-1} and was on par with 7.5 kg Zn ha^{-1}. The piperine content was also maximum (6.46) at 5 kg Zn ha^{-1} and was on par with 7.5 and 10kg Zn ha^{-1}. There was 6.7% increase in oleoresin and 7.13% increase in piperine content over check due to zinc application at 5 kg ha^{-1}. (Table 36). Economic analysis (B/C ratio) showed that, out of the applied levels, Zn @ 5.0 kg ha^{-1} is most remunerative, followed by 2.5 kg ha^{-1} as Zn SO_4. The response function worked out and was $Y = 1.352 + 0.908\ Zn - 0.0072\ Zn^2$. From the response function, the physical optimum was worked out to be 6.3 kg Zn ha^{-1} where as economic optimum was 6.2 kg

Plate 15. Bush pepper (Karimunda)
A. 0.1% foliar sodium molybdate
B. Mo @ 0.5 mg kg^{-1} soil

Plate 16. Bush pepper (Karimunda)
A. Lime @ 20 g pot^{-1}
B. Check

Zn ha^{-1} (Fig. 14). The net profit at optimum rate of Zn application calculated and was Rs. 44861 ha^{-1}.

Summing up, in zinc deficient soil, zinc application though increased nutrient uptake. The optimum rate for economic yield and quality of black pepper is 6.2 kg Zn as $ZnSO_4$ ha^{-1}.

Table 36. Effect of Zinc on soil and leaf zinc concentration, yield, oleoresin and piperine content of black pepper

Zinc levels Kg ha^{-1}	Soil Zn	Leaf Zn	Berry Zn	Yield Kg $vine^{-1}$	Oleoresin	Piperine	B/C ratio
	(………mg kg^{-1}		………)		(……………%	………)	
0	0.75	19	6.1	1.32	8.23	6.03	4.23
2.5	1.63	25	7.1	1.59	8.35	6.26	5.06
5.0	2.28	28	8.4	1.65	8.78	6.46	5.19
7.5	4.08	37	9.4	1.54	8.68	6.33	4.82
10.0	5.57	47	9.9	1.58	8.57	6.44	4.91
CD 5%	0.09	0.93	0.59	0.13	0.16	0.16	--

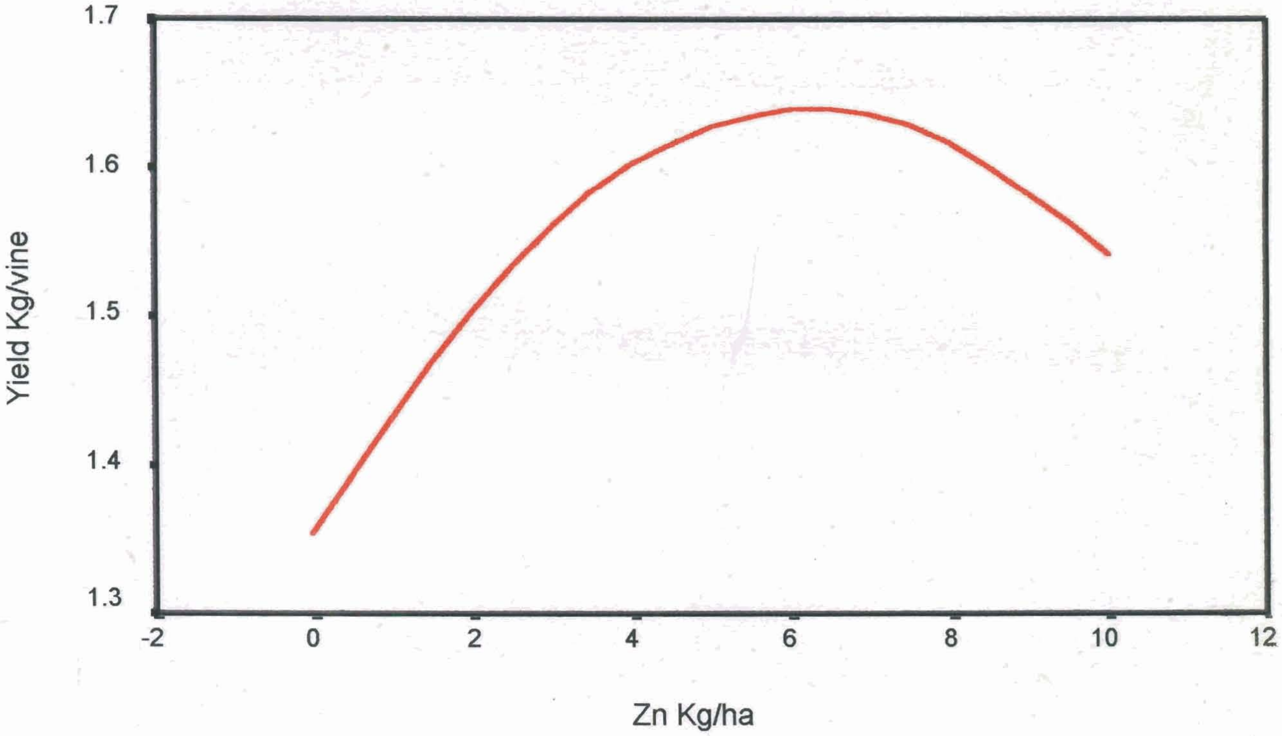
4.4.2 Comparison of different methods and source of zinc application on zinc availability, uptake, yield and quality of black pepper

In a Zn deficient pepper growing soil, availability of zinc was maximum (2.52 mg kg^{-1}) due application of Zn as Zn-EDTA chelate rather than applying $ZnSO_4$+EDTA or $ZnSO_4$ alone at the same rate. Leaf zinc concentration was maximum due to 0.5% foliar spray of $ZnSO_4$ followed by 0.25% $ZnSO_4$, and 0.1% Zn-EDTA chelate application (Fig.15). Berry zinc concentration was also maximum (10.3 mg kg^{-1}) due to 0.5% foliar application of $ZnSO_4$ followed by 0.25% foliar $ZnSO_4$. and 0.1% Zn-EDTA chelate. There was 55% increase in soil availability, 20% increase in leaf Zn and 15% increase in berry zinc due to 2.5 Kg Zn application as Zn-EDTA chelate over 2.5 kg $ZnSO_4$. The yield was maximum (1.68 kg $vine^{-1}$) due to foliar application of 0.5% $ZnSO_4$ and was on par with 2.5 kg Zn application either as $ZnSO_4$ or Zn-EDTA chelate soil application. This was followed by foliar application of 0.1% Zn-EDTA or 0.25% $ZnSO_4$ application. There was 27, 26 and 24 % increase in yield over control due to 0.5% $ZnSO_4$ as foliar , soil application of 2.5 kg Zn as $ZnSO_4$, and 2.5kg Zn as Zn-EDTA chelate respectively (Table 37). The oleoresin content was maximum (8.87%) due to soil application of 2.5kg Zn as Zn

Plate 17. Bush Pepper (Karimunda)
A. 100 g FYM Pot^{-1}
B. Check

37

Fig. 14 Response curve of zinc on black pepper yield



$Y = 1.352 + 0.908Zn - 0.0072Zn^2$ ($R^2 = 0.782$)

38

EDTA and was on par with 0.5% $ZnSO_4$ foliar application, 0.1% Zn-EDTA chelate application, 0.25% foliar $ZnSO_4$ application or soil application of 2.5 kg Zn + EDTA. The piperine content was also maximum (6.42%) due to 2.5 kg Zn soil application as Zn-EDTA chelate followed by 0.1% Zn-EDTA foliar application and was on par with soil application of 2.5 kg Zn as $ZnSO_4$ or foliar application of Zn as $ZnSO_4$. Among sources and methods, soil application of ZnSO4 produced maximum B/C ratio (5.27), which was on par with 0.5 % $ZnSO_4$ foliar spray (Fig.16).

In summing up Zn as Zn-EDTA chelate increased soil available zinc. Foliar application of $ZnSO_4$ or Zn-EDTA produced maximum leaf and berry concentration of zinc. Soil application of 2.5kg Zn as Zn-EDTA Chelate produced maximum oleoresin and piperine. In a Zn deficient pepper garden, soil application of Zn as $ZnSO_4$ produced maximum B/C ratio.

