

**HEAVY METALS IN FERTILIZERS IN RELATION TO THEIR
ACCUMULATION IN SOILS DUE TO CONTINUOUS
FERTILIZER USE**

BY

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THESIS

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for the degree**

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DECLARATION

I hereby declare that this thesis entitled **Heavy metals in fertilizers in relation to their accumulation in soils due to continuous fertilizer use** is a bonafide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship or other similar title at any other University or Society



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Certified that this thesis entitled "Heavy metals in fertilizers in relation to their accumulation in soils due to continuous fertilizer use" is a record of research work done by Sri SATHYAPRAKASAN, S under my guidance and supervision and that it has not previously formed the basis for the award of any degree, fellowship or associateship to him



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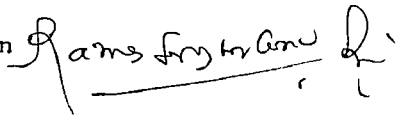
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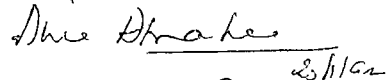


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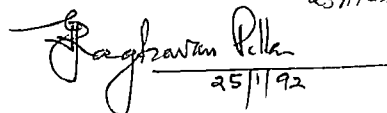
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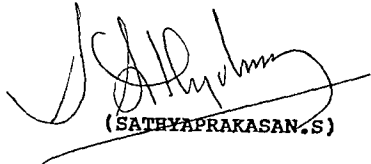
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INTRODUCTION

INTRODUCTION

Heavy metals are those elements whose density is more than 4 g cm^{-3} . Their content in the soil is very low and some of them are essential to both plants and animals in small doses, but becomes toxic when taken up in large quantities. Copper, zinc, manganese, cobalt etc are examples of essential heavy metals. But metals like cadmium, nickel, lead, chromium, mercury etc are elements which are not essential to plants and animals, with the exception of cadmium which is reported to be essential for shellfish (Gunnarsson, 1983). Chromium was also considered to be a non-essential heavy metal element, but it has been found to be essential to plants like shallot and carrot (Bertrand, 1967). Most of the non-essential heavy metals may also be taken up inadvertently by plants, thereby introducing them into the food chain which terminates in man, the ultimate consumer of food of both vegetable and animal origin.

As against the essential heavy metals, metals like cadmium, nickel, chromium, lead and mercury pose an altogether different problem. All these metals turn out to be health hazards when ingested and accumulated in large quantities, in the animal and human tissues. The mercury content of the soil is minimal unless polluted by industrial wastes and fungicides, and therefore poses no problem. But the metals cadmium, nickel and lead deserves much more attention, as the chances of their addition to the soil through fertilizers, are more

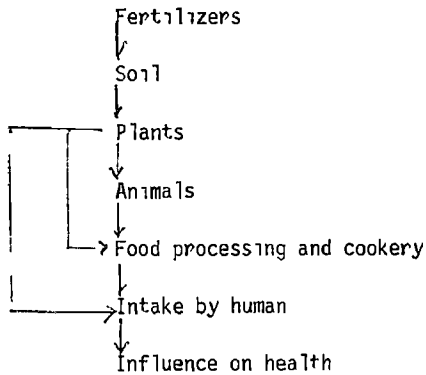
Cadmium is the most toxic element among heavy metals even though acute poisoning is rare. The health hazard attributed to cadmium is related to its long term accumulation in the animal and human tissues. Cadmium is reported to have a half life of 20-30 years in human body (Gunnarsson, 1983). Due to continuous intake even in minute quantities, its heavy build up in liver and kidneys, may lead to diseases like proteinurea, osteomalacia, itai-itai, etc. Tubular proteinurea is postulated to occur when cadmium concentration reaches 200 ppm in the kidney cortex (whole kidney concentration at 400 ppm). The metal is also reported to be

carcinogenic (Gunnarsson, 1983) Since, even smaller levels of cadmium also is found to manifest health problems, the Swedish Medical and Environmental authorities suggested that reasonable measures be taken to reduce cadmium intake.

Of the other heavy metals, lead is an element which is strongly fixed in the soil and hence considerable inflow into the soil is necessary to manifest serious problems. But the problem of lead poisoning may be serious through other sources like automobile exhaust fumes and industrial gases. Nickel also is believed to cause no serious hazards, though little is known about its behaviour (Giordano, 1983)

Food, of both vegetable and animal origin are considered to be the main input agency of cadmium in the human body. Fertilizers, especially phosphatic fertilizers are the easily identifiable source of the metal.

Route of fertilizer cadmium in food chain



Man, in his quest for finding alternative source of plant nutrients other than those of organic origin, has been exploiting geological deposits and making use of them as such or by refining their contents of different elements. Large quantities of phosphorus potassium, calcium and magnesium are thus derived from geological deposits. The use of fertilizers derived from mined materials is on the increase This is very important in view of the increasing demand for fertilizers required for boosting agricultural production, needed to feed the increasing population

The fertilizer industry is using many minerals containing phosphorus (eg Apatite), Potassium (eg Sylvite) Sulphur (eg Pyrites) etc for the manufacture of fertilizers having definite analyses. But the minerals so used for the manufacture

of fertilizers are not clear and often contain impurities which are carried to the soil and consequently to the crops growing on them. Among the finished products potassic fertilizers do not contain appreciable quantities of heavy metals as impurities and therefore are not considered to be hazardous. Phosphatic and sulphur minerals on the other hand cause concern due to their higher content of so called heavy metals. Cadmium is the most important hazardous heavy metal which originate mostly from phosphate rocks.

The problem of heavy metal pollution through fertilizers has become a subject of grave concern only during recent times. In South India this has gained much importance due to the divergent claims put forth by various fertilizer manufacturers. The argument presented from some quarters that the question of heavy metal pollution of arable soils due to continuous fertilizer use and the resultant health hazards are not reported so far in India, need not be a deterrent in undertaking a scientific investigation on the possible health hazards contributed by fertilizers on man. This context makes it imperative to remove the common man's fears, or to warn him about any possible pollution hazards that may become a threat to his survival due to the unscrupulous use of fertilizers.

Even though only negligible work in this field has been carried out in India, it is heartening to note that the scientists and agricultural technocrats elsewhere have paid a lot of attention on the subject. Notwithstanding the useful conclusions drawn by scientists from temperate countries like U S A , Sweden, Japan, U.K., Belgium, Canada, Netherlands etc one has to think that it is high time for conducting similar investigations in the different agro-climatic regions of India also. This is all the more important in view of the fact that the soil properties, climatic conditions and crop management practices differ from state to state and even within a particular state. The nature and quantity of both native, and added heavy metals through fertilizers and their intake by plants and retention by soils are most likely to differ among states, regions and localities.

