Forms of manganese in soils:

Under present investigation, total Mn in the soils of Meerut and Saharanpur regions of Uttar Pradesh ranged from 115 to 240 mgkg⁻¹ with an average value of 179 mgkg⁻¹. These values are fairly comparably to the results reported by Randhaya et al. (1961) Mehta and Patel (1967), Mishra and Tripathi (1972), Singh (1978), Joshi et al. (1981), Saha et al. (1982) and Sharma and Yadav (1986) for total Mn in different Indian soils. According to Swaine (1955) the total content of Mn of most soils lies in the range of 200 to 3000 ppm. Kanwar and Randhawa (1974) while reviewing the work done on various aspects of micronutrients in soils and plants, stated that total Mn in most of the Indian soils varies from 250 to 1600 ppm. In the present study, the soils of Meerut and Saharanpur region showed variation in their contents to total Mn. These variations have most probably arisen due to difference in the local factord in relation to soil genesis, soil climate conditions including texture and cropping system. It seems most likely that high total Mn content of Muzaffarnagar district soils may be due to the lower CaCO₃ content as evident from negative correlation between total Mn and CaCO₃ content. A non significant and negative correlation between total Mn and soil pH was noticed in this study. Joshi et al. (1981) and Singh et al. (2003) also reported similar results. Total Mn was found to be significantly and positively correlated with soluble salt concentration in these soils. It also showed significant and positive correlation with organic carbon content. (Singh et al. 2003)

The water soluble Mn content in these soils ranged from 1.15 to 8.2 mgkg⁻¹. The mean values of water soluble Mn for soils of Ghaziabad,
Meerut, Muzaffarnagar and Saharanpur district were 4.24 4.13, 4.87 and 4.44 mgkg$^{-1}$, respectively. These values are in close agreement to the results reported by Agarwala (1963, 1964) and Mishra and Tripathi (1972) for soil of Uttar Pradesh. A close scrutiny of the data also reveals that appreciable amount of Mn was present in water soluble form usually in soils having low, $P^H$, low amount of CaCO$_3$ and higher amount of organic matter. These soils having $P^H$ greater than 4 and/or more than 2% CaCO$_3$ were often found to possess small amounts of Mn in water soluble state which may be ascribed to the conversion of divalent Mn in to insoluble higher oxides of Mn at higher pH (Leeper, 1947, Sharman and Harmer, 1952) and fixation of soluble Mn on the surfaces of CaCO$_3$ particles as postulated by Boischat and Durroux (1949). Water soluble Mn had significant and negative relationship with pH, EC and CaCO$_3$ content of the soils. On the other hand, it showed significant and positive correlation with organic carbon. Water soluble Mn also showed significant and positive correlations with exchangeable and active forms of Mn.

Exchangeable Mn varied from 1.20 to 2.30 with an average value mgK$^{-1}$. Nevertheless, form point of view of availability to plants, some of the samples, can be rated as deficient in Mn because some samples analysed in this investigation contain less than 1.2 mgkg$^{-1}$ of exchangeable Mn. According to Sherman and Harmer (1942), Mn deficiency in crops in likely to occur on soils which contain less than 3 ppm of exchangeable Mn. The value of exchangeable Mn reported in the present study are fairly comparable to the value reported by Randhawa et al. (1961), Vinayak et al (1967), Mehta and Patel (1967), and Mishra and Tripathi (1972) for soils of Punjab, Kaira district of Gujarat and Uttar Pradesh. Among different district of Meerut and Saharanpur regions the soils from Muzaffarnagar were observed
to be relatively rich in exchangeable Mn. Total Mn has significant bearing on
the level of exchangeable Mn in these soils. Exchangeable Mn did not show
any significant relationship with pH, EC and CaCO$_3$ content of the soils.
Gupta and Shukla (1975) also did not observe any relationship between
exchangeable Mn and CaCO$_3$ content of the soils. It showed significant
and positive relationship with organic carbon content of the soils. Mehta
and Patel (1967) and Mishra and Tripathi (1972) also found a positive
correlation between these two variables.

Easily reducible Mn was found to be the dominant Mn fraction in
these soils accounting for 42.2 percent of average active Mn. This was quite
expected since the distribution of Mn fractions is largely pH dependent
(Leeper, 1947, Sherman and Harmer, 1942) and soils under study had
mostly neutral to alkaline reaction which favours the formation of various
oxides of tri and tetravalent Mn (Dion and Mann, 1946, Leeper, 1947, Jones
and Leeper, 1951). On an average, reducible Mn forms 22.3% portion of
total Mn in these soils. A comparative study of Mn and reducible Mn
indicates that soils rich in total Mn possess abundant quantities of reducibles
Mn, the correlation coefficient between these two being significant
($r = 0.421$). As such soils of Muzaffarnagar and Saharanpur soils were
found to be richer in reducible Mn as well as total Mn as compared to soils
of other tehsils of the district. Regarding the impact of pH, EC organic
carbon and CaCO$_3$ it was found that only organic carbon was found to be
correlated significantly with reducible Mn. There existed no relationship
between reducible Mn and pH, EC and CaCO$_3$ contents of these soils.