Table 37. Comparison of different methods and sources of zinc application on soil, leaf and berry content of zinc, yield, oleoresin and piperine content of black pepper

Treatment	Soil Zn	Leaf Zn	Berry Zn	Yield	Oleoresin	Piperine	B/C ratio
	(........mg kg^{-1}		.......)	Kg/vine	(.........%	.........)	
Check	0.75	19	6.10	1.32	8.23	6.03	4.23
2.5 kg Zn as $ZnSO_4$	1.63	25	7.13	1.66	8.35	6.26	5.27
2.5 kg EDTA chelate	0.84	22	5.73	1.28	8.21	6.06	4.05
2.5 kg EDTA chelate 2.5 kg Zn as $ZnSO_4$	2.24	27	6.67	1.59	8.67	6.15	4.94
2.5 kg Zn as Zn-EDTA chelate	2.52	30	8.2	1.64	8.87	6.42	4.38
0.25% $ZnSO_4$ as foliar	1.21	43	8.90	1.56	8.68	6.25	4.95
0.5% $ZnSO_4$ as foliar	1.54	50	10.30	1.68	8.81	6.25	5.26
0.1% Zn-EDTA as foliar	1.16	37	9.53	1.56	8.80	6.29	4.71
CD 5%	0.09	2.3	0.59	0.11	0.16	0.12	

85A

Fig. 15 Comparison of different methods and sources of Zinc application on soil availability, leaf and berry zinc content (mg kg^{-1}) of black pepper

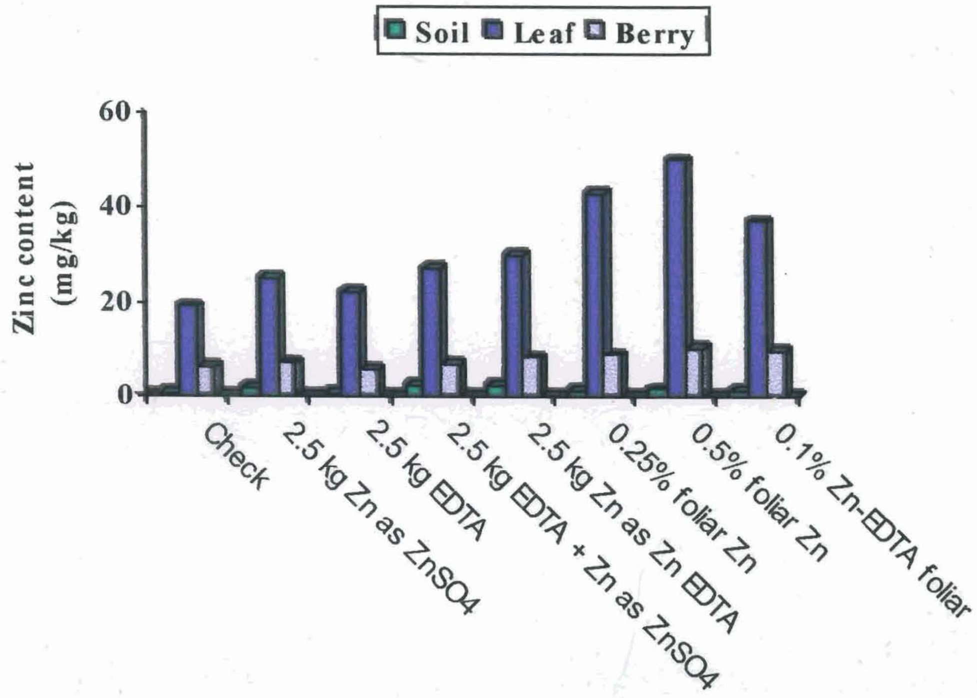
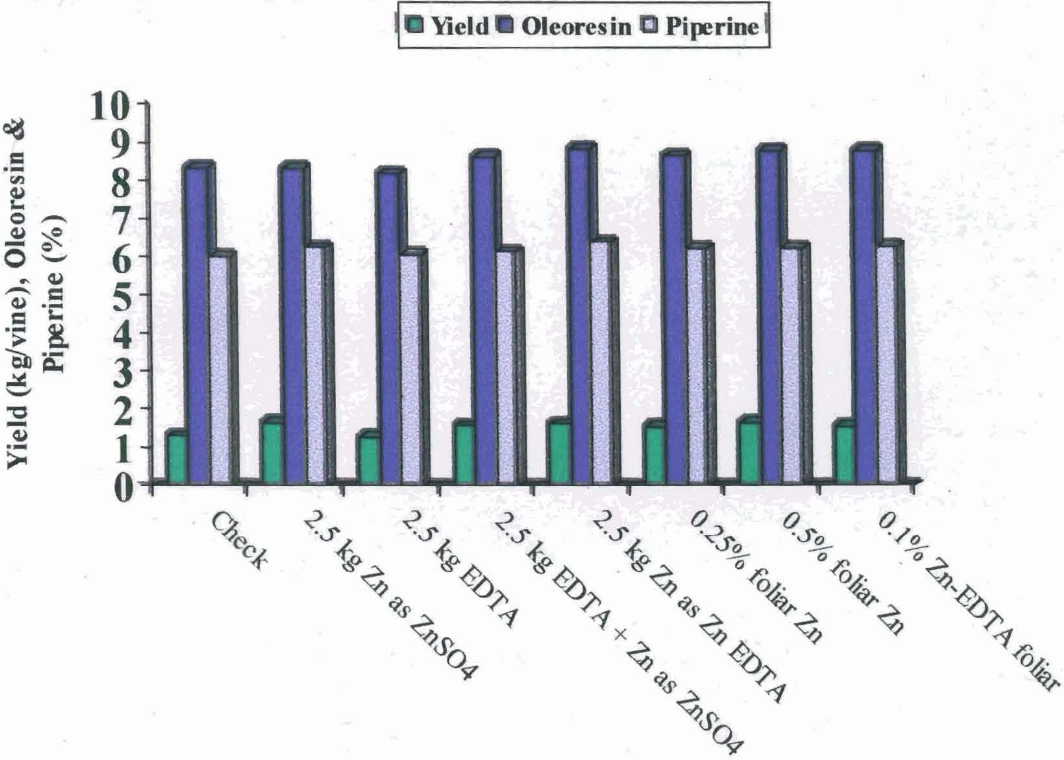


Fig. 16 Comparison of different method and sources of zinc application on yield and quality (oleoresin and piperine) of black pepper



4.4.3 Effect of different levels of molybdenum application on soil availability, leaf concentration, yield and quality of black pepper

In a acidic soil deficient in Mo, soil, leaf and berry Mo concentrations increased significantly with increasing level of Mo application from 0 to 2 kg ha^{-1}. Soil Mo increased from 0.30 to 0.58 mg kg^{-1} leaf Mo from 3.2 to 6.6 mg kg^{-1} and berry Mo from 0.88 to 1.06 mg kg^{-1}. The yield, oleoresin and piperine contents were maximum (1.45 kg vine^{-1}, 8.52 and 6.19% respectively) due to application of Mo @ 0.5 kg ha^{-1} (Table 38). Economic analysis showed that out of the applied levels Mo @ 0.5 kg ha^{-1} is most remunerative followed by Mo@ 1.0 kg ha^{-1}. The response function was worked out and was, $Y= 1.289 +0.296 Mo -0.157 Mo^2$. From the equation, the economical optimum worked out to be 0.94 kg Mo ha^{-1} (Fig. 17). The maximum net profit due to Mo was Rs. 20, 976 t ha^{-1}.

In brief in Mo deficient pepper growing gardens, Mo application increased soil availability and uptake of Mo. For economical yield of black pepper in such garden, Mo application @ 0.94 kg ha^{-1} as sodium molybdenum is optimum.

Table 38. Effect of different levels of molybdenum on soil, leaf and berry content of Mo, yield, oleoresin and piperine content of black pepper