In view of the perspectives elaborated hereto, it was felt necessary to conduct a preliminary investigation on the heavy metal status with special reference to cadmium in some major rice growing soils of Kerala and crops grown on them, so that some insight into the heavy metal status of these soils are obtained.

It is hoped that such a study would be helpful to the common citizen in alleviating his fears about the danger of continuous fertilizer application intended for boosting agricultural production or in encouraging him to ignore the hypothetical health hazards supposed to follow such practices. The objectives of the investigation undertaken are as follows:

(i) To estimate the total cadmium, nickel and lead content of some commonly used fertilizers and fertilizer complexes sold in Kerala.

(ii) To assess the total and extractable cadmium, nickel and lead concentrations of four soil types (paddy growing) of Kerala.

(iii) To assess the content of the above heavy metals in the plant samples of rice grown in these soils.

(iv) To assess the accumulation of these heavy metals in the soils of two permanent manurial experimental plots at RARS Pattambi.

(v) To study the influence of added cadmium in different doses on three crops: a cereal, a leafy vegetable and a forage crop (rice, amaranthus, and guinea grass) using pot culture.

REVIEW OF LITERATURE

REVIEW OF LITERATURE

The problem of heavy metal accumulation in soils by continuous use of fertilizers has gained due attention only during recent years. Even though in India much work has not been done in this regard, scientists elsewhere have done commendable work on this subject and have drawn useful conclusions. A brief review of literature pertaining to the presence of toxic metals in soils and fertilizers, their movement in soil, accumulation in plants and the consequent toxic hazards to animals and human beings etc. are presented in this chapter.

2.1 Heavy metals in fertilizers

Mortvedt (1978) conducted experiments to determine the extractability of Cd after application of P fertilizers which contained Cd as a contaminant. He reported that concentration of Cd in soil extracts decreased in the order DAP + Cd Cl_2 , commercial DAP, Commercial C S P., DAP + Cd $(H_2PO_4)_2$ - Cd (HPO_4) and DAP + Cd $(PO_4)_2$. These results suggested that the form of Cd contained in P fertilizers are in the form of Cd (H_2PO_4) or Cd (HPO_4) .

Reuss et al (1978) noticed that, when reagent grade monocalcium phosphate was used as a P source, the content of edible radish roots and tops were $0.4 \mu\text{g Cd g}^{-1}$ on dry weight basis. The use of concentrated superphosphate (CSP) containing $174 \mu\text{g Cd g}^{-1}$ resulted in a plant Cd content of $2.4 \mu\text{g Cd g}^{-1}$ in radish root and top. But on calcareous soils the Cd content in plant parts was less than this. It was also found that spot placement of DAP almost completely eliminated Cd uptake from fertilizers.

Mulla et al (1980) studied the influence of long term P fertilization at approximately 175 kg/ha/year as T.S.P. over a 36 year period, and found that the total Cd in soil was 1.5 ppm, whereas in the control the Cd concentration was 0.12 ppm. However water soluble Cd ranged from 0.001 to $0.003 \mu\text{g/ml}$ which are normal values for most soils.

Carlson and Rolf (1979) found that growth reduction occurred in rye grass when Cd was applied along with fertilizers. Cadmium content of fertilized plants were higher than that of non fertilized plants. When Cd and Pb were combined, the Cd content of plants increased, but Pb content was not altered.

They also established that when rye grass was grown in fertilized and unfertilized soils treated with Pb and Cd or a combination of Pb and Cd at a ratio 100 Pb : 1 Cd, growth was reduced beyond 10000 µg Pb. The Cd content of plants were greater in Cd + Pb treatment. But the Pb content was not altered by the concentration.

Goodroad and Coldwell (1979) noticed that, when concentrated superphosphate was applied continuously for 19 years, there was no addition of Pb, As or Cr in the soil. Their study revealed that P fertilizers at the rates presently applied would not add substantially to the natural levels of Pb, As or Cr in the soil.

Reuss et al (1978) reported that spot placement of diammonium phosphate almost completely eliminated Cd uptake from fertilizer. In the calcareous soil, spot placement increased Cd uptake from the concentrated superphosphate, but slightly depressed uptake from diammonium phosphate.

Mulla et al (1980) showed that the concentration of total Cd was highly correlated with total P in soils fertilized with triple

superphosphate for 36 years continuously. There was also increase in the concentration of Cd in plant parts.

Mortvedt et al (1981) contended that concentration of Cd in wheat grain and straw was significantly increased with the application of diammonium phosphate containing Cd. But the Cd content of the plant parts were lower in high limed soil. They suggested that the Cd concentration in wheat products were not significantly changed by the generally used phosphate fertilization practice.

Poletschny (1982) observed that, in a soil subjected to long term fertilization with P fertilizers, the Cd concentration was not increased significantly. It was also found that in potatoes, winter wheat and sugar beet the Cd accumulation was not generally affected by the form of P applied and was greatest in the controls without P and K which had lowest yields.

Anderson (1982) found a rectilinear positive relationship between added amount of P and extracted amount of Cd. The rates of increase in the soil Cd levels caused by normal P fertilization ranged from 0.33 to 1.1% annually, depending upon soil type.

Machelite (1984) established with the help of a continuous experiment with P that the application of about 13 tons superphosphate over 31 years did not influence either the soil Cd content, or the amount of Cd taken up by plants.

Mortvedt (1985) conducted studies on Zn fertilizers and found that plant uptake of Cd increased with increasing level of Cd in the Zn fertilizer, in acid soils

It was also noticed by him that the Pb content in plant was not affected with the application of Zn fertilizers containing Pb as high as 5200 mg/kg

Further, he observed that when Zn fertilizers containing heavy metals were applied to soil, the uptake of Ni was not affected even though the Ni levels in some fertilizers were as high as 8950 mg/kg. As Zn fertilizers are not generally used for corn and vegetable crops, the chance of heavy metal contamination is little

2.2 Heavy metals in soils

John, and Laerhoven, (1972) reported that the soil properties particularly soil PH were important when attempting to predict plant lead. Lead availability was found to be related to soil PH, extractable Al and total N, and there was no relation with organic matter.

Takuma et al (1973) analysed soils near zinc mines and reported that the Cd content in soil varied from 0.2 to 10.4 ppm and it had no apparent relation to Cd content in rice grown on the soil. The exchangeable Cd and Zn-Cd ratio in soluble form had negative and positive correlation with rice Cd respectively.

Haghir (1976) investigated the release and availability of Cd to plants from Cd treated kaolinite and illite clays in relation to their Ca and K saturation. He found that the concentration of Cd in the dialyzates from both kaolinite and illite clays increased with a decrease in the per cent Ca or K saturations in the clay suspension. The release of Cd from both clays was greater in the presence of Ca than K.