Active Mn is the sum total of water soluble, exchangeable and easily
reducible Mn and it is often described as a function of total Mn (Leeper,
1947, Biswas, 1953). This relationship was clearly manifested by the soils of Meerut and Saharanpur regions of Uttar Pradesh. The statistical methods used to verify this contention indicated that there exists a significant and positive relationship between these two \( r = 0.603 \) variables. Active Mn also had significant relationships with all other forms of Mn studied in the present investigation. It was also found to have significant and positive correlation with soil pH, EC and organic carbon. On the other hand, it showed significant and negative relationship with CaCO\(_3\) content of the soils.

Under present investigation, DITA - extractable Mn in these soils ranged from 3.2 to 30.0 mg kg\(^{-1}\) with an average value of 13.6 mg kg\(^{-1}\). Mann et al. (1977) while working with soils of Sangrur district, gave the range and average and of manganese as 1-8-30.0 ppm and 10.54 ppm respectively. According to Saha et al. (1982), the range and average of DTPA - extractable Mn in Jute growing areas of Assam and West Bengal were 10 to 86 ppm and 38 ppm, respectively. Singh and Tripathi (1983) while working on citrus growing soils of Agra region reported 7.2 to 32.0 ppm DTPA-Mn. A comparison of the values of Mn obtained in the present study and that of Punjab, Assam and Agra region, shows that the range of variation in DTPA extractable Mn was wider in Assam and West Bengal soils. The soils in the present investigation showed higher average values of Mn as compared to the soils of Sangrur district in Punjab. The values of DTPA extractable Mn obtained in present study were comparable to that of citrus growing soils of Agra region. Follett and Lindsay (1970) have suggested 1.0 ppm. DTPA - extractable Mn as critical limit below which deficiency of Mn may appear for various crops. It is noted that in the present investigation some of the soil samples contained Mn in amount less than the critical
value. Contrary to our findings, Takker et al. (1976) reported manganese deficiency in Sangrur and Gurdarpur districts of Punjab. Katyal and Sharma (1979) have reported that out of 30382 soil samples collected from states of India about less than 1% of the samples were Mn deficient. Singh and Tripathi (1983) reported that citrus growing soils of Agra region were adequate in Mn. The soil samples collected from Muzaffarnagar district were found to contain relatively higher concentration of DTPA - Mn than the soils of other district of the two region. As known DTPA- extractant extracts from the soils chelated or complexed from of Mn whose amount in the soils would depend on soil pH, organic carbon content, CaCO₃ and clay content. A reference to table 4.4 indicate that DTPA-Mn showed significant and negative correlation with PH. Singh and Tripathi (1983), Singh et al. (1983) Bhardari and Rathore (1985) Prashad and Sahi (1989) and Singh et al. (2000) also reported significant and negative correlation between soil-pH and DTPA-Mn. It had positive relationship with total Mn content (Rawat and Mathpal, 1981, Saha et al. , 1982) and soluble salt concentration. The available Mn showed significant and negative correlation with CaCO₃. Rai et al. (1977) also reported similar realtionship between these two variables. It had significant and positive correlation with organic carbon. Joshi et al. (1981), Singh and Tripathi (1983) and Sharma et al. (1985) also reported similar results.

**Extraction of manganese by different methods:**

The capacity of various extractants to extract manganese differs considerably because of the fact that the amount of manganese extracted depends on the nature of reagent contact/shaking time. The various chemical soil test methods employed to assess Mn viz. Water soluble, exchangeable or adsofbed, chelated or complexed forms.
Among six extractants, $\text{NH}_4$, $\text{H}_2\text{PO}_4$ extracted the higher quantity of manganese from soils (Table 4.7 and 4.8). This is due to presence of $\text{H}_2\text{PO}_4$ ion which solubilizes some additional amount of soil-Mn, besides, exchangeable and acid hydrolyzable organic forms (Larsen, 1956, 1964). This reagent is buffered at a higher PH and also has much higher strength (3N) and thus values of available Mn obtained with this extractant were greater than 0.1N $\text{H}_3\text{PO}_4$. Hammes and Berger (1960a) suggested that if soil-Mn extracted with 0.1 $\text{NH}_4\text{PO}_4$ or 3N $\text{NH}_4\text{H}_2\text{PO}_4$ was less than 20 ppm, Mn $\text{NH}_4\text{OAC}$ and Mg (NO$_3$)$_2$ are believed to extract mainly divalent form of Mn viz. Water soluble and exchangeable (Page-1964). DTPA extracted greater amount of soil-Mn than N $\text{NH}_4\text{OAC}$ (PH 7) extracted the minimum amount of Mn from soil. The close relationships among extracting solutions indicate that different solutions had solubilized same forms of iron of manganese to different degrees.

