CHAPTER IV

SOIL GEOCHEMICAL SURVEY

INTRODUCTION : The popularity of residual soil surveys as an exploration method is simple reflection of reliability of soil anomalies as ore guide. Wherever, the parent rock is mineralised, some kind of chemical imprints is mandatory in the residual soil, that results from the weathering of bed rock. Weathering can be chemically described as that the processes of dissolution, hydration, hydrolysis, oxidation, reduction and carbonization of primary mineral. All these processes are based on rules of entalphy and entropy and they lead to the formation of secondary minerals and components that are in the state of equilibrium in the surfacial environment.

Rose et al. (1979) reveiwed the usefulness of soil geochemical exploration in identification of base metal and molybdenite deposits and stated that in the secondary environment a geochemist plays diametrically opposite games of exploration. Using the stream sediment geochemical surveys a geochemist identifys a fugitive indicator element and makes a coarse with arrows of higher values towards some hypothetical source of mineralization. While in the soil surveys the higher values are assumed to be insitu and the anomalies in the soils are close to the target.

Soil samples were collected in the present investigation to evaluate the secondary geochemical 'patterns, associated with sulphide mineralisation in Koheda area. The technique of sampling in given in detail in chapter II. The elements analysed from the minus 80 fraction of soil samples are Cu, Pb, Zn, Ni, Cr, Co, Mo, W, Fe and Mn. The reason for selectively analysing these suite of elements is due to their geochemical affinity, association with base metal and molybdenite mineralisation. Apart ,from these facts, it was felt that the investigation must be cost effective. The details of analysis and geochemical data is furnished in the Table 2.3 of chapter II.

ASSOCIATION OF ELEMENTS : The statistical information of soil geochemical data is given in the Table 4.1. The table provides information about the average, standard deviation and threshold values of the elements analysed from the soils of Koheda area.

As stated in the preceeding chapter, the simplest procedure for correlating multivariate data is to generate the matrix which contains the correlations between all possible pairs of elements being considered. Thus to evaluate the elemental association in soils over molybdenite - copper mineralisation of Koheda area, correlation coefficients were calculated and are given in Table 4.2.

Based on the significant level of correlation being plus 0.5 the groups derived from the Table 4.2 are as follows

Table No. 4.1 : Shows a comprehensive statistical information of geochemical analysis of soils from Koheda area.

Sr.No.	Element	Range (ppm)	Average (ppm)	Standard Deviation (ppm)	Threshold (ppm)
1	Fe	22430 - 82080	39085.33	15826.58	70738.51
2	Mn	110 - 590	191.37	53.26	297.90
3	Ni	22 - 618	42.29	10.63	63.57
4	Cr	32 - 219	58.26	16.35	90.98
5	Co	6 - 28	11.04	3.91	18.86
6	Cu	22 - 1160	54.31	18.99	92.31
7	Pb	26 - 349	41.21	9.45	60.11
8	Zn	27 - 2700	41.81	12.93	67.67
9	Mo	5 - 72	17.62	11.52	40.67
10	W	10 - 80	23.41	9.73	42.87

Table No. 4.2 : Shows the correlation coefficient matrix of the elements analysed in soils from Koheda area.

	Cu	Pb	Zn	Co	Cr	Ni	Fe	Mn	Mo	W
Cu	1.000	0.180	0.657	0.038	-0.018	0.322	0.075	-0.040	0.234	-0.072
Pb	-	1.000	0.207	0.419	0.695	0.161	-0.057	0.076	-0.004	-0.034
Zn	-	-	1.000	0.173	0.001	0.479	0.183	-0.044	-0.065	-0.144
Co	-	-	-	1.000	0.555	-0.037	0.146	0.447	0.235	0.374
Cr	-	-	-	-	1.000	-0.061	-0.066	0.383	-0.077	0.010
Ni	-	-	-	-	-	1.000	0.185	-0.142	0.012	-0.077
Fe	-	-	-	-	-	-	1.000	0.150	-0.024	0.174
Mn	-	-	-	-	-	-	-	1.000	0.160	0.256
Mo	-	-	-	-	-	-	-	-	1.000	0.587
W	-	-	-	-	-	-	-	-	-	1.000

1) Cu - Zn 2) Pb - Cr 3) Zn - Ni and 4) Mo - W. Such correlations in the trace constituents of soils are due to the similar behaviour of these elements in the physio-chemical conditions imposed by the secondary environment.

The total number of elements in each group as compared to lithogeochemical data is drastically reduced. This is largely because of the process of weathering of primary minerals, (Pendias and Pendias, 1984). The gamut of variable in the surfacial environment would result in the reorganisation of elemental association compared to primary environment. Nevertheless, imprints of the primary environment can not be ruled out because of low temperatures, prevailing near the earth's surface and hence reaction rates are often so slow as to permit the primary minerals to co-exist metastably in the soils for some period of geological time.

The association of Cu - Zn in the soils of Koheda area is largely due to their similarity of mobility in the surfacial conditions (Levinson 1974), the common oxidation states found in the secondary conditions for these two elements are + 2 and the pH which influences the insolubility and immobilisation for Cu and Zn are 5.5 and 6.8 respectively. These pH conditions are quite common in the areas of oxidising sulphide deposits (Rose et al. 1979). Observation of pH in Koheda soils reflect the pH conditions favourable for Cu and Zn association. Significant positive correlations was reported between, Cu and Zn apart from Pb and Co in secondary samples over sulphide mineralisation from Rajpura of Rajasthan, by Roonwal and Aneel Kumar (1987). Similar results obtained in soils of Koheda reflects a buried mineralisation. The mobility of Zn being for greater distance than copper, it is found to form wider haloes.

The association of Pb with Cr and Zn with Ni in the Koheda soils reflect partly the imprints of the chalcophilic relationship and of the primary environment. The association of Cr with Pb in the surfacial conditions is largely the reflection of their immobile nature (Levinson 1974, Rose et al. 1979). The causative factors of Zn association with Ni needs further investigation. This might be due to the imprints of mafic minerals in the soil formation process.

Tungsten correlation with Mo is presumably due to their geochemical resemblance (Pendias and Pendias 1984). These two elements in the hypergene conditions form complexes such as MoO_4^{2-} and HWO_4^- in aqueous solutions (Rose et al. 1979). These complexes form hydromorphic dispersion patterns It is inferred that such process would have resulted in the geochemical patterns of Mo and W in soil of Koheda area. The higher values and association of Mo - W in the soil of investigated area might be due to the presence of porphyry copper deposit.

The hydromorphic dispersion of Mo - W as compared to Cu over mineralised granites and granodiorites in Ireland was studied, by Talbot and Ryan (1988) found the Mo - Cu - W haloes in overburden to be reasonable drill target. Therefore, such studies in Koheda area might prove similar results.

DISTRIBUTION OF pH IN THE SOILS : The pH values for the soil samples is listed in the Table 2.3 of chapter II. The Fig. 4.1 illustrates the pH contours of 6, 7, 8 and 9 for the soils of the investigated area. It is noticed from the figure that acidic environment has developed in soils around Maisampalli, Kurella, east of Gotlamitta and Ramachandrapuram. The pH values for the soils in these areas are below six. Apart from the said areas, there are some zones representing acidic soils. The rest of the area have alkaline pH values. The Table 4.3 shows the combination of anomalous elements with pH values of the soil from some target localities in the area of investigation.