In a separate experiment he has found that the concentration of Cd in soybean shoots decreased with increasing per cent Ca or K saturation of the soil. The results indicated that the Cd uptake by soybean could be impaired to a great extent by K application.

According to Giordano and Morvedt (1976) cation movement in soils under leaching conditions has been associated with N fertilization. Studies were conducted by them to determine the mobility of heavy metals applied in inorganic form and in sewage sludge in the presence of various N sources. In a column study they found that mobility of heavy metals from inorganic source was slightly greater than that from sewage sludge. Nitrogen fertilizers did not affect the downward movement of Zn, Cd, Cr, Pb and Ni through the soil, while the uptake of these metals by crop (Fescue) grown in the column was found to be enhanced. They are of the opinion that the probability of heavy metal contamination of ground water is not likely in heavy textured soils, when sewage sludge accompanied by N fertilizers is applied to the soil.

Symeonides and Mc_Rae (1977) assessed the plant availability of Cd from soil and reported that the most sensitive of several possible indices to Cd uptake by plant is the amount extracted by shaking with 1 N ammonium nitrate solution. The pH also got marked effect on cadmium availability.

Miller et al (1977) noticed that Cd uptake decreased as soil pH and CEC increased. But availability of Cd increased with increase in acidity.

Reddy and Patrick (1977) studied the influence of pH on Cd uptake and concluded that the total Cd uptake increased with an increase in suspension redox potential and a decrease in pH. So, by altering these parameters, behaviour of some heavy metals can be manipulated.

Street et al (1978) reported that increasing the pH of the soil amended with inorganic Cd, decreased the Cd concentration in corn leaves by 67%. There was 100 fold decrease of Cd solubility with every unit increase in pH.

Woggan (1978) found that Cd movement in soil was decreased with increasing soil pH. But time and moisture content have no influence on Cd recovery. It was also observed that the presence of P reduces Cd diffusion.

Bollag and Barabasz (1979) studied the effect of Cd, Cu, Pb and Zn on denitrification of pseudomonas in liquid medium and denitrifying activity of the soil. They reported that Cd concentration at 50 $\mu\text{g/ml}$ strongly inhibited growth of Pseudomonas sp while Zn and Pb did not inhibit even upto 500 $\mu\text{g/ml}$.

White and Chaney (1980) stated that high organic matter was more effective in reducing the metal uptake. The soil type also has got strong influence on Cd and Zn uptake. But organic matter is more important in limiting the Cd uptake.

Rashid et al (1981) reported that a change from alkaline to acidic pH under moderately oxidised to well oxidised condition resulted in 109% Cd transformation from potentially available organic form to more mobile and readily available dissolved and exchangeable form.

Chubin and Street (1981) observed that Cd retention in soil depends not only on aqueous chemistry of Cd and surface chemistry of adsorbant but also the chemistry of synthetic complexing agents

Emmerich et al (1982) reported that when sewage sludge was treated with soil, the metals did not move out of sewage sludge layer and the chemical forms of the metals were found in the organically bound carbonate or residual forms. According to this it appeared that Cd, Zn and Ni were shifting to the residual form

In another work they observed from a column study that essentially, no metal moved below the depth of incorporation and 100% of the metal could be recovered from the treated soil layers

Hickey and Kittrick (1984) extracted heavy metals after massive addition of the metals and found that the highest amount of exchangeable form was associated with Cd (37%). The residual fractions were 15, 34, 55 and 14 percent Cd, Cu, Ni and Zn respectively. The amount of Cd in residual form was 50 times higher than typical for unpolluted soils. Mobility and potential metal bio-availability for the highly contaminated soils and sediments was in the order of Cd, Zn, Cu Ni

Elliott (1984) investigated the adsorption behaviour of Cd, both as Cd⁺⁺ and Cd-EDTA, Cd was adsorbed by the positively charged soil. This suggested that strong chelation does not necessarily preclude substantial metal adsorption, and complexed heavy metals may be less mobile and available than their unbound counterparts.

Bingham et al (1984) reported that Cd was found to exist principally as Cd⁺⁺ and CdCl⁺. Multiple regression analysis of leaf Cd in relation to Cd, Cd²⁺ and CdCl₂⁺ that leaf Cd to be a primary function of Cd concentration.

Clune et al (1984) observed from short and long term leaching studies that Cd movement is limited to one or two cm below the zone of sludge (109 Cd) incorporation. In calcareous soils mobility of Cd was very much limited.

Turner et al (1985) reported that atmospherically deposited Pb in McDonald branch watershed, New Jersey, Pinebarrens was 140 g/ha/year and the falling Pb was retained by organic floor by 75%, and 25% by mineral soil. The total Pb content of biota was 335 g/ha. They also noted that Pb did not appear physiologically accumulated by vegetation.

2.3 Heavy metals in plants

Baumhardt and Welch (1972) observed that, after application of Pb ranging from zero to 3200 kg/ha, emergence, plant height and grain yield were not affected by added Pb. The added Pb increased the Pb content in stover. Even though the plant is unaffected the plant material could contain enough Pb to be harmful when ingested.

John and Laerhoven (1972) reported that soil application of Pb increased its uptake by lettuce to a greater degree than oats. Application of lime depressed the uptake of added Pb by both plants.

Based on works conducted in tree crops Gary and Rolfe (1973) observed that when Pb was tried at four levels ranging from zero to 600 ppm the uptake was affected by soil concentration of Pb. There was higher uptake with higher concentration and most of the Pb accumulates in the root system.

Hagihira (1973) reported that growth and Cd concentration of soybean and wheat tops were influenced by soil applied Cd. The Cd toxicity began to occur in both the crops at 2.5 ppm. The relative concentration in descending order for various vegetables was lettuce, radish tops, celery stalk, celery leaves, green pepper

* As lead acetate

and radish Cadmium in various plant parts decreased in the order of stem, leaves, pods, beans

Investigations conducted by Turner (1973) revealed that, in the case of vegetables, tomato was found to be sensitive to Cd damage. For all species tried, Cd in tops tended to increase with increased Cd levels in solution. Most species tolerated Cd levels upto $0.10 \mu\text{g/ml}$

Roof et al (1975) reported that the uptake from solution containing one to forty mg/l Cd was correlated with leaf chlorophyll content, dry matter production and tissue concentration of Zn and Fe. Cadmium concentration in roots and shoots increased with increased time of treatment. With increased Cd, Zn concentration was found to decrease and the Fe concentration was increased.

Iwai et al (1975) studied the Cd uptake in corn plants and concluded that, with increased Cd concentration, the Cd content of plant increased and total dry weight and grain yield decreased in the absence of Ca. Under these conditions, addition of Ca or Fe caused a decrease in Cd content and increase in dry weight. The relationship between dry weight and Cd content indicated that the critical Cd content above which plants suffer from Cd toxicity was about 20 ppm.