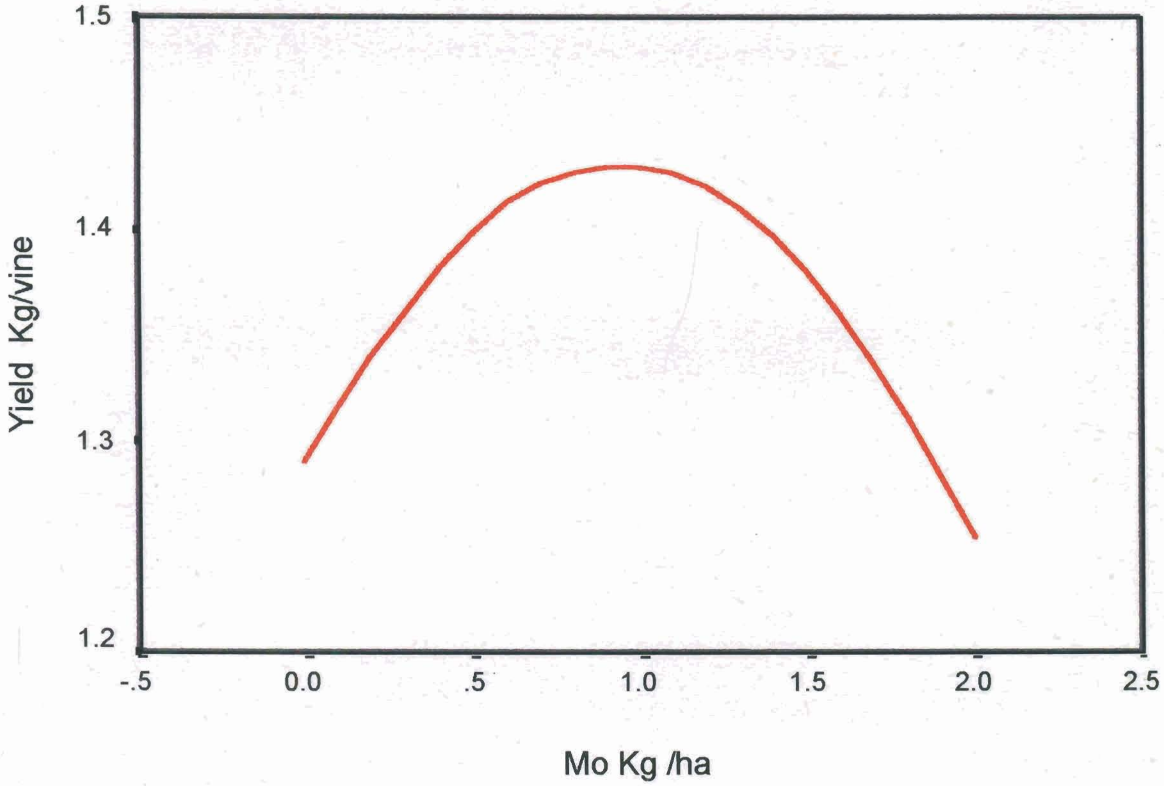
Mo levels	Soil Mo	Leaf Mo	Berry Mo	Yield	Oleoresin	Piperine	B/C ratio
Kgha^{-1}	(----------mg kg^{-1}------------)			Kg vine^{-1}	(------------%----------)		
0	0.30	3.2	0.89	1.27	8.03	5.76	4.06
0.5	0.35	3.9	0.93	1.45	8.52	6.19	4.57
1.0	0.45	5.0	0.99	1.39	8.16	5.88	4.32
1.5	0.49	6.1	1.04	1.38	8.26	5.99	4.22
2.0	0.58	6.6	1.06	1.26	8.32	6.12	3.80
CD 5%	0.02	0.14	0.10	0.10	0.16	0.19	--

4.4.4 Comparison of different amendments and methods of application of molybdenum on soil availability, leaf and berry concentration, yield and quality of black pepper

In Mo deficient pepper growing acidic soils, application of 0.5 kg Mo ha^{-1} after lime application (half ton ha^{-1}) recorded maximum soil availability of Mo (0.47

86A

Fig. 17 Response curve of Mo on black pepper yield



$Y = 1.289 + 0.296Mo - 0.157Mo^2$ ($R^2 = 0.830$)

mg kg^{-1}), followed by 0.25 kg Mo application after the application of lime. Application of 0.5 kg Mo ha^{-1} or half ton lime alone were on par with regard to soil Mo availability (Fig.18). Maximum leaf and berry Mo were recorded in 0.2% foliar molybdenum application, followed by 0.1% foliar molybdenum and 0.5 kg soil Mo+lime. The yield was maximum (1.47 kg vine^{-1}) due to half ton lime application alone but was on par with 0.5kg Mo or 0.25 kg Mo+lime or 0.5 kg Mo+lime application or 0.1% foliar molybdenum. There was 14 & 16 % increase in yield over check due to 0.5 kg Mo or lime application respectively. The oleoresin and piperine contents were maximum (8.52 and 6.19% respectively) due to Mo application 0.5 kg ha^{-1} (Fig.19). Economic analysis (B/C ratio) showed that application of lime @ half ton or Mo application @ 0.5 kg ha^{-1} were almost on par (Table. 39).

In summing up, in a molybdenum deficient acid soil as that of Coorg, lime application @ half ton is as good as 0.5 kg Mo ha^{-1} application, for augmenting soil Mo availability, economic yield and quality of black pepper.

Table 39. Comparison of different amendments and method of application of molybdenum on soil, leaf and berry content of Mo, yield, Oleoresin and piperine content of black pepper

Treatment	Soil Mo	Leaf Mo	Berry Mo	Yield	Oleoresin	Piperine	B/C ratio
	(…….mg kg^{-1}		……)	Kg/vine	(……….%	……….)	
Check	0.30	3.2	0.89	1.27	8.03	5.76	4.06
FYM 10 t ha^{-1}	0.33	3.4	0.90	1.38	8.25	5.91	4.02
0.5kg Mo ha^{-1}	0.35	4.0	0.93	1.45	8.52	6.19	4.57
Lime @ 0.5 tha^{-1}	0.35	3.4	0.87	1.47	8.29	6.09	4.58
0.25 kg Mo + lime	0.39	3.5	0.91	1.43	8.31	5.76	4.41
0.5 kg Mo+lime	0.47	4.0	0.97	1.45	8.40	5.92	4.43
0.1% foliar Mo	0.32	4.8	1.02	1.40	8.05	5.93	4.31
0.2 % foliar Mo	0.33	5.3	1.11	1.33	8.36	5.75	3.98
CD 5 %	0.02	0.14	0.10	0.09	0.16	0.19	--

Fig. 18 Comparison of different amendments and method of application of molybdenum on soil availability, leaf and berry Mo content (mg/kg) of black pepper

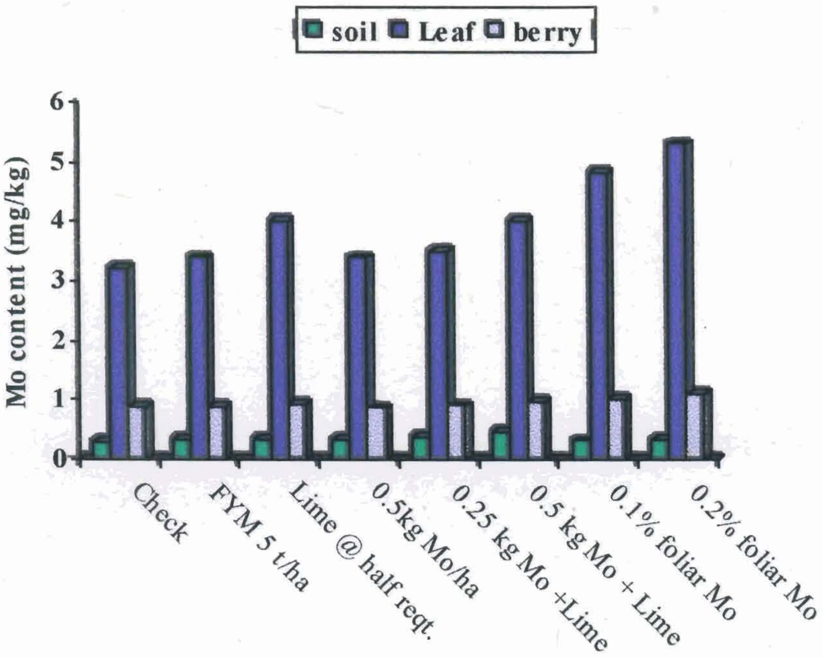
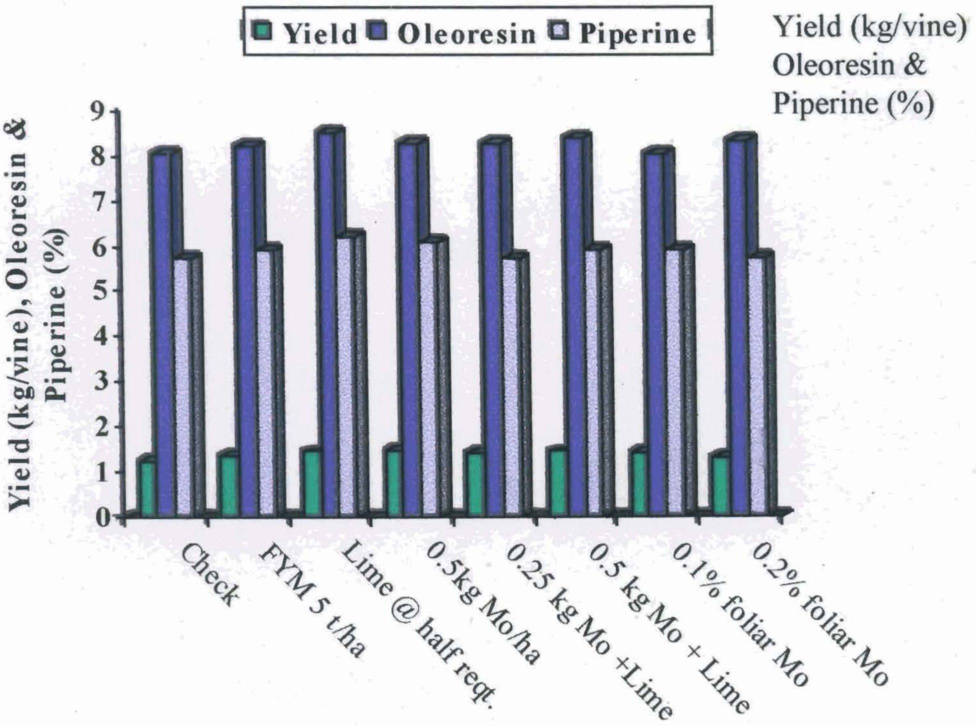


Fig. 19 Comparison of different amendments and methods of application of molybdenum on yield and quality content (oleoresin and piperine) of black pepper.