It is well known fact that oxidation of pyrite, chalcopyrite and other sulphides, provide abundant amount of sulphuric acid to the ground and surface waters. This acidified water dissolves large quantity of many elements which are associated with the sulphide deposits. The dissolved elements are dispersed in the surfacial environment by the

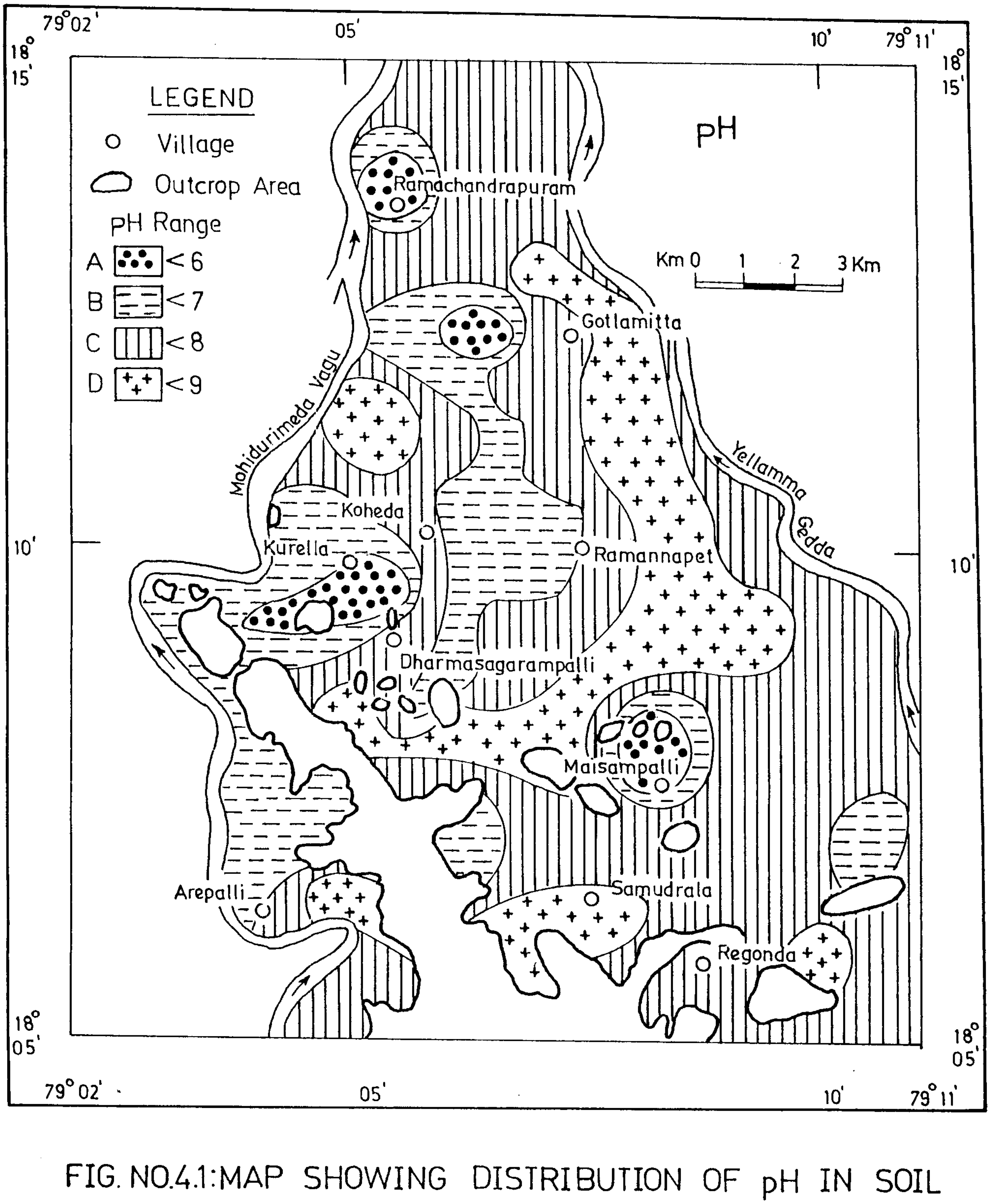

FIG. NO.4.1:MAP SHOWING DISTRIBUTION OF pH IN SOIL

Table No. 4.3 : Shows the combination of anomalous elements with pH values of soils from some target localities.

Sr.No.	Soil samples	pH	Elements	Localities
1	65	6	Cu, Zn, Mo	Kurella
	70	7	Cu, Zn, Mo	Kurella
2	1	7	Cu, Zn	West Kurella
3	86	9	Cu, Zn	South Dharmasagarapalli
	90	9	Cu, Zn	South Dharmasagarapalli
	93	8	Cu, Zn	South Dharmasagarapalli
4	50	6	Cu, Zn, Co, Mo, W	Maisampalli
	53	7	Cu, Zn, Co, Mo, W	Maisampalli
5	165	9	Mo, W	Reganda
6	105	7	Zn, Co, Mo, W	Arepalli
7	126	6	Cu, Zn	North Ramachandrapuram
8	14	9	Cu, Pb, Zn, Ni	North-East Ramannapeth

ground water. The distance to which different elements are dispersed is related to the pH of hydrolysis of the elements (Levinson 1974). During this process the soils become acidic around the oxidising sulphide body (Bateman 1979, Levinson 1974, Govett 1976 and Rose et al. 1979). Rose et al. (1988) have used the soil pH as a guide for identification of sulphide deposits. Govett (1976) have used the pH in conjunction with the soil trace constituents for the identification of buried sulphide deposits.

As mentioned in the Table 4.3 the low pH zones and anomalous concentrations of some target elements, in the investigated area might prove the proximity of oxidising sulphide body.

DISTRIBUTION OF ELEMENTS IN SOILS : As mentioned earlier, the average, standard deviation and threshold values for the elements, Cu, Pb, Zn, Cr, Ni, Co, Mo, W, Fe and Mn is given in the Table 4.1. The threshold value needs to be fixed to define the upper limit of normal background value. Threshold and background values differ for each element analysed. The higher values than threshold are considered anomalous and worthy of careful examination.

Hawkes and Webb (1962) have proposed mean plus twice the standard deviation as threshold value. This has proved worthy in many geochemical exploration (Rose et al. 1979). The same has been presently adopted. Using the background and threshold concentrations contouring was carried out for each element. The Figures 4.2 to 4.11 depicts areas of below background, above background and above threshold concentration for the elements analysed. The distribution of elements in the soils from the Koheda area is discussed in four major groups. The groups are made based on the geochemical similarities of the elements. They are as follows;

1) Fe Mn 2) Ni Cr Co 3) Cu Pb Zn and 4) Mo W

DISPERSION PATTERNS OF IRON AND MANGANESE : The distribution of iron in soils collected from Koheda area is shown in Fig.4.2. The background and threshold values for iron are 3.9 % and 7.07 %, respectively. The total anomalous region having above threshold concentration is about 7.8 km^2. This is distributed in and around Arepalli (4 km^2), Ramachandrapuram (1.5 km^2), Gotlamitta (1.2 km^2) and west of Maisampalli (1.1 km^2).

The Fig. 4.3 illustrates the distribution of manganese in the soils of Koheda area. The background and threshold values for this element are 191.37 ppm and 297.9 ppm, respectively. The total anomalous region for this element is 23.4 km^2. This anomalous pattern formed by Mn appears to be the widest halo compared to the haloes of any element under consideration. The anomalous pattern of Mn is noticed