Bingham et al (1975) reported that Cd sensitive plants such as spinach, soybean and lettuce were injured by soil Cd levels of approximately 170 $\mu\text{g Cd/g}$ without exhibiting symptoms. But rice was tolerant at all levels tested. Leafy plants accumulated 175 to 354 $\mu\text{g Cd/g}$ in tissue. Paddy exhibited no ill effect upto 640 $\mu\text{g Cd/g}$ soil and at this level the tissue concentration was 2 $\mu\text{g Cd/g}$.

Cuningham et al (1975) compared the metal uptake of Cr, Cu and Ni and reported that the treatment involving inorganic salts of these metals resulted in lower yield and higher metal concentration.

Giordano et al (1975) found that concentration of Ni in grain and forage ranged from 2.6 to 6.9 ppm with the application of municipal waste.

Honma and Hirata (1976) reported that, in rice the Cd concentration above 0.5 ppm depressed plant height, tiller and weight of shoots. It was also reported that the co-existence of Zn stimulated the Cd transport to shoots in both soil and water experiments in a certain Zn/Cd ratio.

According to Miller et al (1976) Cd uptake decreased as soil pH increased while available P was related to increased Cd accumulation. The growth of soybean shoots were generally depressed when concentration reached 3 to 5 μg Cd/g dry weight.

They also observed that high levels of available P reduced Pb uptake while studying the accumulation of heavy metals and its effect on vegetable growth.

Lee et al (1976) investigated the effect of Pb and reported that Pb treatment resulted in increased respiration rate, increased activity of acid phosphatase, peroxidase, alpha amylase and an increase in soluble protein and ammonia. Increased activity of hydrolytic enzymes and peroxidase indicate that Pb treatment enhanced senescence.

Foroughi et al (1976) noticed that high concentration of heavy metals particularly Cd and Ni caused wilting, necrosis of older leaves, weak growth, small fruits and early ripening. Nickel also caused brown spots on fruits. Yield depression occurred with 1.5 to 3.0 ppm Cd, 2.5 Ni, and 5.0 ppm Cr.

Ito and Imura (1976) found that in rice plants grown in culture solutions containing zero to 30 ppm of Cd in pots on a paddy soil containing 0.30 (native concentration) to 2000 ppm of Cd, that tillering and root hair elongation were inhibited and grain yield decreased at the higher Cd concentration. The lower limit of Cd concentration for bringing about the growth disorder was about 20 ppm in straw and 2 ppm in brown rice. The water culture experiment with Cd in rice plant showed that the Cd concentration was in the order of root, stem, leaves and brown rice.

According to Maclean (1976) the Cd concentration of 10 plant species grown in a neutral surface soil (0.65 ppm Cd) varied from 0.18 ppm in potato tuber to 0.97 ppm in soybean roots on dry matter basis. Addition of 5.0 ppm Cd resulted in a corresponding concentration of 10.36 ppm in lettuce and 11.57 ppm in tobacco leaves.

Bigham et al (1976) raised rice plants to maturity in pots with soil amended by 1% sewage sludge enriched with $CdSO_4$ ranging upto 640 μg Cd/g in two sets of soil conditions viz flooded and non-flooded. They found that grain products for rice under flooded management was relatively unaffected by Cd treatment. But there was 25% yield decrement with treatment of 320 μg Cd/g under non-flooded conditions.

According to Lamoreaux and Cheney (1977) leaf, stem and root dry weight were significantly reduced and strongly correlated with applied $CdCl_2$ levels. The Cd treatment also resulted in the reduction of relative conductivity of excised stem.

Reddy and Patrick (1977) found that almost all Cd entering rice plants accumulated in shoots and water soluble Cd in soil solution was significantly correlated with total plant Cd.

Miller et al (1977) reported that there is a tendency for soil Pb to increase both the plant Cd concentration and the total Cd uptake of the corn shoots. But the soil Cd reduced the total Pb content.

Nakajima (1978) conducted investigations on Cd concentration in brown rice which suffered Cd pollution and found that soil Cd was not correlated to brown rice Cd.

Dabiri et al (1978) noticed that when rice plants were grown in Hoagland Arnon-1 nutrient solution containing different concentration of Cd (0.005, 0.010 and 0.100 ppm) and one concentration of Zn (0.070 ppm) with ^{109}Cd and ^{65}Zn , Cd remained fixed by radicular sites and its translocation index was very low.

Mitchell et al (1978) reported that Cd was most toxic followed by Ni, Cu and Zn. Yield reduction was noticed when the leaves contained Cd at 36 to 43 ppm in wheat.

Spalding (1979) in an experiment, monitored Hg, Cd, Pb, Ni, Zn and Cu @ 10, 100 and 1000 µg/g and reported that all metals except Pb inhibited respiration at higher levels. Cellulose activity was found depressed by Hg and Cd after four weeks.

Mills and Parker (1979) reported that germination, survival, height and dry weight exhibited a negative response with increased Cd application and there was variation according to species.

Kelly et al (1979) reported that shoot elongation and root and shoot dry weight were reduced by Cd. There was increased content of Cd in plants with increased dose.

Austen, G.A. (1979) examined the effects of increasing levels of NiSO₄ on development of Phaseolous vulgaris in a solution culture and found that with increasing concentration, both heavy metals were absorbed and translocated to the shoots. At higher concentrations Co uptake was noticeably reduced compared with that of Ni.

The specific organ distribution of Ni led to a concentration gradient being, root, leaf, fruit and stem. Plant development was inhibited by NiSO₄.

Mills and Parker (1980) observed that Cd effect was an initial delay in growth rather than reduction in overall growth. Generally heavy metal contamination resulted in reduced growth and this is not due to Cd alone.

Mulla et al (1980) established that, in a soil fertilized with 175 kg of P/ha/year for 36 years, the surface soil concentration of Cd can well be correlated with concentration of total P. Cd levels in plants were elevated over that of control plots and no yield depression was noticed in case of barley.

Khalid and Tonsley (1980) observed depression of shoot yield by Ni except at lower level (30 µg Ni/g soil). Nickel concentration of 50 µg/g in shoot did not reduce dry matter production although slight chlorosis appeared at this level. Increase in Ni concentration in shoot was not proportional to the reduction in yield.

Preet et al (1980) analysed garden vegetables for their content in heavy metals and found that garden fruits were lower in

heavy metals than leafy or root vegetables. Species difference in Pb and Cd uptake among leafy vegetables were also observed. Higher Pb content occurred in leafy vegetables grown near heavy traffic.