DISCUSSION

DISCUSSION

5. DISCUSSION

Results of laboratory, greenhouse and field experiments carried out on zinc and molybdenum nutrition on yield and quality of black pepper have been briefly enumerated in preceding chapters. From those results, it is possible to draw a few broad conclusions. Some of the results needed more work for interpreting the results. These have not been attempted. The significant results obtained from the study are discussed below.

5.1. Soil site suitability for black pepper

5.1.1 Assessment of soil physico-chemical properties in relation to altitude

The survey revealed that, at higher altitude (Wynad and Idukki) soils, sand and silt fractions, pH, base saturation, exchangeable base, cation exchange capacity, available major, secondary and micro nutrient status was higher compared to that of lower altitude areas (Calicut and Cannanore). Pepper yield was found to be higher in high altitude, compared to low altitude areas. Since the clay content is minimum at high altitude, fixation of nutrients would also be minimum. Root penetration and growth of pepper vines is likely to be maximum in such areas. As in other crops, for black pepper also the optimum temperature required for photosynthesis, may be lower than that for respiration and would be one of the reasons for the higher yield in high altitude & cool areas like Coorg and Wynad compared to warmer lower altitude areas as that of Calicut and Cannanore.

Low decomposition of organic matter due to low temperature leading to high fertility at high altitude area may be yet another reason. It was reported that principal factors determining micronutrients uptake by plants was the degree of saturation of clay (Epstein 1949). At higher altitude, utilization of organic matter and nutrients were maximum due to better availability that favors growth of pepper. Sand fraction was found to be high, clay and available sulphur status were found to be lower in high altitude. Heavy rainfall at high altitude, results in loss of clay and soluble sulphur, leaving behind sand and silt fractions. It is reported that availability of nutrients would be reduced with increasing clay content. (Modalish 1990, Brennan 1992, Muneera Siddiqui *et al* 1993). Permeability of parent materials influence the rate of weathering, control the effectiveness of leaching which in turn depends on rainfall, temperature, slope and vegetation. At low altitude area where soil is highly acidic, rich in clay and sulphur content, low in essential nutrients, water stagnates and hence the root growth limitation leading to poor pepper vine growth. Chottopadhyay *et al* (1996) reported that soils in higher altitude contain more micronutrients, than those in lower altitude. Temperature will also alter the composition of soil, air and microbial activities. Normal development of plants can also be restricted due to the presence of toxic substances like Al, Mn, S, Cu etc though many are beneficial and essential at optimum levels. The available nutrients status and soil fertility is higher at high altitude, that favors better root growth and higher uptake of nutrients, and these may be the reasons that black pepper thrives well on high altitude areas like Wynad, Idukki and Coorg areas.

5.1.2 Assessment of soil physico-chemical properties in relation to soil depth

It was found that from surface to bottom clay fractions increased, sand, and silt fractions decreased. Natural and man made disturbances in top soil resulted in accumulation of sand and silt fractions in top soil leaving clay fractions to settle at the bottom layers. Varadan and Mammen (1999) reported that the illuviation under laterisation is one of the reasons for increasing clay content in bottom layers. The properties like pH, CEC, exchangeable bases, and base saturation also decreased from top to bottom. Among essential nutrients, O.C., Bray-P, exchangeable K, Ca, Mg, available Zn, Cu and Mo also decreased from top to bottom, whereas iron and manganese remained constant and sulphur was maximum at bottom soil. The farmers' cultivation practices (manuring as organic and chemical fertilizers) and fungicide application (like copper oxychloride drenching) mainly confined to the topsoil. The sulphate ions, which are highly leachable, accumulated at the bottom layers, causing higher levels of sulphate at bottom. The increase of soil pH from top to bottom of soil profile would support this fact. Singh *et al* (1998) reported that greater concentration of native zinc desorbed from surface soil and hence Zn availability was maximum in surface compared to sub soil. These corroborate the findings of other workers.

Muneera Siddiqui *et al* (1993) reported that clay-rich soils had high nutrient adsorption capacities (especially for Zn) and hence the availability will be minimum at bottom soil where clay content and fixation of nutrients will be maximum. Anand Swarup *et al* (1994) reported that most of the applied metals (87 to 96%) remained in the top 10 cm of the soil, resulting in lower recovery in leachate. Zhang *et al* (1997) reported that total concentration of micronutrients were greater in Ap horizon and decreased with depth. Above reports, also support accumulation of nutrients in surface soil compared to bottom layers. Similar results were also reported by many other workers (Castro *et al* 1992, Pramasivam and Gopalaswamy 1994).

5.1.3 Assessment of soil physico-chemical properties in relation to pepper yield

The survey also showed that from high yielding to low yielding pepper gardens, sand and silt fractions, base saturation, exchangeable base, soil pH, CEC, organic carbon, available P, K, Ca, Mg and DTPA-extractable zinc were decreasing. Significant positive correlations were also obtained between these physicochemical properties and pepper yield. Mathew *et al* (1995) reported significant positive correlations of soil pH, organic carbon, exchangeable Ca, Mg and negative correlations of available Fe and S with pepper yield. There was not much difference with regard to availability of Fe, Cu and Mo between high and low yielding locations. Sulphur and manganese content were low in high yielding locations. To maintain soil fertility and replenish nutrients removed by the crops, application of manures and fertilizers even in fertile soil, is an important necessity. It was reported that red and lateritic soils of Kerala, though possessing good physical properties, are acidic, low in OC, and CEC and other nutrients and their productivity can be increased only by judicious application of fertilizers both organic and inorganic (Harikrishnan Nair and Koshi 1983). From the above report it is clear that one of the reasons for the low productivity of black pepper, in some areas is low status of major, secondary and micronutrients, higher clay and sulphur contents and highly acidic reaction of soils. These would indicate that appropriate management of soils could increase black pepper productivity. These underline the findings of Sadanandan (1994, 2000) and Deward (1969) in which they reported that for black pepper, highly fertile soil with good drainage as in Western Ghats are very essential. Sivaraman *et al* (1999) also reported that due to heavy rainfall and unsustainable soil management practices, the soil become poor and balanced manuring is essential for good production and growth of pepper.

5.2 Zinc and molybdenum deficiency in black pepper

Zinc deficiency in black pepper produced retardation in shoot growth, chlorosis of younger leaves in interveinal areas with reduction in size of lamina, petiole and internode, a symptom similar to little leaf disease with chlorosis (Plate 6). Zinc is required mainly for tryptophan and indole acetic acid synthesis, and is essential for plants (Maze 1914, Somner and Lipman 1926, Somner, 1928). It is directly or indirectly required for several enzymes involved in protein synthesis, seed production and maturity. It was reported that zinc deficiency causes reduction in biosynthesis of proteins and hydrolysis of carbohydrates (Agarwal and Chatterjee 1996). Low available zinc caused rosette disease in apple trees (Naumov *et al* 1984). Hence, lack of zinc in nutrient solution creates disturbance in metabolism and produces chlorosis in many plant parts leading to stunted growth of plant. Zinc is considered an immobile element and hence the symptoms are found in younger plant parts. Similar results were reported by Nybe (1986) in rooted pepper cuttings also. Veloso *et al* (1998) reported critical deficiency of zinc in black pepper at a tissue zinc concentration of < 16 mg kg^{-1}.

Molybdenum though required in smallest amounts, crops like legumes, citrus, maize, cotton, cauliflower, clover, lettuce, spinach etc. are considered highly sensitive to molybdenum deficiency among all micronutrients. Mo deficiency results in marginal scorching and rolling or cupping of leaves with chlorosis (Cox 1992). In black pepper Mo requirement is very small and that may be the reason that the black pepper did not show clear deficiency symptoms as evidenced from the present study.

5.3 Soil and leaf nutrients in relations to black pepper yield

Survey showed great variation among different locations in both soil and leaf nutrient status. The soil pH varied from 4.4 to 6.7, lime requirement from traces to 7.1 t ha^{-1}, soil organic carbon from 0.51 to 3.7%, Bray-P from 1.6 to 154 mg kg^{-1}. Exchangeable K from 61 to 2094 mg kg^{-1}, Ca from 244 to 3310 mg kg^{-1}, Mg from 24 to 455 mg kg^{-1}, available S from 14 to 193 mg kg^{-1}and zinc varied from 0.62 to 14 mg kg^{-1}, Fe from 26 to 60 mg kg^{-1}, Mn from 5.8 to 31 mg kg^{-1}, Cu from 1.5 to 55 mg kg^{-1} and Mo from 0.02 to 0.66 mg kg^{-1}. Leaf N varied from 1.9 to 2.7%, leaf P varied from 0.06 to 0.50%, K from 0.9 to 4.7%, Ca from 1.1 to 4.9%, Mg from 0.12 to 1.6%, S from 0.08 to 0.53%, Fe from 110 to 537 mg kg^{-1}, Mn from 33 to 810 mg kg^{-1}, Zn from 18 to 46 mg kg^{-1} Cu from 7.6 to 750 mg kg^{-1} and Mo from 0.23 to 2.6 mg kg^{-1}. The pepper yield also showed wide variations ranging from 0.10 kg to 8 kg vine^{-1}. The wide variation in soil and leaf nutrient composition and yield of pepper may be due to the wide variation in soil fertility, temperature, rainfall, elevation (Table 40), farmer's package of practices etc in different locations.