Statistical analysis of the data to determine the extent of relationship between Mn uptake by oats and level of available Mn in soils as determined by 6 chemical extractants indicated that DTPA is superior to all other five reagents. The method employing this extractant also showed highest correlation with percent yield of oats. In view of these, DTPA can be considered to offer the best index of Mn availability in soils of Muzaffarnagar district. Lindsay and Norvell (1969) and Dhane and Shukla (1995) also reported DTPA method as a best method to predict Mn availability. Gajbhiye et al. (1984) also reported similar results. Deci-normal phosphoric acid also showed highly significant relationship with percent yield and Mn uptake by oats. View of good correlations between 0.1N $\text{N}_3\text{PO}_4$ and Mn uptake and percent yield of oats, it is fairly reasonable to believe that this method can
also serve as satisfactory for the appraisal of available Mn. Hammes and Berger (1960a, 1960b) also reported that 0.1NH₃PO₄ method is the most reliable and obtained by Hoff and Mederski (1985) showed that 0.1N H₃PO₄ method provided an equally good measure of Mn availability in soils of Ohio. Mishra and Tripathi (1971) also made similar observations. Under present investigation, 3N NH₄H₂SO₄ which has been claimed by Hoff and Maderski (1958) and Mehta and Patel (1969) as most suitable extractant was found to be of limited applicability in these soils as it showed lower degree of correlation with Mn uptake and percent yield of oats. These results are in agreement with the findings of Mishra and Tripathi (1971). The soil manganese extracted by 1N NH₄OAC did not show any significant relationship with percent yield of oats. Thus it can be outrightly rejected for the present group of soils.

**Critical limits of available soil Mn:**

Since the highest correlations were recorded between DTPA extractable manganese and percent yield and uptake of manganese by oat crop, attempts have been made to fix the critical limits as per cate and Nelson (1965) procedure. The critical limit of available manganese (DTPA-extractable) was found 11.1 ppm (Fig-4.23). Lindsay and Norvell (1978) reported 1 ppm DTPA-extractable manganese as critical limit for demarcating the manganese responsive from soil. All the soils giving value below this critical limit responded markedly to Mn application. Critical limit of 2.65 ppm DTPA - extractable Mn have been reported by Katyal (1985). The critical limit of available Mn (0.1NH₃PO₄ extractable) was 16.3 ppm (Fig-4.23). The critical limit for plant Mn content was 68.2 ppm (Fig-4.24).
Phosphorus - manganese interaction:

The results obtained from the field experiment, described in the preceding pages, indicate that green foliage and dry matter yield of oat crop increased significantly with the application of manganese. The increases in dry matte yield of oats due to 10, 20 and 40 ppm Mn over control were 11.4, 21.0 and 13.7 per cent, respectively. Responses to Mn application in oats have also been reported by Singh and Pathak (1968), Mishra and Tripathi (1973) Sakal et al. (1981) and Datiya et al. (1990). The highest dose of Mn (40ppm) failed to produce additional yield of dry matter as compared to 20 ppm Mn addition. The green foliage and dry matter yield of oats also increased significantly with the addition of phosphorus to soil. The percentage increases in dry matter yield with 25, 50 and 100 ppm phosphorus addition were 22.8, 37.4 and 26.6 over control, respectively. The highest yield of oat was recorded with 50 ppm phosphorus application. Singh and Raina (1981) Malik and Singh (1994) also reported an increase in yield of oat with phosphorus application. The interaction effect of P x Mn was found to be significant (Fig - 4.5) and the maximum dry matter yield was recorded with 50 ppm P and 20 ppm Mn treatment. The higher levels of P and Mn failed to produce higher yields.

The nitrogen concentration in oat plants decreased significantly with Mn and P addition. However, a slight increase in N content was noted with 10 ppm Mn addition. The increasing levels of P depressed the concentration of N at all the levels of Mn. Similarly higher levels of Mn also tended to decrease N content showing an antagonistic effect of higher levels of Mn on the absorption of N by plants. The concentration of P in oat plants increased significantly with its application. Pathak et al. (1972) and Mishra and Tripathi
(1973) also reported that the applied P had a favorable effect on its content in oat plants. On the other hand, the application of Mn tended to decrease the P content in oat plants significantly as also reported by Singh and Raina (1981). The increased levels of Mn decreased P content of oats at all the levels of P. This was possibly due to antagonistic relationship as evident by significant interaction between P and Mn (Fig - 4.6). Application of Mn progressively enhanced its concentration in oat plants. Mishra and Tripathi (1973) and Singh and Raina (1981) also reported similar results. The phosphorus applications reduced the content of Mn in oat plants significantly as also reported by Singh and Raina (1981). The phosphorus application reduced the Mn content of oat plants irrespective of the presence of absence of Mn which showed an antagonistic relationship. The phosphorus application increased P/Mn ratio in oat plants. With the addition of Mn, this ratio decreased over that in control. The critical P/Mn ratio for oat plants was 35.0 (Fig - 4.7).