Weich (1981) reported that even though the essentiality of Ni has not been established for higher plants, there are some beneficial effects. Nickel may function in the utilization and translocation of N and it is used for anabolic reaction in growing tissues. Nickel may have an essential function in symbiotic N_2 fixation for the growth of rhizobia or for utilisation of fixed N_2 by plants.

Lund et al (1981) observed that residual soil material developed from shale parent material had the greatest Cd concentration with a mean value of $7.5 \mu\text{g/g}$, whereas soil developed from sandstone and basalt had a Cd concentration with a mean of $0.84 \mu\text{g/g}$. Alluvial soils from parent materials of mixed sources had a mean Cd content of $1.5 \mu\text{g/g}$. Vegetables grown on these soils contained Cd sufficient to be of public health concern.

In an experiment conducted on beans, to determine the toxicity of Cd, Vigue et al (1981) noticed that the total N content of

shoots, nodule weight, nodule number and nitrogen fixation were significantly reduced at 10 μM Cd/litre. Nodulation was completely inhibited at 500 μg Cd/l. They also observed that Cd uptake and translocation were slow and so Cd levels were high in roots, much lower in nodules and lowest in shoot tissue.

Deviprasad and Deviprasad (1972) reported that in fresh water algae Cd and Pb had stimulating effect at lower concentrations (0.10 to 1.0 ppm) whereas they were lethal at higher concentrations (5 ppm).

Wallace et al (1982) studied the effects of excess Cu, Ni, Co or their combination on Phaseolus vulgaris. They reported that the yield of trifoliolate leaves were reduced by 72, 42 and 68 per cent respectively when they contained 89 μg Cu, 76 μg Ni and 54 μg Co/g dry matter. Combination of Ni and Co induced chlorosis which was not given by Ni or Co alone.

Khan observed (1983) that there was some beneficial effects for Cd and Pb at their lower doses and toxicity at higher levels, when tomato plants were grown under green-house conditions. It was also reported that tomato is more tolerant than egg plant to heavy metals.

Vlams et al (1985) reported that when barley plants were grown with the addition of sludge containing Cd and Zn for 7 years, no toxic effect was noticed. For the first two years Cd and Zn concentration was not increased in plants. In the last four years Zn and Cd concentration was found to increase in grain and straw.

2.4 Heavy metals and animal toxicity

Underwood (1971) has stated that common pastures contain 0.5 to 3.5 ppm Ni on dry basis and the concentration of Ni in soil and plant is higher than in animals. Human consumption is estimated as 0.5 mg/day. The Cd content in human body is 30 mg and the maximum Cd accumulation is at the age of 50. Milk contains 20-30 µg Cd/litre and the daily intake by human adult is 200 to 500 µg with variation in type of food. It is also stated that lead content in pasture in industrial area is 0.3 to 1.5 ppm which may increase to 10.0 to 40.0 ppm in winter. To a certain level the ingested Pb will be excreted and beyond that it is retained in tissues.

Martz and Cornatzer (1971), found that Ni content is higher in rice, legumes, vegetables, tea, coffee, cocoa etc and low in apple, milk, corn meal etc. There are a number of pathological conditions that result in an increase in Ni.

Based on a study in corn, Baumhardt and Welch (1972) concluded that added Pb increased the concentration of Pb in plants and even though the plant is unaffected the plant material could contain enough Pb to be harmful when ingested. According to them, dry matter concentration of 150 ppm Pb is harmful when ingested.

Clerk and Myra (1975) stated that occasional Cd poisoning has been reported following use of Cd plated vessels and pasture contamination in the vicinity of zinc mines and the metal is readily absorbed from guts and then fixed by tissues. In cattle 82% of the Cd ingested is excreted in faeces and 0.022% is occurring in milk. Regarding Pb, high concentration of pasture occurs near lead mines and the herbage in this area may contain upto 580 ppm Pb on dry weight basis. Gasoline causes Pb pollution near highways and the vegetation in such area are found to contain upto 500 ppm Pb.

Casarett and Doull's (1975) in their book 'Toxicology' have narrated that the major routes of absorption of Pb are gastrointestinal and respiratory systems. The overall Pb consumed through inadvertently contaminated food is approximately 8% of the total consumption. Considering cadmium, the percentage of Cd absorbed by

humans through gastrointestinal tract is 0.5 to 12.0. About 50% of the Cd is concentrated in liver and kidneys and the major Ni content in body is 70 mg and there is a mechanism for limited internal absorption is suggested for this metal.

Williams and Wollum (1981) evaluated the effect of Cd on soil procaryotic population and found that low levels of media, Cd retarded procaryotic growth, whereas higher levels did not. This depends on the protection mechanism that is operative at high levels of Cd. They also noticed that the DTPA TEA extractable soil Cd had no influence on the development of Cd tolerant soil population on media amended with Cd.

In a study conducted on earth worms, Bayer et al (1982) found that the earthworms were containing 12 times more Cd than that of control sites. Concentration of Cd in soil and earth worms were correlated. Concentration of Cd as high as 10.0 ppm (dry weight) were detected in earth worms from soil containing 2.0 ppm Cd. These concentrations were found hazardous to wild life that eat earth worms. They suggested that dietary Cd concentration of more than 100 ppm is harmful to a variety of species.

Bisessar (1982) noted that the Cd, Pb, As and Cu decreased with increasing distance from the source of pollution and the population of bacteria actinomycets, fungi, nematodes and earth worms increased with distance

Baxter et al (1982) observed that, when diet containing zero and 12% anaerobically digested sewage sludge was fed to animals for nine months, the Cd concentration in tissues increased from one to 20 ppm which did not decrease by withdrawal of the feed Cadmium in kidney increased from 5 ppm to 55 ppm Onset of proteinurea has been postulated to occur when Cd concentrations in kidney cortex reaches 200 ppm This is equivalent to 400 ppm in the whole kidney

Impact of sewage sludge fertilized corn feeding on goats were studied by Bray et al (1985) and found that there was accumulation of trace metals in tissues Cornsilage contained 5.3 mg Cd/kg, and Cd concentration in goat liver after 3 years feeding was 2.94 mg/kg, Kidney concentration was 10 times more than liver But this amount was less than that suggested for renal dysfunction Critical Cd level for renal dysfunction was 300 mg Cd/kg

Gupta and Salunkhe (1985) suggested that Pb may cause neuritis and alteration in red blood cells and Cd may affect the mitotic

activity of T cells. Once absorbed Cd is well retained with a half life of 10-40 years. Nickel will cause pulmonary oedema, bronchitis and intestinal pneumonitis.