Table 40. Meteorological data of major black pepper growing areas

Location	Altitude (m) Above MSL	Rainfall (mm)	Rainy days (No.)	RH (%)	Temperature ^{0} C
Idukki	1100	2124	204	65-98	16.4 to 29.8
Wynad	975	2142	121	56-91	15.5 to 31.6
Coorg	1175	2899	132	83 - 95	14.3 to 32.4
Calicut	55	4069	132	45-94	23.6 to 35.7
Cannanore	95	4259	124	71-94	19.4 to 38.8

The survey showed that 57% soils and 13% leaf samples collected from typical pepper growing areas are deficient in zinc and 38% soil samples deficient in Mo. These findings would corroborate the findings of other workers on zinc nutrition.

Wide spread Zn deficiency in Indian soils is reported by many workers. (El Fouly *et al* 1984, Rathore 1992). Surveys in major spices growing tracts especially cardamom growing areas of Kerala, Karnataka and Tamil Nadu reported that 68% soils are deficient in zinc (Srinivasan *et al* 1998). Sadanandan *et al* (1996,1998) also stressed the importance of maintaining optimum soil and leaf nutrient status for increasing productivity of black pepper where zinc is one of the major components. Chauhan (1995) also reported that about 50% cultivated Indian soils are deficient in Zn and need Zn dressing in variable quantities for crop production. These findings underline the importance of zinc in pepper production.

5.4 Correlations of zinc with major, secondary, micronutrients and yield of black pepper

Studies on correlations of soil Zn with other nutrients, in locations of differential yield, revealed that soil available zinc was significantly and positively correlated with soil pH, exchangeable bases, base saturation, cation exchange capacity, organic carbon, Bray P, exchangeable K and Ca in high and moderate yielding locations. It is a fact that in high and moderate yielding locations high levels of pH, base saturation, organic carbon, CEC and Ca results in corresponding increase in all cations and hence available Zn status. At low yielding locations CEC, organic carbon and base saturation were in low ranges and correlations were non significant. Such correlations were reported by many workers (Arriechi and Ramirez 1997, Kanwar *et al* 1984, Mukopadhyay and Halder 1992). Significant correlations of available zinc with CEC, Org. C and clay content were reported by Singh *et al* (1999). Soil Zn was positively correlated with soil Cu at moderate and low yielding locations and not in high yielding locations. At high yielding locations Cu status was very high in soil solution due to the use of copper fungicides. This higher level of Cu might have produced antagonistic effect and hindered Zn^{2+} ion in soil solution by a shift in equilibrium in opposite direction. At moderate and low yield locations, both Cu and Zn status were comparatively low and hence they might have acted synergistically producing positive correlations. Similar results were reported by Saha *et al* (1996). Soil Zn was negatively correlated with available sulphur in moderate and low yielding locations. One possibility is that the excess sulphur might have formed $ZnSO_4$ salt with the available zinc in soil solution, which is highly soluble and leachable without chance of replenishment.

Studies on correlations of soil Zn with other nutrients in different altitudes revealed that soil zinc significantly and positively correlated with organic carbon, Bray P, exchangeable K, Ca and Mg in high elevation like Idukki, Coorg and Wynad. This is because at higher altitudes, organic carbon and base saturation are high and correspondingly the concentrations of soil zinc will increase, resulting in positive relations among them. Soil available zinc was positively correlated with total soil zinc in Idukki, Wynad and Calicut. Significant correlations and dynamic equilibrium among different fractions of Zn in red and lateritic soil was reported by Mete *et al* (1996). Khan *et al* (1997) also reported high correlations of DTPA extractable Zn , Cu, Fe, and Mn with their total amounts indicating a genetic relationship among them. Available zinc was positively correlated with pepper yield in Idukki area. The findings of Randhawa and Singh (1995) and Saravanan and Ramanathan (1988) confirm these facts. They reported increase in yield of crop due to Zn application in Zn deficient soils.

Leaf zinc was negatively correlated with leaf N in Coorg soil. Higher availability of N might have produced higher N uptake and hence more foliage and dry matter production, which might have caused reduction in leaf zinc due to dilution effect. It was reported that judicious application of N results in increased plant growth, which can dilute the Zn concentration and can cause Zn deficiency (Hemantharanjan 1996). It was found that leaf Zn significantly and positively correlated with leaf Mn and Cu at Idukki, Coorg and Wynad soils. This is because in place like Coorg and Wynad, the availability of these elements including zinc are high compared to low altitude areas, which would have caused higher uptake Synergic interactions between Cu and Zn, have also been reported.

5.5 Correlations of molybdenum with major, secondary, micro nutrients and yield of black pepper

Soil Mo was found to be correlated positively with organic carbon. This is because, higher organic matter status will contribute for molybdenum availability in soils. Soil Mo was found to be negatively correlated with exchangeable base, base saturation, exchangeable Ca, Mg, available Fe, Mn and Cu. Higher base saturation, exchangeable base, N, Ca, Mg, Fe, Mn and Cu concentrations will increase the availability of ions in the soil solution, which will reduce the availability of Mo due to the antagonistic effect of these nutrients in acid soil. Total soil Mo was found to be negatively correlated with soil pH and leaf zinc. Soil available Mo was negatively correlated with soil available Zn. This is because MoO_4^{2-} anions would predominate in near neutral soil pH where $Zn^{2'}$ ion concentration will be minimum due to formation of insoluble salts. Gupta and Potalia (1987) reported similar relation between zinc and Mo. In a green house study 10 mg kg^{-1} Zn application decreased Mo concentration by 73% and vice versa. Higher pH and P increased the solubility of MoO_4^{2-} ion in soil solution, which, in turn decreased due to the increased uptake by plant and due to leaching.

Leaf Mo was found to be significantly and positively correlated with soil exchangeable Ca and Mg in soil solution. This may be due to the fact that increases in Ca^{2+} and Mg^{2+} decrease H^+ ions and hence increase the soil pH. This in turn increases the concentration and hence uptake of MoO_4^{2-} anion, as molybdenum is absorbed by plants in anionic form. Similar correlations were also reported by other workers (Falke *et al* 1988, Vinay Singh *et al* 1995). Leaf Mo was found to be positively correlated with leaf P and Ca. This is due to the synergistic effect of these nutrients on Mo, which results in the formation of a complex phosphomolybdate anion, which is absorbed more readily by plants. Leaf Mo was found to be negatively correlated with leaf iron and pepper yield. Hechanova and Curayag (1987) reported decrease in yield of azolla due to Mo application. This is because excess Mo will enhance the assimilation of nitrogen and hence foliage and the excess foliage normally reduce pepper yield either due to low exposure of laterals to sunlight or due to excess dry matter production of leaves. Leaf Mo correlated negatively with leaf Fe and Zn. Similar antagonistic relations between Zn and Mo has been reported. This is because excess molybdenum would have increased nitrogen uptake and morphological growth producing dilution effects on the absorbed Zn and Fe. Further leaf Mo was found to be positively correlated with leaf N, P, Ca and Mg. Synergistic effects of Mo with N, P, and Ca are reported by several workers (Falke *et al* 1988). Increasing Mo concentrations might have increased N utilization due to its favorable effects on nitrogen metabolism and phosphomolybdate complex formations.

5.6 Adsorption-desorption and extraction of zinc and molybdenum in major black pepper growing soils

Adsorption studies in different black pepper growing soils showed that zinc adsorption was maximum at lower concentrations of applied zinc and increased with increasing concentrations of zinc. At lower concentrations, more surface area is available for adsorption, which gradually gets filled up and get saturated with increasing concentrations. Under such condition, precipitation may occur and all the soils behaved almost similarly. At low concentration, all the added metals were adsorbed regardless of solution pH whereas at high concentration, adsorption correlated positively with soil pH. It was reported that application of Zn simultaneously increased the equilibrium concentration, adsorption, percent saturation of adsorption capacity and supply parameter of zinc in all type of soils (Diatta and Koclakowski, 1998). Among the soils, adsorption was maximum in lower altitudes as that of Peruvannamuzhi and Cannanore, compared to that of higher altitude areas viz., Coorg, Idukki and Ambalawayal. This is due to the variation in clay content.