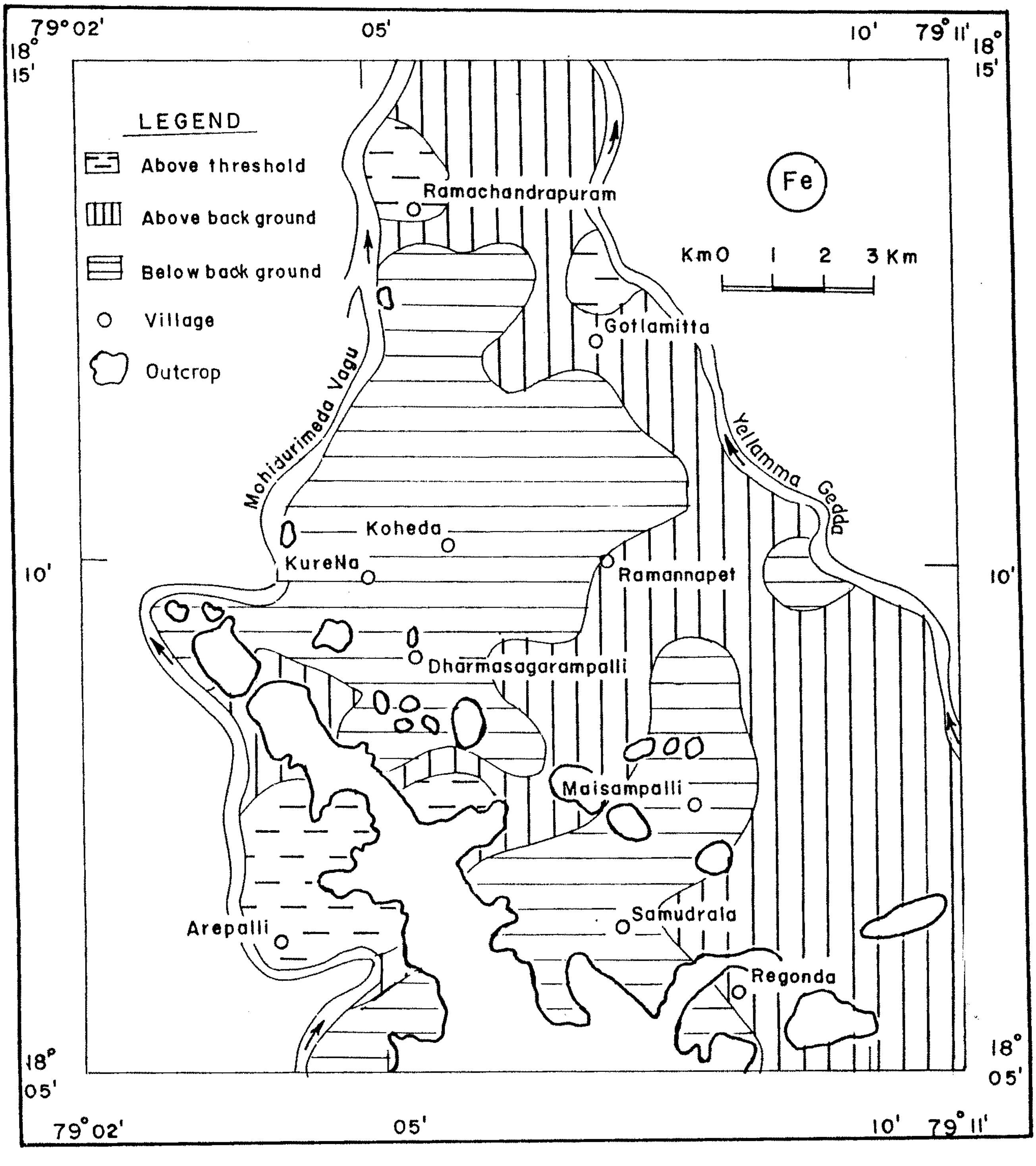

FIG. NO.4.2: DISTRIBUTION OF IRON IN SOILS

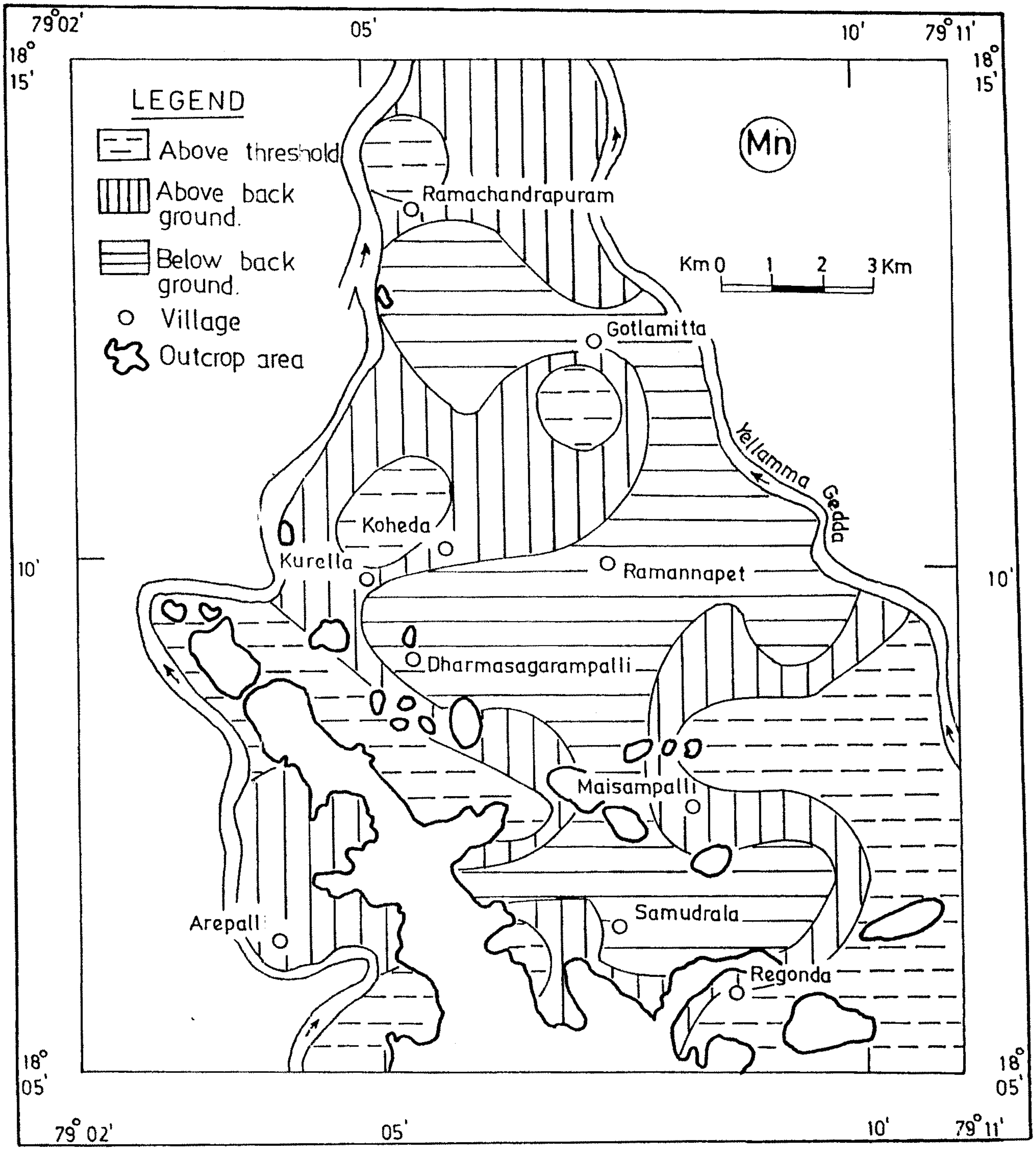

FIG. NO.4.3:MAP SHOWING DISTRIBUTION OF MANGANESE IN THE SOILS.

all around the outcrop regions in the southwest and south-east parts of the area of investigation. The smaller anomalous haloes of Mn are noticed near Koheda, south of Gotlamitta and north of Ramachandrapuram. These are of insignificant in nature.

The behaviour of iron and manganese was investigated by many exploration geochemist. Of them Theobald et al. (1963), Taylor and Mckenzie (1966, 1968, 1979), Hem (1978), Carpenter et al. (1975), Cameron (1975) and Chao and Theobald (1976) were the poineering researcher. They all opined that Fe and Mn form hydroxides and oxides. Between the two elements, the mobility of Mn is greater then Fe (Levinson 1980).

Studies related to Fe and Mn dispersion in soils helps in understanding the mobility and stability of secondary minerals of trace constituents in soils. Hem (1970) attributes the trace elemental concentration in secondary environment is due to their co-precipitation with Fe and Mn oxides.

Although the haloes of Fe and Mn do not indicate mineralisation but are diagonistic in the speciation of trace elements in the soil environment.

DISPERSION PATTERNS OF NICKEL, CHROMIUM AND COBALT : Fig. 4.4 illustrates the distribution of nickel in soils from Koheda