They also stated that river water polluted with Cd used for irrigating rice fields in Japan resulted in the increase of Cd content in rice 10 times of the normal. The average Cd content in earth's crust is 0.15 to 0.2 ppm and 50% of the soil Cd is as free Cd⁺⁺. Cadmium is released in the environment by Cd plated metals, incineration of plastics, the wear of automobile tyres, use of P fertilizers, use of coal and heating oil, use of sludge and consumption of tobacco. About 5.2% of the total Cd processed is annually released to the environment.

2.5 Controlling heavy metal concentration in soil

Takizuma and Katsumi (1973) noticed that the Cd uptake after ear forming stage by rice was reduced remarkably by a basal application of the soil amendments followed by top application. Combined use of calcium silicate and fused magnesium phosphate was most effective in producing rice with lowest Cd content, i.e. one fifth of the control. Solubility of Cd appeared to be depressed by the addition of ammonium sulphate also.

The efficiency of barley straw in removing heavy metals was investigated by Larsen and Schierup (1981) who concluded that one gram of straw was able to absorb amounts of Zn, Cu, Pb, Ni and Cd ranging from 4.3 to 15.2 mg. The efficiency of straw was improved by 10 to 90% when mixed with CaCO₃.

MATERIALS AND METHODS

MATERIALS AND METHODS

The primary aim of this investigation is to assess any possible accumulation of heavy metals especially cadmium in some of the heavily and continuously fertilized major rice soil types. An insight into the health hazards if any, consequent to continuous fertilizer use was also necessary, either to substantiate or alleviate the apprehensions raised from some quarters. It was also necessary to investigate the difference among different crops in taking up heavy metals when present in excess quantities in the soil. Some of the common fertilizers available in the market were also analysed for their heavy metal content. The materials and methods for achieving the above explained objectives are presented in this chapter.

3.1 Fertilizers investigated for their heavy metal content

The following fertilizers available in the market were collected at random and their mean heavy metal determined.

Sl No	Name of fertilizers	Analysis %			NO of samples collected
		N	P ₂ O ₅	K ₂ O	
1	Mussoorie phosphate (Rockphosphate)	0	24	0	6
2	Superphosphate	0	16(WS)	0	5
3	Factamphos	16	20	0	4
4	Muriate of potash	0	0	60	6
5	Urea	46	0	0	6
6	Ammonium sulphate	20.5	0	0	6
7	Rock phosphate (Imported origin not known)	0	35	0	2
8	17 17 17 complex	17	17	17	4

3 2 Soil and Plant sample

The type of soils, their location and number of soils and plant samples collected from each location^{are} presented below

Surface soil (0 15 cm) samples were collected during the Punja season of 1985 from the Karappadam, Kayal and Kari soils Kuttanad region Mature paddy plants (straw and grain) were also collected from these locations along with the soil samples Soil and plant samples of the Loamy soil type were collected during the rabi season of 1985 Soil and plant samples from the PMT plots^{were} also collected during the rabi season^{of} 1985

Sl No	Type of soil	Locality from which collected	No of samples collected (Equal NO of soil and plant samples)
1	Karappadam soil (Sulfaquent)	Mankottapadom at Edathuva in Alleppey District	30
2	Kayal soil (Sulphaquept)	Monkombu and Pulinkunnu areas of Alleppey District	36
3	Kari soil (Sulphaquept)	Malayathodu Thekkuvasam Padom at Ambalapuzha in Alleppey District	36
4	Loam soil (Tropudults)	Seed farm and surroundings at Chirayinkil in Trivandrum District	14

3 3 Samples from permanent manurial experiments

Samples ^{were} collected from two permanent manurial experiments, the plots under each treatment receiving the same dose and type of fertilizers and their combinations including organic manure for 25 years and 13 years respectively and hence could give valuable data on the difference between treatments with reference to their heavy metal status. Because large number of plant and soil samples had to be analysed from both permanent manurial experiment plots, soil, plant and grain samples from the new permanent manurial experiment and soil alone from old PME were collected and analysed. *The experimental plots are located at IARS Pattambi.*

3 3 1 Old permanent manurial Expt with fall indica rice

Year of starting	1961
Year of sample collection	1985 rabi
No of soil samples collected	32
Fertilizer recommendation adopted	40 20 20 (per acre) (44 22 22 kg/ha)

Treatments

Treatment No	Details of organic Fertilizer applied	manure/ per ha	Nutrient applied		
			N	P	K
T ₁	Cattle manure	8820 kg/ha	44	-	-
T ₂	Green leaves	8820 kg/ha	44	-	-
T ₃	Cattle manure Green leaves	4410 kg/ha and 4410 kg/ha	44	-	-
T ₄	Ammonium sulphate	220 kg/ha	44	-	-
T ₅	Cattle manure Ammonium sulphate Superphosphate Muriate of potash	4410 kg/ha 110 kg/ha 137 kg/ha and 36 kg/ha	44	22	22
T ₆	Green leaves Ammonium sulphate Superphosphate Muriate of potash	4410 kg/ha 110 kg/ha 137 kg/ha and 36 kg/ha	44	22	22
T ₇	Cattle manure Green leaves Ammonium sulphate Superphosphate Muriate of potash	2205 kg/ha 2205 kg/ha 110 kg/ha 137 kg/ha and 36 kg/ha	44	22	22
T ₈	Ammonium sulphate Superphosphate Muriate of potash	220 kg/ha 137 kg/ha 36 kg/ha	44	22	22

Year of starting	1973
Year of soil collection	1985
No of soil samples collected	16
No of plant samples collected	16
No of grain samples collected	16

Treatments

Treatment No	Details of organic manure/ Fertilizer applied per ha	Nutrients applied		
		N	P	K
T ₁	Cattle manure 18,000 kg/ha	90		
T ₂	Green leaves 18,000 kg/ha	30		
T ₃	Cattle manure Green leaves 9,000 kg/ha 9,000 kg/ha	90		
T ₄	Ammonium sulphate 450 kg/ha	90		
T ₅	Cattle manure Ammonium sulphate Superphosphate Murate of Potash 9,000 kg/ha 225 kg/ha 281 kg/ha 75 kg/ha	90	15	45
T ₆	Green leaves Ammonium sulphate Super phosphate 9,000 kg/ha 225 kg/ha 281 kg/ha	90	45	0
T ₇	Cattle manure Green leaves Ammonium sulphate Super phosphate Murate of potash 4,500 kg/ha 4,500 kg/ha 225 kg/ha 281 kg/ha 75 kg/ha	90	45	15
T ₈	Ammonium sulphate Super phosphate Murate of potash 450 kg/ha 281 kg/ha 75 kg/ha	90	45	45

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3.4 Pot culture experiment

A completely randomised design experiment with four replications in glazed porcelain pots filled with 5 kg homogenised red loam soil was carried out with rice, amaranthus and guinea grass (a cereal crop, a leafy vegetable and a forage crop) to observe differences if any in the uptake of cadmium. The basal application of recommended fertilizer was thoroughly mixed with $CdCl_2$ equivalent to 0, 10, 20 and 30 g Cd per hectare. No organic manure or plant protection chemicals were used in the experiment to avoid possible heavy metal contamination.