Study showed that adsorption of zinc in major black pepper growing soils though fit to both Langmuir and Freundlich isotherm, it is highly confined to Langmuir equation as indicated by high value correlation coefficients. Zinc adsorption maximum was highest for Thamarassery and least for Idukki soil. This is due to the variation in CEC, organic carbon, and clay content in these soils. It is reported that zinc adsorption in soils is confined to the linear form of Langmuir and

Freundlich equation (Dhane and Shukla, 1996, Krishnaswamy and Krishnamoorthy, 1991, Manjunathaiah *et al* 1992, Abbas *et al* 1996). Maximum adsorption capacity and bonding energy increases with increase in pH (Machado and Pavan, 1987). The difference in the content and nature of clay mineral and organic matter in soil might be the reason for difference in isotherm constant as stated by Ramanathan and Krishnamoorty (1976). Vasudeva and Ananthanarayana (1999) reported that raising the soil pH by liming would increase both the amount and affinity of zinc adsorption.

According to Krishnaswamy and Krishnamoorthy (1991b), soil texture, organic matter, and cation content influence Zn adsorption. It was reported that soil with high organic matter content had high Zn adsorption capacities (Muneera Siddiqui *et al* 1993). The dominant role of CEC, clay and organic matter content towards zinc sorption and desorption was reported by other workers also (Singh *et al* 1997, Rupa and Shukla 1998 and Cunha *et al* 1994).

Studies on the adsorption of applied Mo in major black pepper growing soils showed that at equilibrium concentration of 5 to 25 mg kg^{-1} Mo, Ambalawayal soil showed the lowest and Peruvannamuzhi soils the highest adsorption. Adsorption increased with increasing concentration of Mo in the soil. As in the case of zinc, molybdenum adsorption was fit to Langmuir equation as indicated by high value correlation coefficient. Adsorption was highest for Ambalawayal soil and least for Peruvannamuzhi soil. Goldberg *et al* (1996) reported from adsorption studies that molybdenum adsorption was higher for the oxide minerals having higher specific surface area and lower in crystalline minerals. According to Reddy *et al* (1997), adsorption of Mo is highly pH dependent. The variations in CEC, O.C, P, Cu status, clay content type of clay minerals in different black pepper growing soils are the reason for variations in adsorption.

Desorption of zinc either with 0.01M $CaCl_2$ and DTPA extract was found to increase with applied levels in all the experimental soils. Increasing levels of applied zinc increased water soluble and exchangeable fractions of Zn which in turn increases DTPA and $CaCl_2$ extractable Zn. Increase in Zn availability with increasing levels of zinc application was reported by several workers (Savithri 1978, Thenmozhi 1990)

Desorption was more with DTPA than 0.01M $CaCl_2$. DTPA has higher extracting capacities due to the chelating effect of acetic acid in addition to calcium chloride. Rupa and Shukla (1998) also reported that DTPA will extract relatively higher amount of Zn compared to $CaCl_2$. Antil and Dahiya (1986) reported that increasing application of Zn would increase DTPA extractable Zn. Desorption was found to vary in different soils. This is due to the difference in CEC, clay content, organic carbon status, and type of clay minerals present. For example, CEC was maximum in Pulpally soil and least in Thamarassery. Clay content was maximum in Peruvannamuzhi and least in Coorg soil.

Desorption of zinc by both DTPA and 0.01M $CaCl_2$ though fit to both Langmuir and Freundlich isotherm, it is highly confirmed to Freundlich equation as indicated by the high value of Correlation Coefficient. Desorption was maximum and was highest for Thamarassery soil and least for Idukki soil. This is due to the variation in soil physico-chemical property like clay, silt and sand content, organic matter and CEC status as reported by Rupa and Sukla (1998), Krishnaswamy and Krishnamoorthy (1991). At higher applied Zn, all soils behaved equally in desorption. This is because at a very high concentration of applied zinc, fixation site will be saturated in all the soils and the applied Zn will contribute directly to the soil solution zinc. With addition of increased amount of zinc, there was a simultaneous increase in the equilibrium concentration, adsorption, percentage saturation of adsorption capacity and supply parameter of zinc in all soils (Diatta and Koclakowski, 1998). The following finding will also support the variation in adsorption-desorption in different soils. Sakal *et al* (1988) reported that the depletion of soil available zinc will enhance with increasing soil fertility. It was reported that added Zn desorbed from Alfisol, slowly due to their greater fixing ability, compared to Inceptisols (Hazra and Biswapati Mandal 1996). Further, desorption of adsorbed Zn decrease with an increase in pH (Anjana Srivastava and Srivastava, 1990). Soil pH, CEC and Organic Carbon are the dominant soil variable, contribute towards sorption and desorption of zinc (Singh *et al* 1997, Cunha *et al* 1994). According to Ladonin (1997) trioctachedral montmorillionite, vermiculite, chlorite, and biotite showed highest affinity for Zn. According to Deopal and Sastry(1988) in alfisol of Kerala, zinc was preferentially sorbed throughout the range of surface coverage on both sodium and magnesium clays. Further Desorption decreases with rise in pH and became a trace at pH > 6.0.

5.7 Transformation and availability of applied zinc in black pepper growing soils

The Zn fractionation study in black pepper growing soils showed that out of the fractions residual fraction was the predominant one, where as water soluble + exchangeable, complexed and organically bound will form a small fraction. Applied zinc increased water-soluble + exchangeable fraction, and organically bound fraction to a smaller extent but that of complexed, carbonate amorphous oxide and crystalline oxide bound fraction to a moderately large extent, and increased the residual fraction to a very high extent in all the soils. This is in accordance to the results of Mandal and Mandal (1986). They reported that a larger fraction (44.6 to 71%) of the applied zinc found its way to the mineral pool leaving only 2 to 6.5 % and 3 to 22.4% in water soluble+exchangeable and organic complexed forms respectively. Soils having higher CEC retain higher proportion of the applied zinc in exchangeable and water-soluble form. A larger proportion of applied zinc will bound to amorphous and crystalline sesqui oxides due to their higher scavenging action for the element. Moreover, amorphous sesquioxides have greater ability to retain the trace metals due to their high specific surface area. Chandrasekaran and Kedlay (1988) reported that most of the total zinc in soil existed in the residual form, the amount of water-soluble exchangeable and complexed forms of zinc diminished due to crop removal, while addition of zinc to the soil increased these three forms considerably. Similar results were reported by Edward Raja and Iyangar (1986) and Murthy and Schoen (1987) where bulk of the native Zn (amounting to 86 to 90 %) was in the residual fractions strongly bound to the soil minerals, being not extractable by any of the reagents used for fractionation. The soils generally had negligible quantities of native Zn as water-soluble and very low amounts in exchangeable and complexed forms. Mandal and Mandal (1986) reported that major amounts of soil zinc were associated with the clay minerals fractions of the soils as residual fractions and that Zn associated with oxides and other primary and secondary minerals are relatively unavailable to plants.

Among the soils studied, it was found that Idukki soil contain maximum water-soluble + exchangeable fraction, Thamarassery soil had maximum complexed and organically bound, carbonate and amorphous oxide and crystalline oxide bound forms, where as Coorg soil had maximum residual fraction. This is because the equilibrium among different fractions is influenced by pH and concentration of other cations. Soils having comparatively low pH value contains a higher amount of water-soluble + exchangeable fractions. Cupric acetate extractable (complexed fraction) vary directly with organic carbon content of the soil. Crystalline and amorphous oxide bound fractions is related directly to the free Fe_2O_3 content of the soils. Pal *et al* (1997) reported that clay, organic carbon, CEC, and free Fe_2O_3 content influence availability of various zinc fractions. Acid soils contained greater amount of water-soluble and non-specifically adsorbed Zn, while those with neutral pH contained greater quantity of specifically adsorbed and residual Zn (Bogaez 1993).

Correlations of zinc fractions in major black pepper growing soils showed that, most of the Zn fractions viz., water soluble, exchangeable, complexed, crystalline and amorphous oxide bound and residual correlate significantly and positively among themselves. This is due to the dynamic equilibrium with each other in soil solution as suggested by Mandal and Mandal (1986). Decrease or increase in concentration of one fraction will adjust among themselves to keep the equilibrium. Further, these fractions were found to be significantly and positively correlated with DTPA and $CaCl_2$ extractable Zn and Zn uptake. Obviously, the Zn needed by plants is actually extracted by $CaCl_2$ and DTPA and they are related to zinc supplying capacity of soils. Edward Raja and Iyangar (1986) reported that complexed form is the major source of available zinc to plants in soil and that zinc strongly bound by organic matter and that associated with carbonates and other amorphous oxides are less available. Dahiya *et al* (1991) reported that different forms of Zn had positive significant correlations among each other and with Zn uptake. Many other workers reported similar correlation. (Dhane and Shukla 1995, Gowrisankar and Murugappan, 1998, Sen *et al* 1997, Mete *et al* 1996). When zinc is applied to soil from external sources, it undergoes transformation to various chemical forms, the nature and magnitude of which differ in different soils depending on their physico- chemical properties and environment. These fractions later attain equilibrium amongst themselves.