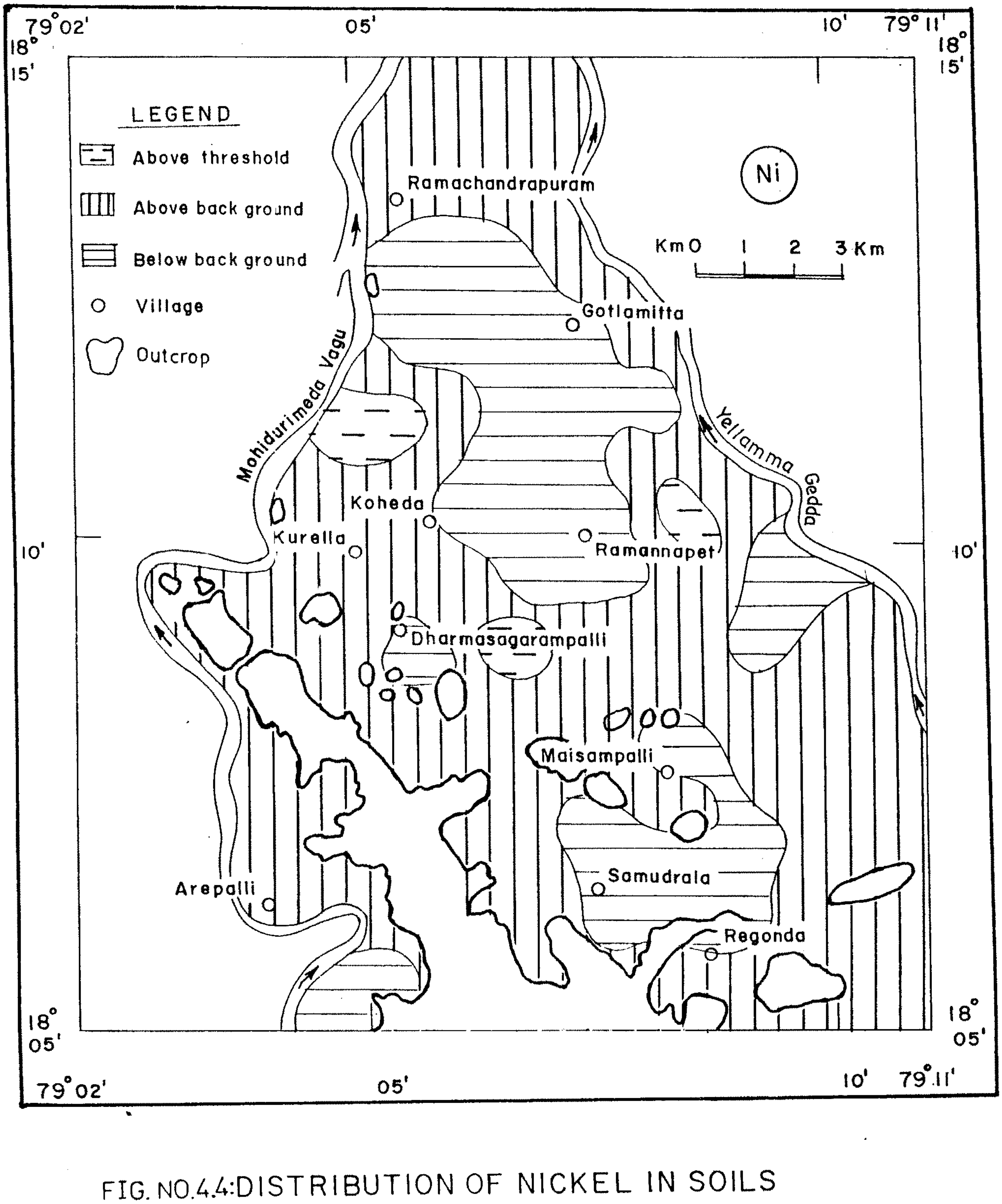

FIG. NO.4.4:DISTRIBUTION OF NICKEL IN SOILS area. The background and threshold values for this element are 42.29 ppm and 63.57 ppm, respectively. The area of interest having threshold concentration was measured for this element and is about 3.5 km^2. This is sproidically scattered towards northwest of Koheda (1.5 km^2), east of Dharmasagarpalli (1 km^2) and east of Ramannapeth (1 km^2).

The distribution of chromium is shown in Fig. 4.5. The values 58.36 ppm and 90.98 ppm are background and threshold concentrations, respectively. Anomalous regions of chromium are found towards northwest of Koheda (1.5 km^2). This region is similar to the nickel halo. The other zones of above threshold values are noticed between villages - Koheda, Kurella and Dharmasagarpalli. The third and fourth anomalous areas of one km^2 each are observed west and eastnortheast of Maisampalli.

The distribution of cobalt in soils of Koheda area is depicted in Fig. 4.6. The background and threshold values for cobalt in the area of investigation are 11.04 ppm and 18.86 ppm, respectively. The total area above threshold concentration is 10.10 km^2. Part of this is distributed towards northwest of Koheda covering an area of about 2 km^2. It is similar to the anomalous region noticed for Ni and Cr. Other soil anomalies for cobalt are noticed at eastnortheast and west of Maisampalli. Their areas are 3 km^2 and 2.5 km^2, respectively. Apart from these regions, village Arepalli is

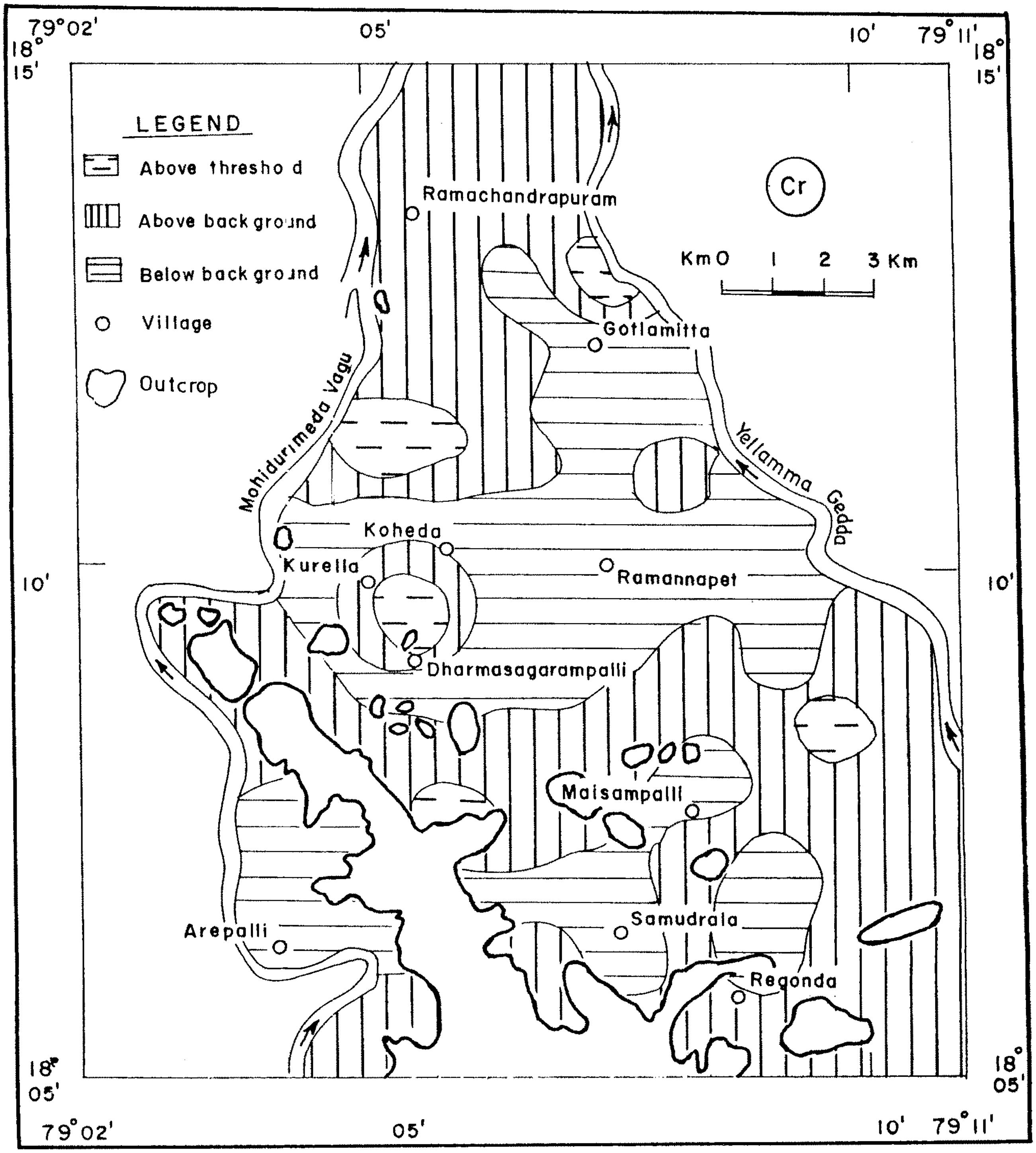

FIG. NO. 4.5: DISTRIBUTION OF CHROMIUM IN SOILS.