3.5 Preparation of samples

3.5.1 Preparation of soil samples

Composite soil samples were collected just after harvest. The soils were dried in shade, broken with wooden mallet and sieved through a 20 μ m plastic cloth and kept aside for analysis.

3.5.2 Preparation of plant samples

Grains were removed from the shoots and plant parts were cleaned and cut with a clean stainless steel scissors, dried in a hot air oven at 70 ± 5 C to a constant weight and representative samples were drawn. Again the samples were dried in the oven and

pulverised in a Retsch ultra centrifugal mill, using 0.75 mm mesh and stored in small polythene containers

3.5.3 Preparation of grain

The grains separated from the plants were cleaned of chaff washed with dilute acid and then in dilute alkali alternatively and again washed several times in distilled water and then dried in an oven till the moisture content was 12%. Then the whole grains were powdered in the Retsch ultra centrifugal mill using a 0.75 mm mesh and stored in polythene jars for further analysis

3.6 Soil analysis

3.6.1 Measurement of pH

pH was measured in a 1:2.5 soil water system using a combined electrode and a portable Elmer pH meter

3.6.2 Total Nitrogen

The total nitrogen status of the soils were determined by the micro kjeldahl digestion and distillation method using Parnas and Wagner apparatus (Jackson, 1973)

3 6 3 Available phosphorus

The available P_2O_5 was determined from an aliquot of soil extract with Bray No 1 reagent as per the chlorostannous reduced phosphomolybdic blue colour method in hydrochloric acid system. The colour was read in a spectronic 2000 spectrophotometer at 640 nm (Bray and Kurtz, 1945)

3 6 4 Total Potassium

The HCl extract was diluted and the Potassium in the extract was estimated in an EEL Flame photometer

3 6 5 CEC, organic matter and clay content

The CEC, organic matter and clay content were determined by standard procedure described by Jackson (1973)

3 5 6 1 Total Heavy metals

One gram of soil was digested with 15 ml of double acid (H_2SO_4 10 ml + $HClO_4$ 5 ml) and evaporated to incipient dryness, dissolved in 50 ml 1N HCl and then boiled. The heavy metal concentration in this extract were measured in a Perkin Elmer (PE 3030) Atomic Absorption spectro photometer, using electrodeless discharge lamps as the light source

3.6.6.2 D T P A - TEA extractable heavy metals

Ten gram of soil was mixed with 20 ml of D T P A - T E A solution (0.005 M) in polythene bottles and were shaken for two hours filtered through No 42 Whatman filter paper. The filtered solution was set aside for the determination of extractable heavy metals, using the Perkin Elmer (P E 3030) Atomic Absorption Spectrophotometer. Electrodeless discharge lamps and Hollow cathode lamps were used as the light source for determination of the metals.

3.7 Plant analysis

Five hundred milligrammes each of powdered samples were digested with 10 ml of double acid (prepared in the ratio of 2:1 H_2SO_4 and $HClO_4$) until the contents were clear, cooled and diluted with triple distilled water and made up to 100 ml and the heavy metal contents were determined with the aid of the A A S as described above.

RESULTS

RESULTS

The results of analyses of eight commonly sold fertilizers, 116 each of soil and plant samples collected from four major rice soils of Kerala, 32 soil samples from one permanent manurial experiment and soil, plant and grain samples from another permanent manurial experiment of the Regional Agricultural Research Station, Pattambi are presented in this chapter. The two permanent manurial experiments investigated were 25 and 13 years old at the time of sample collection and were having different combinations of fertilizer doses as treatments. Since exact data and cropping history of these experiments were systematically and meticulously kept, an insight into the comparative accumulation of heavy metals as related to different treatment combinations could be brought out. The result of one pot culture study conducted to bring out crop to crop variation in the uptake of cadmium from fertilizers made impure by adding cadmium in the form of $CdCl_2$, is also presented. The results of analyses are presented in Tables 1 to 11.

4.1 Fertilizer analysis

The mean content of total heavy metals in eight commonly sold fertilizers are presented in Table -2

Basic details of Soil samples collected from cultivators'

fields

Table - 1

Sl.No.	Type of Soil	Nos. Collected	Fertilizer nutrients applied for 6 years			Nutrient present in the soil			PH	CEC meq/100g	Organic matter %	Clay content %
			Kgs /ha			%						
			N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O				
1	Karappadam Soil	30	281	249	255	0.209	0.0024	0.354	4.51	26.470	5.605	38.10
2	Kayal Soil	36	404	285	243	0.227	0.0022	0.323	4.41	21.600	3.860	23.0
3	Kari Soil	36	238	231	117	0.194	0.0034	0.182	3.61	36.900	15.910	62.70
4	Trivandrum Sandy loam soil	14	630	315	315	0.133	0.0088	0.197	5.82	4.200	0.727	5.80

4.1.1 Cadmium content of fertilizers

The highest mean total content of Cd was observed in the case of Factamphos (7.160 ppm) while the minimum value was noted in Ammonium sulphate (0.658 ppm). The Cd content in fertilizers decreased in the order of Factamphos (7.160 ppm), 17-17-17 complex (6.254 ppm), Super phosphate (4.879 ppm), Mussoorie phosphate (1.873 ppm), Muriate of potash (1.842 ppm), Imported Rock phosphate (0.925 ppm) and Ammonium sulphate (0.658 ppm).

The analysis of variance showed that there was significant variation in the cadmium content of different fertilizers. The Cd content of Factamphos, 17-17-17 complex and super phosphate were significantly higher as compared to other fertilizers.

4.1.2 Nickel content in fertilizers

The mean total nickel content was found to be highest in Mussoorie phosphate (45.190 ppm) while the minimum content was noted in Ammonium sulphate (0.730 ppm). The nickel content of different fertilizers was in the decreasing order of Mussoorie phosphate (45.190 ppm), Factamphos (10.967 ppm), Superphosphate (9.146 ppm), 17-17-17 complex (5.817 ppm), Rock phosphate (imported) (5.417 ppm), Muriate of potash (2.788 ppm), Urea (0.950 ppm), Ammonium sulphate (0.729 ppm).

Analysis of variance showed that the N₁ content of Mussoorie phosphate was far higher as compared to all other fertilizers. Factamphos and super phosphate were on par in N₁ content while being superior to all other fertilizers. But the N₁ content of super phosphate was found to be on par with 17 17 17 complex and imported rock phosphate.