5.8 Response of black pepper to zinc for yield and quality

Under both green house and field conditions increase in levels of applied zinc increased the soil availability, leaf and berry concentrations of zinc. The optimum dose of zinc for pepper was found to be 6.2kg Zn ha^{-1} and then yield remained almost constant with further increasing levels. The soil of Coorg where field experiment was conducted is acidic, low in base saturation and CEC and deficient in Zn and medium to low in P and medium to high in K (Anon. 1997). In such soils the optimum concentration of Zn is 6.2 kg ha^{-1} to get higher yield as no further economic yield increases was noticed above 6.2 kg Zn ha^{-1}. Beyond optimum concentration by way of ion antagonism, and imbalances in the uptake of other nutrients might have reduced the yield. With increase in levels of zinc applications, there will be more than a proportional increase in the residual zinc fraction and that results in saturated crop response beyond a certain level of zinc application. According to Ananthanarayana and Vasudeva (1999) in a heavy rainfall agro climatic zones of Karnataka (where the field experiment on black pepper was carried out) application of $ZnSO_4$ @ 20 kg ha^{-1} in soil having DTPA extractable zinc 2.0 mg kg^{-1} produced maximum grain and straw yield of rice. According to them, though the DTPA extractable zinc is 2.0 mg kg^{-1} due to heavy rainfall in such area, zinc become deficient by hydroxide formation in addition to leaching loss. Under green house condition also increasing levels of zinc from 0 to 10 mg kg^{-1} increased soil, leaf and berry zinc status of bush pepper. The number of spike and yield was maximum at 5 mg kg^{-1} applied zinc levels. This is because, in zinc deficient soil where green house experiment was conducted, zinc might have produce beneficial effect up to 5 mg kg^{-1} and then become toxic and or antagonistic to other nutrients uptake as in the field conditions.

The quality viz. oleoresin and piperine content was found to be increased with increase in zinc levels, and was maximum at 5kg Zn ha^{-1} under field condition and at 5 mg kg^{-1} levels for potted bush pepper. Zinc might have enhanced the amino acid protein synthesis and hence increased the concentrations of oil, oleoresin and piperine in pepper. Increase in yield and quality of produce due to zinc application @ 5 to 10kg Zn ha^{-1} was reported by many workers in plantation crops (Balasubramanyan *et al* 1992, Eaorashvili *et al* 1991, Khera *et al* 1985, Joom *et al* 1984, Kumaresan *et al* 1985). It has reported that zinc is involved in many metallo-enzymes in plants. These enzymes, like carbonic anhydrase, play important role in photosynthesis. Zinc is also involved in the activation of protein synthesis through RNA and ribosome. These might be the reasons for getting improvement in yield and quality of black pepper due to zinc application.

5.8.2 Zinc use efficiency in black pepper

Under field condition, soil availability of zinc was maximum due to Zn-EDTA chelate application @ 2.5 kg Zn ha^{-1} rather than Zn+EDTA or $ZnSO_4$ alone. This is because zinc availability is high in chelated form of Zinc. In zinc EDTA chelate, leaching loss and fixation of zinc in soil will be minimum. Hence, Zn availability will be maximum. EDTA will increase Zn concentration in exchangeable form by solubilisation from organic matter fractions and converting to exchangeable fraction. Alvarez *et al* (1997) reported that chelating makes the Zn in soil solution available in more favorable form for uptake by plants. Application of $ZnSO_4$ alone or $ZnSO_4$+EDTA might have caused fixation of Zn in soil due to non-formation of chelate.The superiority of Zn-EDTA chelate was also reported by many workers (Mehdi *et al* 1990, Prasad and Sarangathan 1992, Ferrandon and Chamel 1998, Chatterjee and Mandal 1985).

Leaf and berry zinc concentration was maximum due to foliar application of 0.5% $ZnSO_4$ rather than 0.25% $ZnSO_4$ or 0.1% Zn EDTA chelate. This is because 0.5% $ZnSO_4$ will contain more zinc and absorption by leaf will be maximum in this rather than 0.25% $ZnSO_4$ or 0.1% Zn-EDTA. Response to foliar zinc as 0.5% $ZnSO_4$ or 0.1% Zn-EDTA was reported by many workers (Little More *et al* 1991, Pons 1996, Basso *et al* 1990, Arulmozhizhan *et al* 1993). Zinc sulphate is the extensively used zinc fertilizer, due to its higher water solubility and low cost, as reported by Rajkumar *et al* (1997). Brennan (1991) reported that foliar spray as Zn-EDTA increased yield of Wheat and Zn-EDTA was 1.4 to 1.7 times more effective than zinc sulphate.

Under greenhouse condition, application of foliar zinc @ 0.5% $ZnSO_4$ or soil application of Zn @ 2.5 mg kg^{-1} $ZnSO_4$ or Zn-EDTA chelate were on par with regard to pepper yield. The oleoresin and piperine content of black pepper also increased due to zinc application either as soil or foliar application as $ZnSO_4$ or Zn-EDTA chelates. The application of zinc might have increased its availability and uptake by pepper plants, which in turn might have helped in protein synthesis and hence quality up gradation as enhanced oleoresin and piperine. Geetha and Sivaraman Nair (1990) reported that foliar spray of 0.5% $ZnSO_4$ to black pepper increased berry volume and weight and reduced spike shedding by 48.4%. Foliar spray of 0.2 to 0.4% $ZnSO_4$ significantly increased growth, height, yield, and quality of betel vine (Anon. 1993). According to Arambari *et al* (1944), basic salts of Zn and Fe are as effective as the chelates and are more environmentally safe. Brennan (1991) reported that foliar spray of Zn-EDTA or $ZnSO_4$ increase the yield of maize, however Zn-EDTA was more effective. Modalish (1990) reported that the rate of zinc diffusion and zinc extractability were considerably higher with Zn-EDTA than with $ZnSO_4$ fertilizer. Increases the yield of pepper due to micronutrients were also reported from Malaysia (Anon. 1989, 1990). The present findings also support the need for zinc application for better yield and quality of black pepper either as chelated forms or as zinc sulphate, but chelated form is costlier compared to other source. Similarly, though foliar application can correct zinc deficiency, soil application is practical for black pepper.

5.9 Response of black pepper to Molybdenum

Soil, leaf and berry concentration of Mo increased with increasing Mo application. This is due to the increased availability in soil solution and hence its uptake by black pepper. Application of Mo was also found to increase yield and quality of black pepper. From the response function worked it was found that Mo @ 0.9 kg ha^{-1} as sodium molybdate is optimum for economic yield. Application of Mo might have increased the uptake and hence growth and better N utilization for amino acid and protein synthesis. Further, the location where field experiment was conducted, the soil is acidic and high in Cu status (due to continuous drenching and spraying of copper fungicides) and there may be chance of molybdenum deficiency, response to applied molybdenum. For bush black pepper, in green house condition, increase in Mo level has increased soil, leaf, and berry concentration. In pots molybdenum @ 0.25 mg $kg^{-1}$was found to be optimum. The green house experiment conducted in a molybdenum deficient acidic soil, and hence responded to the applied molybdenum. The reduction in yield beyond 0.9 kg ha^{-1} might be due to the toxic effect of molybdenum at higher levels as reported by Hunashikatti *et al* (2000). They also found that increase in protein and ascorbic acid content of cabbage due to involvement of molybdenum in nitrogen metabolism and synthesis of ascorbic acid. Many workers reported similar results of increasing yield and quality of crops. (Adams *et al* 1990, Pradhan and Sarkar 1985, Nayak *et al* 1989). Alluvial acidic soil responds very well to Mo application. Jongruaysup *et al* (1994) reported good response to Mo in sandy loam soil. Significant increase in yield and quality through increase in oil, protein, vitamin C and sugar content due to Mo application has been reported by many workers (Guseva, 1991, Cheng 1994, Dey and Ghosh 1986, Tomar *et al* 1990, Verma *et al* 1988).

5.9.2 Molybdenum use efficiency in black pepper

Under field condition, soil availability of Mo was maximum due to 0.5kg Mo + lime @ 0.5 t ha^{-1} (half the lime requirement to get 6.5 pH). However individual application Mo @ 0.5 kg ha^{-1} or liming @ half lime requirement were found to be on par. This is because liming might have increased the soil pH and hence Mo availability, as Mo is the nutrient element absorbed by plants in anionic form viz., MoO_4^{2-}.Maximum leaf and berry Mo was recorded in 0.2% foliar molybdenum application followed by 0.1% foliar molybdenum. The yield of pepper was maximum due to lime application @ 0.5 t ha^{-1} and was on par with 0.5 kg Mo ha^{-1}. The contribution of Mo to pepper either due to 0.5 kg Mo or due to increased availability of Mo by lime might be the same.

Under the field condition, the maximum oleoresin and piperine was recorded due to the application of 0.5 Kg Mo ha^{-1} followed by 0.5 kg Mo + lime. Piperine content was maximum for 0.5 kg Mo application. The B/C ratio was highest for lime alone treatment followed by Mo @ 0.5 kg ha^{-1}. Gupta (1997) reported that Mo could be applied as seed treatment, soil application or as foliar spray. As the Mo requirement of plants is very small, application of Mo even as low as 0.5 Kg ha^{-1} or liming alone might have contributed sufficient Mo in soil solution for plant requirement.