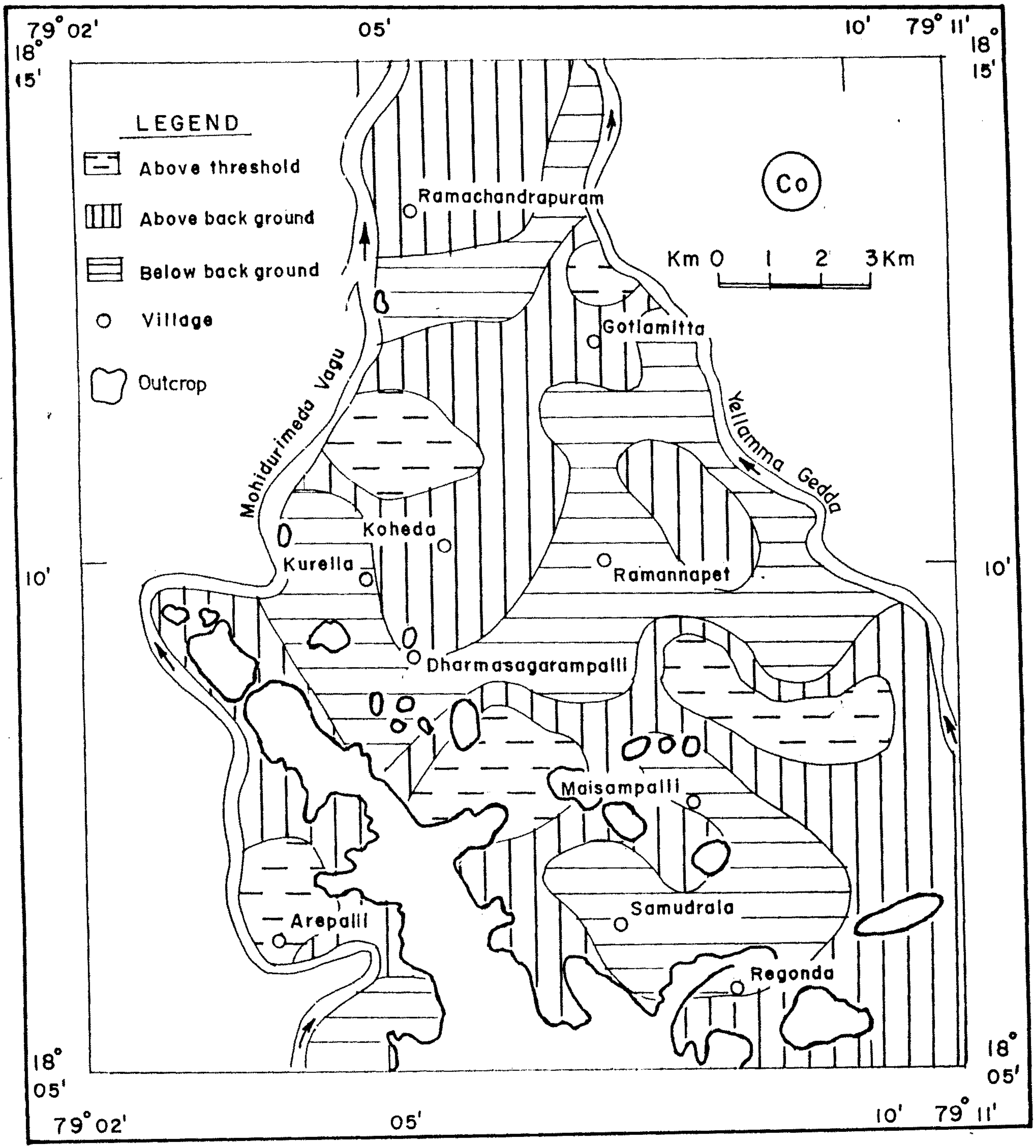

FIG. NO.4.6:DISTRIBUTION OF COBALT IN SOILS situated on an anomalous halo of 1.6 km^2 and a small halo of one km^2 is located north of Gotlamitta.

On examination of total anomalous areas for Cr, Ni and Co, it is noticed that cobalt has wider haloes followed by Cr and Ni. Nickel distribution in soils was studied by Pandias and Pandias (1984) who stated that this element appears to occur mainly in organically bond form, which may be a soluble complex in aqueous systems. Bloomfield(1981) and Norrish (1975) found the concentration of soil nickel in oxides of Fe and Mn. Thus, the nickel distribution in soils is related to either organic matter or amorphous Fe and Mn oxides. Information about nickel species in soil solution is rather limited except the work of Garrell and Christ (1975). They described Ni^{2+}, $NiOH^+$, $HNiO_2^-$ and $Ni(OH)_3^-$ are the principle complexes to occur when nickel is not completely chelated. The solubility of nickel is inversely related to the soil pH (Levinson, 1974 and Rose et al. 1979). Relatively low mobility of nickel in soils appear to be reflected in the form of small anomalous regions in the ,soil of Koheda area.

Vinogradov (1959) and Shirley Dreiss (1986) advocated that the Cr behaviour is complex in surfacial environment and is related to reactions controlling the Cr transport in soil waters. Chromium shows variable oxidation states from

Cr^{2+} to Cr^{6+} and is also known to form anionic complexes. Cr^{3+} is slightly mobile in very acid media and at pH 5.5 it is almost completely precipitated. On the other hand Cr^{6+} is very unstable in soils and is easily mobilised in both acid and alkaline environments (Bloomfield and Pruden 1980, Groove and Ellis 1980). Hem (1977) found Cr in anionic species when oxidised and cationic species when reduced. The anhydrous crystalline species of Cr_2O_3 is much insoluble over the range of pH 4.7 to 14 and is the limiting factor for Cr mobility. On comparison of Cr solublity with that of Ni, it was reported by Pandias and Pandias (1984), that Cr is relatively more soluble and mobile than Ni. It is obvious to expect wider anomalous patterns of Cr than Ni. The total area of above threshold concentration for Cr and Ni in Koheda area are 4.6 km^2 and 3.5 km^2, respectively. This is in accordance with the discussion of Pandias and Pandias (1984). The element Co resembles Fe and Mn in secondary environment. The investigations of Tiller and Hedgeson (1962) and Taylor and Mckenzie (1966) revealed that the solubility and availability of soil cobalt is controlled by sorption mechanism by crystalline Mn-oxides. The mobility of cobalt is strongly related, apart from Fe and Mn - oxides, to organic matter and clay content of the soil.

Canney and Wing (1966) evaluated cobalt as a useful but neglected element in prospecting for sulphides by secondary geochemical prospecting methods. They found that the relative mobility of Co is higher than Cr followed by Ni. Cobalt appears to be an excellant pathfinder element for sulphide deposits. In the present studies, the total anomalous areas of Ni, Cr and Co are 3.5 km^2, 4.6 km^2 and 10.1 km^2, respectively. This is partly due to their relative mobilities. Levinson (1980) states that pH of hydrolysis for divalent ions of Ni, Cr and Co are 3, 4.5 and 6.8, respectively. Thus if these ions are let free from oxidizing sulphide ore then the first to precipitate is Ni followed by Cr and Co. This is reflected in the halo sizes of these elements in the soils of Koheda area.

DISPERSION PATTERNS OF COPPER, LEAD AND ZINC : The Fig. 4.7 illustrates the distribution of copper in soils from the area of investigation. The background and threshold values for Cu in soils of Koheda area are 54.31 ppm and 92.31 ppm, respectively. The total anomalous area measured for this element is 16.80 km^2. The anomalous concentrations are distributed in three major regions viz; Kurella - Maisampalli (14 km^2), Ramachandrapuram (1.5 km^2) and Ramannapeth (1.3 km^2).

The dispersion of lead in the soils is depicted in the Fig. 4.8. The background and threshold values are 41.21 ppm and 60.11 ppm, respectively. The total area having above threshold values of lead is 11.9 km^2. It is distributed