The utilisation of nitrogen by oat plants was enhanced with lower level (10ppm) of manganese addition significantly. But higher levels of Mn addition declined N uptake significantly over control. Nitrogen uptake by oat plants increased significantly with the addition of phosphorus. The per cent increased in nitrogen uptake by plants with 25, 50 and 100 ppm P levels were 21.2, 33.2 and 10.1 over control, respectively. Singh and Raina (1981) Malik and Singh (1994) also made similar observations. The interaction between P and Mn had a significant effect on the utilisation of N by oat plants and maximum value N uptake was recorded with 50 ppm P and 10 ppm Mn treatment. The higher values of Mn showed an antagonistic effect on the uptake of N by oat plants. The applications of phosphorus to the levels of manganese addition. Singh and Raina (1981) and Malik and Singh
(1994) also reported an increase in P uptake with its addition. The lower levels of manganese (10 and 20 ppm) increased phosphorus uptake by oat plants significantly. But highest level (40ppm) declined P uptake significantly over control. Increasing rates of phosphorus fertilisation enhanced the utilisation of manganese by oat plants. On the basis of these results it may be concluded that phosphorus addition augmented Mn absorption by the plants as evident from the values of Mn uptake. Similar results were also reported by Page et al (1963), Larson (1964), Mishra and Tripathi (1973), Singh and Raina (1981) and Singh (2001). Manganese uptake was also increased with increasing levels of Mn addition to soil. Higher values of Mn uptake with increasing rates of Mn are apparently the results of favourable effect of these treatments on Mn absorption coupled with greater dry matter production. Singh and Raina (1981), Malik and Singh (1994) also reported similar results. The interaction between P and Mn was also found to be significant. The maximum uptake value of Mn uptake by oat plants was recorded under 50 ppm and 40 ppm Mn treatment.

Potassium - Manganese:

The green foliage and dry matter yield of Oat crop increased significantly with the application of manganese. These results are in agreement with the opinion of Pandey et al.(2001), Tomar et al. (2001), Singh and Pathak (2002), Singh and Singh (2002) and Singh et al.(2003).

The nitrogen concentration in Oat plants increased with increasing levels of potassium. Similar results were also observed by Tomar et al. (2001). The nitrogen content of Oat increased with increasing levels of Mn as compared to each preceding lower levels of Mn. Similar results were reported by Singh (1996). The concentration of P increased with each
higher level of potassium. The maximum phosphorus content was observed with 100 ppm level of potassium. Similar results were observed by Tomar et al. (2001). Phosphorus content increased with increasing levels of Mn similar results were reported by Sharma and Singh (1999). Potassium content increased with increasing levels of potassium and Mn also. Similar to these findings were also reported by Tiwari (2001), Tomar et al. (2001), Singh and Singh (2002). The concentration of Mn in Oat plant increased with increasing levels of potassium and manganese. Similar findings were also reported by Sharma and Singh (1999) and Maibaum and Orlovivs (2001).

The utilization of N by Oat crop increased significantly with increasing levels of potassium in comparison to control. These results are in accordance with those of Pandey et al. (2001) and Singh and Singh (2002). In case of nitrogen uptake by Oat crop the further reveal that the each higher level of Mn resulted more uptake of N by Oat crop was recorded at highest levels of manganese Mn 3 (40ppm) as compared to control. Similar results were observed by Singh (1994) and Sharma and Singh (1999). The potassium application significantly increased the phosphorus uptake by Oat over control and proceeding lower levels of potassium. Similar to these finding pandey et al. (2001) and Verma and N and Ram (2003). The manganese application influenced the utilization of potassium by Oat. The uptake of potassium increased significantly with increasing levels of manganese in comparison to control. Similar results were also noted by Sharma and Singh (1999). The uptake of manganese increased with increasing levels of potassium. It might be concluded from the finding that the increased uptake of manganese by Oat crop due to potassium application is attributed to enhanced dry matter production and an increase in manganese content. A further study of manganese utilization by Oat crop increased significantly with increasing
levels of manganese. Each higher level of manganese resulted more significant utilization of manganese in comparison to control and preceding lower level of manganese. Similar to these findings Singh and Singh (1995) and Singh (1996).