Bush pepper under greenhouse condition also behaved in more or less similar to that of field pepper with regard yields and soil Mo availability. Mo application @ 0.5 mg kg^{-1} was on par with 0.25 mg kg^{-}1 Mo applied with lime. The leaf and berry Mo content was maximum due to 0.2% foliar application, followed by 0.5 mg kg^{-1} Mo as soil application. Dhankar *et al* (1993) reported that acid soils are apt to be more deficient in Mo. Sulphur and Mo had antagonistic effect on each other with respect to concentration, uptake and utilization. Molybdenum is absorbed by plants in the form of MoO_4^{2-}. The increase in molybdenum availability in acid soils by liming is because of exchange of MoO_4^{2-} and $HMOO_4^-$ anion for OH group of clay. Hence, molybdenum requirement of plants can be met by liming the soil (Anderson 1956). Lindsay (1972) stated that MoO_4^{2-} concentration increase 100 fold for each unit increase in pH. Adams (1990) also reported response of crops to liming without Mo application. Dey and Ghosh (1986) reported significant increase in yield of crops due to lime and molybdenum application. Organic fertilizers like FYM will also contribute to the availability of micronutrients in soil. Molybdenum is normally required for N-metabolism in plants. Adequate availability of Mo could lead to increased N metabolism resulting in increased protein, amino acids, and oil production in black pepper. Increase in oil, oleoresin and protein due to increased Mo availability either due to liming or molybdenum application as soil/foliar, was reported by many workers in many crops (Dey and Ghosh 1986, Hiev and Ivanin 1988, Sharma and Minhas 1988, Sasirekha *et al* 1998) The experiment on black pepper was carried out in a molybdenum deficient acid soil. Hence, molybdenum application at 0.9 kg ha^{-1} has enhanced the yield and quality of black pepper in the experimental field.

SUMMARY AND CONCLUSION

6. SUMMARY AND CONCLUSION

Black pepper (*Piper nigrum* L.) is one of the important spice crops of India, which contributes to the economy of India as foreign exchange earner (Rs. 865 crores in 1999-2000). The productivity of black pepper is lowest in India compared to competing countries *viz.*, Indonesia, Brazil, Malaysia, and Thailand. The reason for low productivity is attributed mainly to poor nutrition and improper management practices. Research work on nutrition of black pepper, especially that of zinc and molybdenum is very scarce.

Black pepper is mainly grown in Kerala and Karnataka (Coorg district), where the soils are acidic and deficient in zinc. Mo is also deficient as its availability decreases with increase in acidity of soil. In addition, constant use of copper fungicides against *Phytophthora* disease of black pepper and the acidity of soil, aggravates the situation due to antagonistic behavior of sulfur and copper on Mo uptake. Keeping these views, the present investigation was conducted with the following objectives.

- Evaluation of total and available Zn and Mo in major black pepper growing soils and their relation ship with other nutrients and yield.
- To find out the soil site suitability for black pepper production
- Studies on the adsorption desorption dynamics and transformation of applied Zn and Mo in major black pepper growing soils.
- To find methods of increasing availability of Zn and Mo in soils for black pepper through application of amendments
- Determination of optimum level of Zn and Mo fertilizers for increasing yield and quality

The results of the investigations are summarized below under the following heads

Survey

- The survey carried out in the major pepper growing areas in 130 gardens showed that 57% of the soils and 13% of the leaf samples are deficient in Zn. Thirty eight percent of soils were deficient in molybdenum. The yield assessment revealed that 22% of the gardens had less than one kg berry yield per vine. The soils were acidic, medium in organic carbon, P, K, Ca and Mg and high in S, Fe and Mn status.

- A critical assessment of the pepper growing areas revealed that there is a wide variation in soil physicochemical properties and yield among the lower and higher elevated areas. Higher elevated areas that favor better yield are having higher sand fractions, organic carbon, CEC, base saturation, and nutrient status.

- Soil site suitability evaluation of major black-pepper growing areas showed that high yielding areas have pH near neutral, higher sand and silt fractions, exchangeable base, base saturations, CEC, organic carbon, major, secondary and micro nutrients except sulphur, and clay content compared to low yielding locations. The acidity of the soil, low status of major, secondary and micro nutrients especially zinc and high status of Mn were found to be some of the causes for low productivity of black pepper.

- Assessment of soil nutrient status in the soil profiles of major black pepper growing areas showed that top soil contains comparatively higher amount of sand and silt fractions, base saturation, extractable bases, CEC, organic carbon, major, secondary and micro nutrients, compared to bottom layers.

Transformation and availability of applied zinc in black pepper growing soils

- Zinc fractionation studies showed that there exists a dynamic equilibrium among different forms of zinc in soil solutions. They are correlated positively among themselves and with soil available zinc. The availability of different fractions of zinc in different soils follows more or less the order, carbonate and amorphous oxide bound Zn > complexed Zn > crystalline oxide bound Zn > water-soluble + exchangeable Zn.

- Incubation studies of zinc in different soils showed that, at lower levels of zinc, DTPA extractable Zn was maximum in Idukki soil, followed by Ambalawayal, Coorg and Thamarassery soils, and least in Peruvannamuzhi soil. At higher levels of zinc, application, Thamarassery, Ambalawayal and Idukki soils showed similar behavior and recorded maximum availability.

Adsorption-desorption studies

- Zinc adsorption increased with increase in levels of Zn application and more confined to Langmuir equation than Freundlich equation.

- Percentage desorption of adsorbed zinc decreased with increasing adsorption and more confined to Freundlich equation than Langmuir equation

- Desorption of Zn by DTPA was higher than that with 0.01 M $CaCl_2$

- Adsorption-desorption of Zn was found to vary from soil to soil depending on soil pH, CEC and clay content.

Zinc and molybdenum deficiencies in black pepper

- Zinc deficiency is characterized by interveinal chlorosis of young leaves, retardation of the growth of terminal shoots, shortening of internodal length resulting in chlorotic little leaves appearance which on advanced stage gave rosetted appearance. Zinc concentration in deficient stem was less by 42%, in leaves by 60% and in berries by 53% compared to healthy vines.

Response of zinc and molybdenum on yield and quality of black pepper

- In zinc deficient soils as that of Coorg, application of Zn @ 6.2 kg ha^{-1} as zinc sulphate to black pepper was optimum producing a yield increase of 25%.

- For bush black pepper application of Zn @ 5 mg kg^{-1} of soil was optimum and recorded 31% increase in yield.

- The quality of black pepper (oleoresin and piperine) increased due to Zn application. The increase in oleoresin and piperine content were 6.7 and 7.1% respectively over no zinc application.

- In molybdenum deficient soils, application of Mo @ 0.9 kg ha^{-1} as sodium molybdate to black pepper was optimum and produced 14.2% increase in yield. There was 6.1% increase in oleoresin and 7.5% increase in piperine over control.

- For bush black pepper application of Mo @ 0.25 mg kg^{-1}soil was optimum

Zinc and molybdenum use efficiency in black pepper

- Studies on the use efficiency of zinc showed that, soil application of Zn as Zn EDTA chelate was better than application of $ZnSO_4$ alone and produced 56% increase in soil and 20% increase in leaf Zn over $ZnSO_4$.

- Foliar spray of 0.5% $ZnSO_4$ produced maximum leaf and berry zinc status in black pepper.

- Foliar application of 0.2% sodium molybdate produced maximum leaf and berry Mo content.

- Studies on the effect of different amendments to increase Mo availability in soil showed that application of half ton lime followed by Mo @ 0.5 kg ha^{-1} produced maximum soil Mo availability.

Correlations

- Correlation studies of Zn with other nutrients in soil showed that soil Zn is significantly and positively correlated with base saturation, CEC, organic carbon and exchangeable K, Ca, Mg and total zinc status of soil. The Soil Zn significantly and positively correlated with black pepper yield.

- Leaf Zn significantly and positively correlated with soil available sulphur, zinc, leaf manganese, and copper and negatively with soil pH, exchangeable magnesium, and leaf nitrogen.

- Soil Mo significantly and positively correlated with soil organic carbon and exchangeable K and negatively correlated with Fe, Mn, Zn and Cu. Total soil Mo is correlated positively with soil lime requirement, organic carbon, exchangeable K, available S, Fe, Mn and Mo. Leaf Mo significantly and positively correlated with leaf N, P, Ca and Mg and negatively with leaf Fe and Zn.

The study revealed the importance of zinc and molybdenum in nutrition of black pepper and suggests further line of study in following aspects

- Development of a theoretical basis for understanding the equilibrium relationship of zinc and molybdenum on other metal chelating agents and natural organic complexes in soils, that may provide sound basis for understanding and interpreting the behavior of chelating agents in soil and their effect on availability and yield.

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