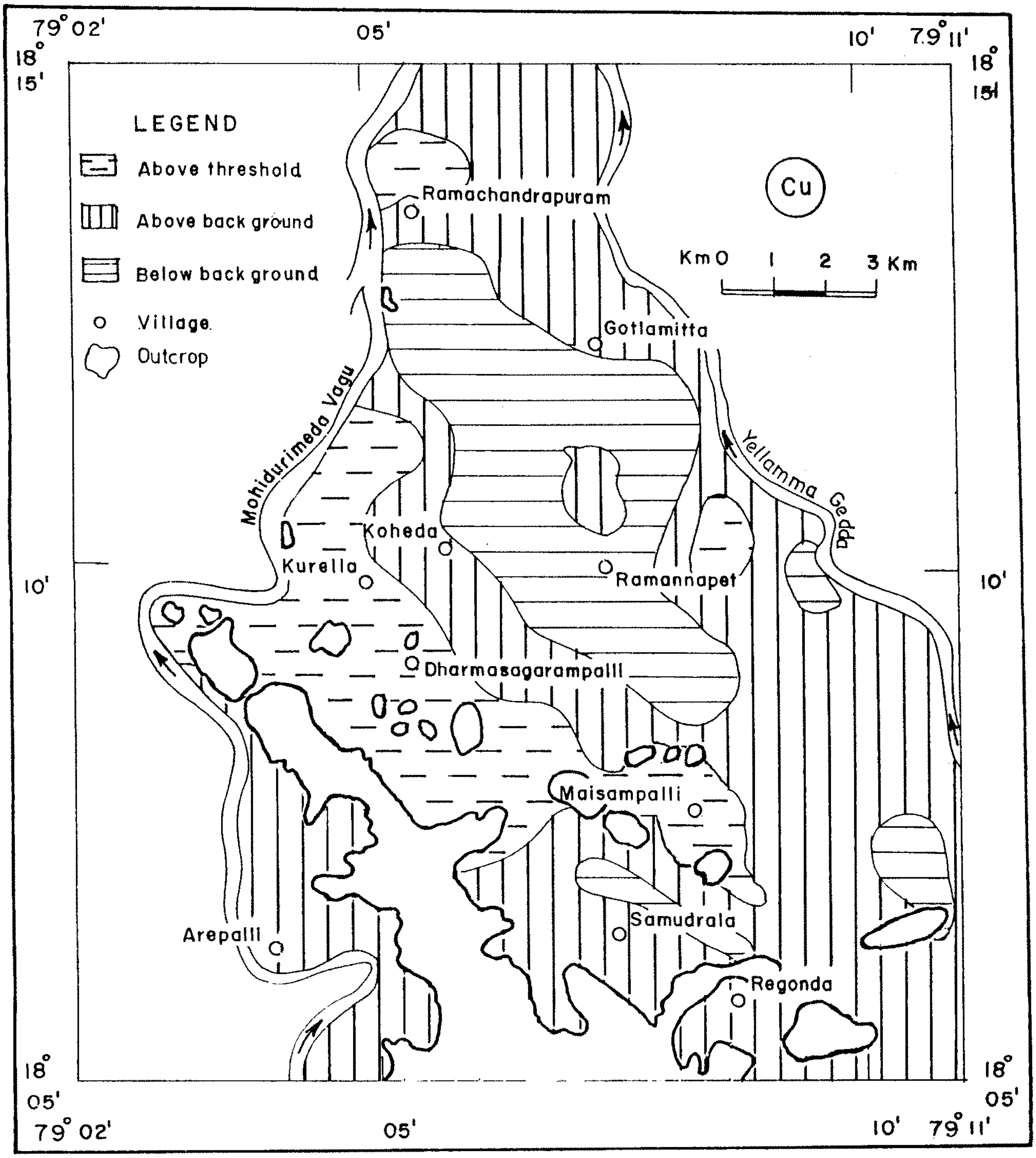

FIG. NO.4.7: DISTRIBUTION OF COPPER IN SOILS

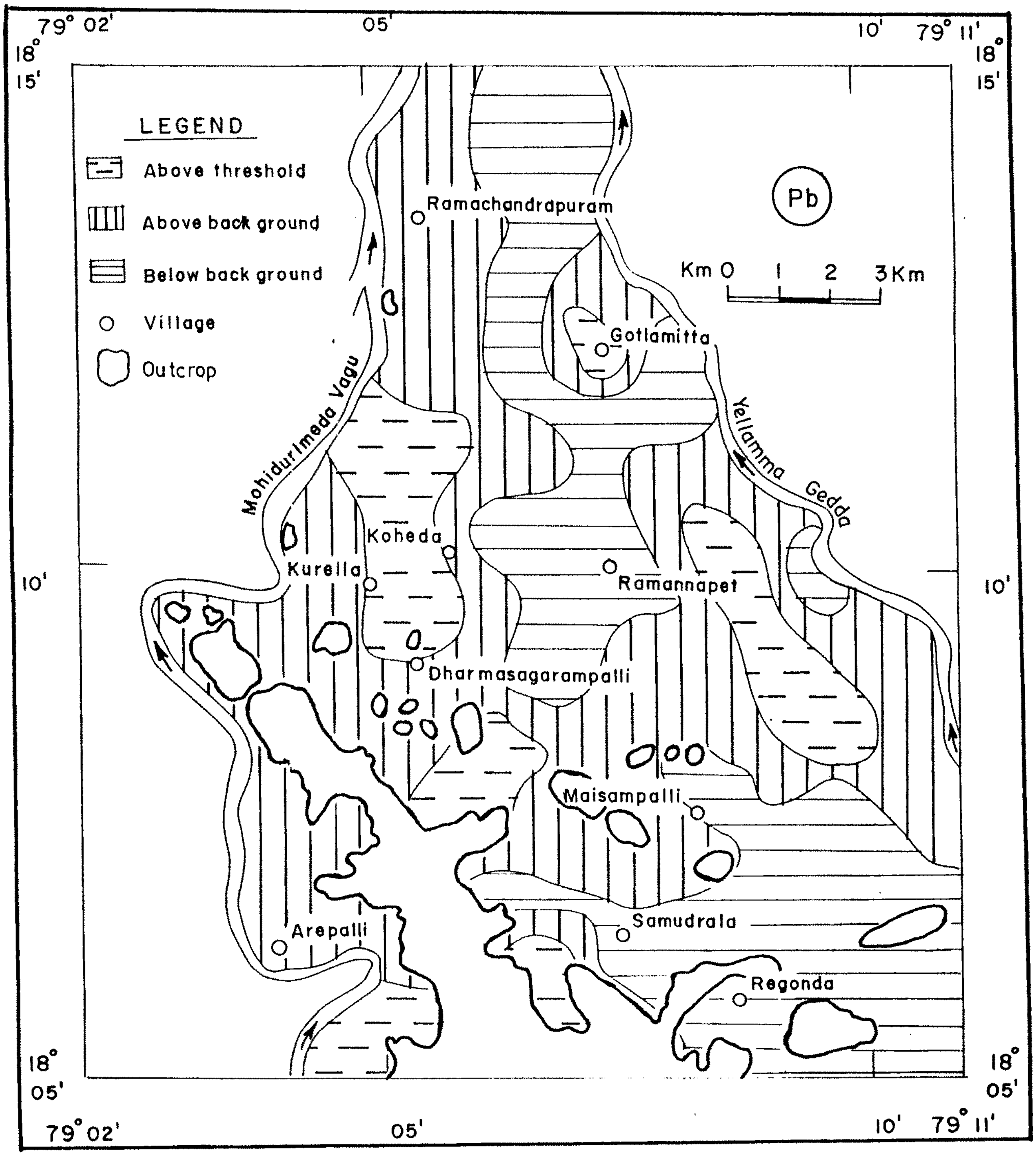

FIG. NO.4.8: DISTRIBUTION OF LEAD IN SOILS around Koheda (3.5 km^2), Maisampalli (2 km^2), Ramannapeth (3.6 km^2), Arepalli (1.8 km^2) and Gotlamitta (1 km^2). On comparison of this elemental pattern with copper distribution, it is observed that the lead has sproidic distribution.

The Fig. 4.9 illustrates the distribution of Zn in the soils collected from Koheda area. The background and threshold values for this element are 41.81 ppm and 67.67 ppm, respectively. The localities Kurella, Koheda, Dharmasagarpalli and Maisampalli are found to have soils with above threshold concentrations of zinc. The total anomalous area in these localities together amounts to 18 km^2. Apart from these haloes, the soils in and around Arepalli show anomalous region of 6 km^2. The total of the anomalous haloes for Zn is 24 km^2.

The anomalous areas for Cu, Pb and Zn are 16.8 km^2, 11.9 km^2 and 24 km^2, respectively. Thus, it appears that Zn is most mobile followed by copper and lead. The anomalous concentration of these elements at Koheda and Maisampalli reflect the proximity of oxidising sulphide deposit.

The solution geochemistry of base metal was investigated by Mann and Deutescher (1977, 1980). They reported the solution of these elements is influenced by the formation of soluble complexes with hydroxyl, carbonate, sulphate and chloride ions These complexes are formed because of acidic environment

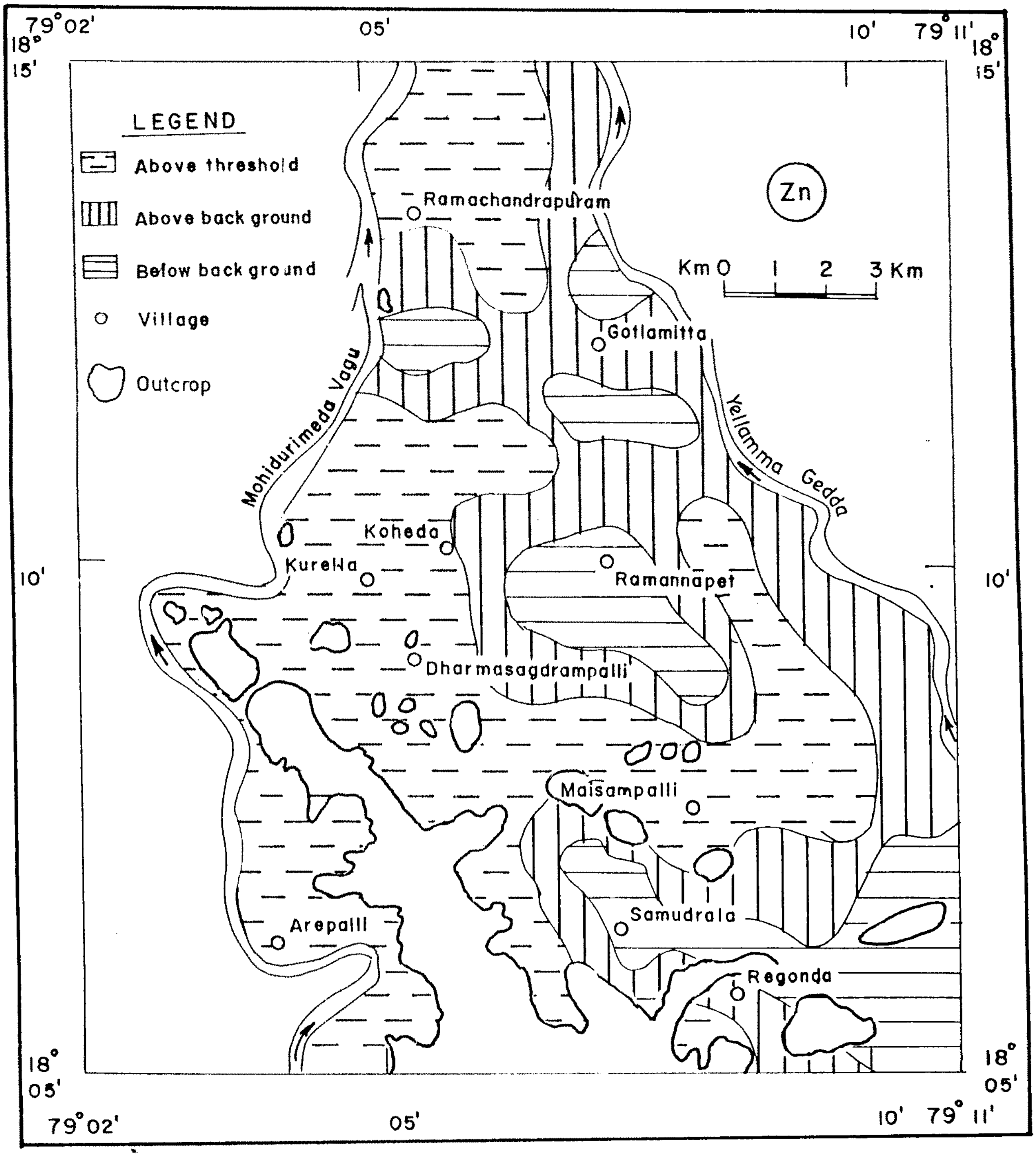

FIG.NO.4.9:DISTRIBUTION OF ZINC IN SOILS developed around an oxidising sulphide body. Under varing conditions, the complexes such as tenorite Cu $(OH)_2$, azurite $Cu_3(OH)_2\ (CO_3)_2$ and antlerite $Cu_3(OH)_4SO_4$ can be the dominant copper containing species in aqueous solutions. The secondary complexes such as cerrusite $PbCO_3$, anglesite $PbSO_4$ and $Pb_2Cl(OH)_3$ are the phases which limit the solubility of lead. Zinc complexes in aqueous solutions are sulphates, carbonates and hydroxyl ions. These are $ZnSO_4(OH)_6$, $ZnSO_4$, $ZnCO_3$ and $Zn(OH)_2$ (Mann et al. 1980).

Andervev and Chernyavev (1975) studied the migrational capacity of metals in the supergene zone of sulphides and confirmed the formation of sulphates, carbonates and oxides. The mobility of Cu, Pb and Zn is facilitated by clay minerals due to their cation exchange capacity, (Wolfe 1973, Loring 1976, Shumann 1977, Levelli and Wilhelm 1989). The total activity of Cu, Pb and Zn in solution was calculated by Cameron (1977) and Mann and Deutscher (1980) who have stated that the relative mobility of base metals from the source as Zn $>$ Cu $>$ Pb. Levinson (1980) supports this phenomenon by stating that the pH of hydrolysis of divalent ions of Pb, Cu, Zn are 3.6, 5.5 and 7, respectively.

The relative sizes of anomalous patterns of these elements from Koheda area, indicate zinc as most mobile, followed by copper with intermediatory mobility and lead as least mobile.

This results corroborates with the Levinson (1980) studies who found the usefulness of Zn as pathfinder for sulphide mineralisation.

DISPERSION PATTERNS OF MOLYBDENUM AND TUNGSTEN : The Fig. 4.10 depicts the distribution of Mo in the soils collected from Koheda area. The background and threshold values for Mo are 17.62 ppm and 40.67 ppm, respectively. The total anomalous area for this element is 8.2 km^2. This is distributed in localities Maisampalli and east of Maisampalli (2 km^2), Kurella and its surroundings (2.5 km^2), north of Arepalli (1.5 km^2) and east of Regonda (2.2 km^2). Apart from these anomalous patterns, there are pockets of anomalous concentration of Mo near Gotlamitta and Ramannapeth which are of less significance.

The distribution of W from the soils of Koheda area is shown in the Fig. 4.11. The background and threshold values for W are 23.41 ppm and 42.87 ppm, respectively. The anomalous pattern of 3.5 km^2 at Maisampalli is similar to the Mo halo at that place (see Fig. 4.10). Similar size halo is noticed to have formed east of Regonda. Apart from these regions, W is found to be above threshold concentrations near Arepalli and forms a halo of 2 km^2. All these haloes are similar to the Mo distribution pattern.

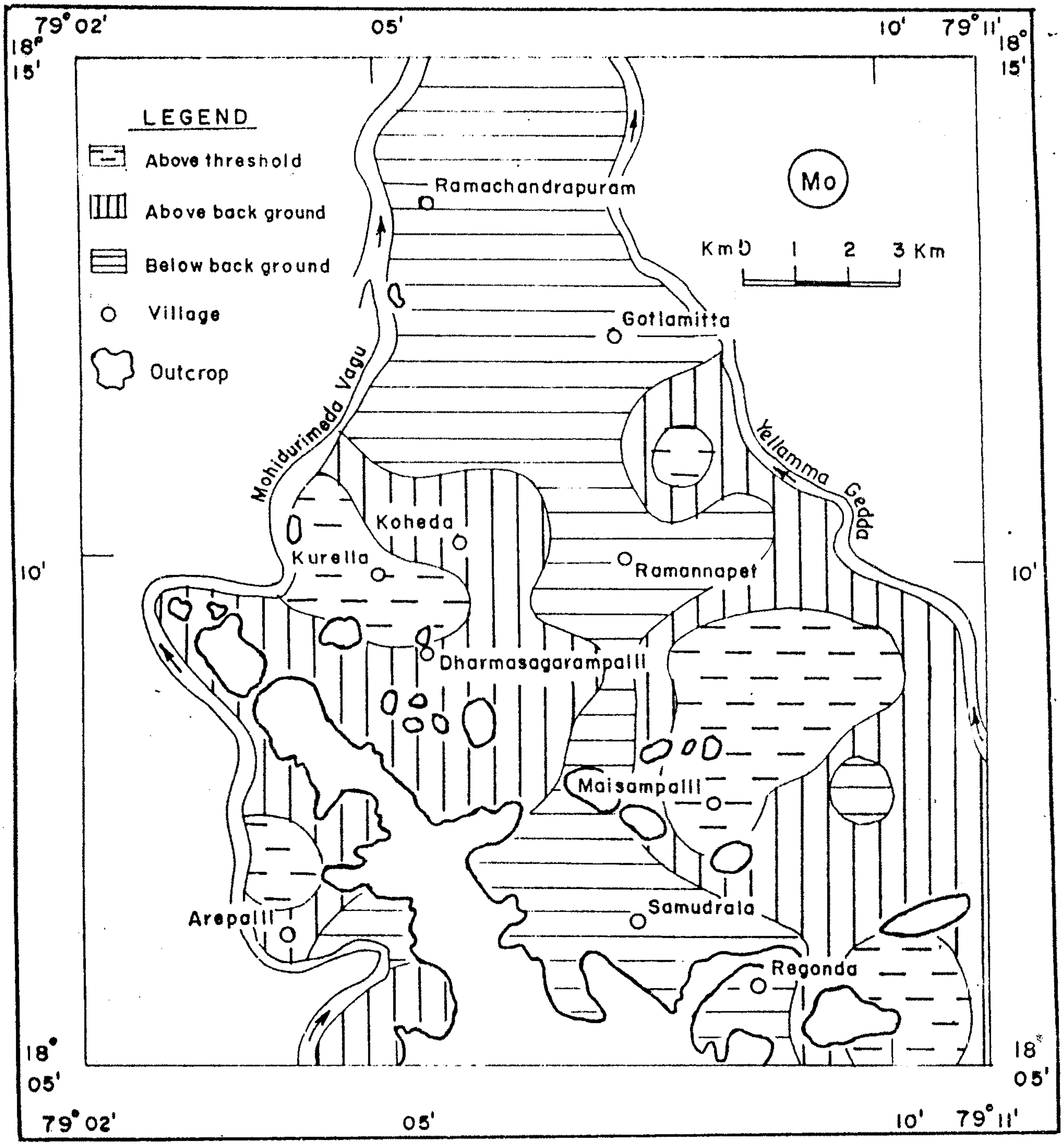

FIG.NO.4:10:DISTRIBUTION OF MOLYBDENUM IN SOILS

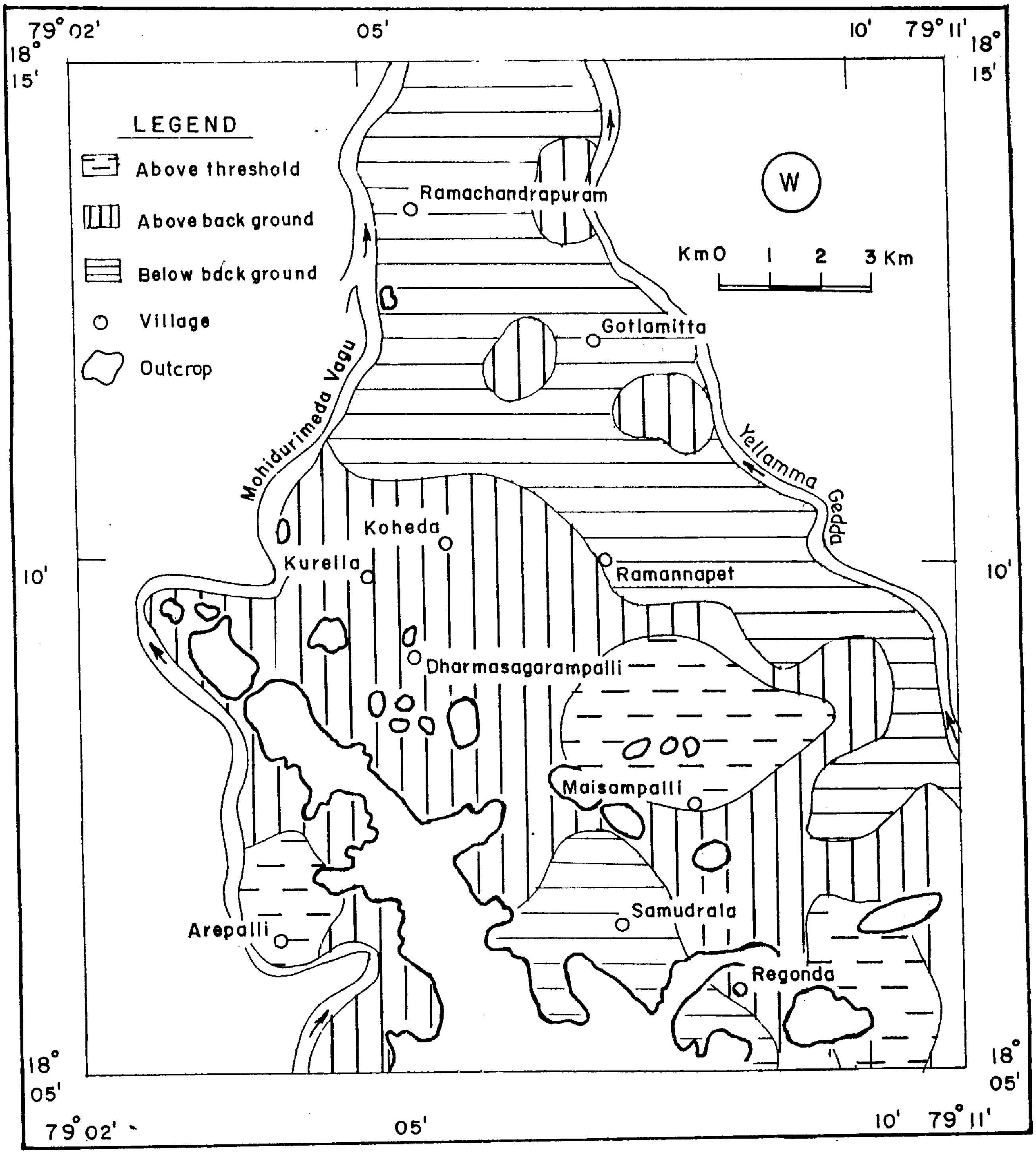

FIG. NO.4.11:DISTRIBUTION OF TUNGSTEN IN SOILS

Molybdenum has affinity to both chalcophilic and lithophilic groups. Its geochemistry in the surface environment is related mainly to the anionic species (Pandias and Pandias 1984). This element has affinity to form organo-metallic complexes : MoO_4^{-2} and $HMoO_4^-$. These are soluble species in aqueous solutions (Kubata 1977). Differential adsorption of Mo by hydrous oxides of Fe and Mn, contribute to the relation of Mo in surfacial environment. The behaviour of Mo in soils have been extensively studied by Krauskof (1967), Garret (1971), Barakov and Bradshaw (1971), Wolfe (1973), Norrish (1975), Vlek and Lindsay (1977) and Talbot and Ryan (1988) who justified that this element is mainly associated with iron oxides and form ferrimolybdate $Fe_2(MoO_4)_3 8H_2O$. Ferrimolybdate which appears bright yellow is insoluble in pH conditions less than 6. However, Mo becomes mobile in alkaline condition and in presence of lime. Talbot and Ryan (1988) have demostrated the use of Mo over Cu for identification of porphyry Cu - deposit. This is because of higher mobility of Mo than copper.

Hansuld (1966), Wolfe (1973) and Rose et al. (1979) reported the efficacy of molybdenum over copper in the surfacial environment and can be used as pathfinder to molybdenite bearing porphyry copper deposit. In the present study area the haloes defined by Mo in soils of Kurella, Maisampalli and east of Regonda could potentially prove the presence of mineralisation in the proximity.

Shcherbina (1971) investigated W in acidic zone and reported that it forms complexes such as HWO_4^- and WO_4^{-2}. Presumably, the geochemical behaviour of tungsten resembles that of the dispersion pattern of Mo and hence it has been found that the anomalous haloes of both these elements have similarities. The general behaviour and anomalous patterns formed by Mo, W, Cu and Zn in the Koheda area, reflect the presence of ore deposit in the proximity.

CONCLUSIONS : The soil geochemical survey carried out in the Koheda area brings forth the following features :

* The acidic pH in conjunction with anomalous values of some target elements - Zn, Cu, Co, W and Mo - at Kurella, Maisampalli, Ramachandrapuram and Gotlamitta, represent proximity of oxidising sulphide deposits.
* The relative sizes of anomalous haloes for the target elements are Zn (24 km^2), Cu (16.8 km^2), Co (10.1 km^2), W (9 km^2) and Mo (8.2 km^2) indicates their relative mobilities in the mineralised soils and reflect their genetic association with ore deposit.
* From the statement mentioned above, it is inferred that Zn, Co and W could be regional pathfinders, while Cu and Mo can be used as local indicators.