4.1.3 Lead content of fertilizers

Mussoorie phosphate was found to contain the maximum amount of total Pb (8.03 ppm) and the minimum content was noted in urea (0.28 ppm). The Pb content in different fertilizers was in the decreasing order of Mussoorie phosphate > super phosphate > Factamphos > Ammonium sulphate > Muriate of potash > 17 17 17 complex > Imported rock phosphate > urea.

As brought out by the analysis of variance, Mussoorie phosphate was found to contain higher Pb as compared to all other fertilizers, at the same time the value was on par with super phosphate. The Pb content of super phosphate was found to be on par with Factamphos while Factamphos was again on par with Ammonium sulphate.

Table -2 Heavy metal content in commonly used fertilizers(mean values)

Sl No	Name of fertilizer	No of samples analysed	Mean heavy metal content in ppm		
			Cd	Ni	Pb
1	Mussoorie phosphate	6	1 873	45 192	8 025
2,	Superphosphate	5	4 879	9 146	6 317
3	Factamphos	4	7 163	10 967	4 675
4	Muriate of potash	6	1 842	2 788	2 492
5	Urea	6	1 150	0 950	0 275
6	Ammonium sulphate	6	0 658	0 729	3 075
7	Rock phosphate (imported)	2	0 925	5 147	0 971
8	17 17 17 complex	4	6 254	5 817	0 971

4.2 Heavy metal content of four types of rice soils

The result of analyses of 30 Karappadam soils and 36 each of Kaya1 and Kari soils and 12 Trivandrum sandy loam soils for their total and DTPA extractable heavy metal content and NPK content are presented in Table 3. The percentages of DTPA extractable heavy metals in relation to their total content in different soils are presented in Table 4.

4.2.1.1 Total Cd content in different soil types

The mean total Cd content ranged between 2.270 ppm to 0.370 ppm among the four soil types studied. The maximum content of 2.270 ppm was present in Karappadam soils, followed by Kaya1 soils (1.680 ppm), Kari soils (0.920 ppm) and Trivandrum sandy loam soils (0.370 ppm). Analysis of variance showed that each soil type varied significantly from the other in total Cd content.

4.2.1.2 DTPA Extractable Cadmium in different soil types

The DTPA extractable Cd content was in the order of Kari soil (0.026 ppm), Kaya1 soils (0.024 ppm), Karappadam soils (0.013 ppm) and Trivandrum sandy loam soils (0.011 ppm). Kari and Kaya1 soils yielded significantly higher DTPA extractable Cd as compared to the other two types of soils.

Kari and Kayal soils were on par in this respect, whereas the other two soil types were also on par

4 2 2 1 Total Ni content in different soil types

The maximum total Ni content was obtained in Kayal soils (53 160 ppm) while the lowest value was observed in Trivandrum sandy loam (14 020 ppm) while the value for Karappadam soils was 48 720 ppm and for Kari soils 30 270 ppm

In total Ni content, Kayal and Karappadam soils were significantly superior to Kari and Trivandrum sandy loam soil

4 2 2 2 DTPA Extractable Ni in different soil types

The maximum DTPA extractable Ni was found in Kayal lands (1 280 ppm) followed by Karappadam (1 240 ppm), Trivandrum sandy loam (0 680 ppm) and Kari soil (0 610 ppm)

The Kayal and Karappadam soils were on par in DTPA extractable Ni and superior to Kari soil and Trivandrum sandy loam soil

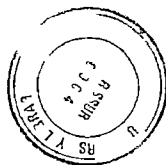
4 2 3 1 Total Pb content in different soil types

Total Pb content was found to be the highest in Kari soil (17 560 ppm) and the lowest value was obtained in the Trivandrum

Table -3

Mean heavy metal content of four different types of soil

Sl No	Soil type	No of samples	Heavy metal content in ppm					
			Total Cd	D T P A Extractable Cd	Total Ni	DTPA extractable Ni	Total Pb	DTPA extractable Pb
1	Karappadam	30	2 271	0 014	48 717	1 245	9 306	1 623
2	Kayal	36	1 679	0 024	53 158	1 278	17 474	1 144
3	Kari	36	0 919	0 026	30 265	0 614	17 561	8 144
4	Trivandrum sandy loam	12	0 371	0 011	14 018	0 067	5 965	0 500



sandy loam soil (5 970 ppm) The total Pb content of Kayal soil was found to be 17 470 ppm and for Karappadam soils it was 9 310 ppm

The total Pb content of Kar and Kayal soils were significantly higher when compared to the other two soil types

4 2 3 2 DTPA extractable Pb content in different soil types

The DTPA extractable Pb ranged between 8 140 ppm 0 500 ppm among the four soil types The maximum amount was present in Kar soils The maximum in Tiruvandrum sandy loam soil The DTPA extractable Pb in Karappadam and Kayal soils were 1 62 ppm and 1 11 ppm respectively

Analysis of various showed that all the soils were significantly different from each other in DTPA extractable Pb content

4 2 4 The percentage of DTPA extractable heavy metal content to the total heavy metal content

The percentage of DTPA extractable heavy metal content of different soil types to their total content is worked out and presented in Table - 4

Of the total Cd in Karappadam, Kayal, Kar and Tiruvandrum sandy loam soils, 0 62, 1 43, 2 83 and 2 96 per cent respectively

Table -4 Per cent DTPA extractable heavy metals in relation to their total content in soil.

Sl No	Soil type	Percentage of D T.P A extractable heavy metal content to the total content		
		Cd	Ni	Pb
1	Karappadam	0.62	2.56	17.46
2	Kayal	1.43	2.40	6.55
3	Kari	2.83	2.03	46.38
4	Trivandrum sandyloam	2.96	0.48	8.38

were found to be DTPA extractable. This fraction was highest in Trivandrum sandy loam soil, followed by Kari and then Kayal soil. Karappadam registered the lowest per cent of DTPA extractable Cd.

With reference to Ni, the DTPA extractable to total Ni in Karapadam, Kayal, Kari and Trivandrum sandy loam soils were in the order of 2.56, 2.40, 2.03 and 0.48 per cent respectively. While the first three types of soils did not show any substantial difference among them in the extractability of Ni, the DTPA extractable Ni in Trivandrum sandy loam soil was found to be the lowest.

In the case of Pb, highest extractability was observed as compared to the other two heavy metals studied. The DTPA extractability of Pb with reference to the soil types were in the order of Kari soils (46.38%), Karappadam soils (27.44%), Trivandrum sandy loam soils (8.38%) and Kayal soils (6.55%). Wide variation is noted among the four different soil types in the percentage of extractable Pb to total Pb. The highest value was in Kari soil followed by Karappadam soils. Trivandrum sandy loam soils yielded the least extractable lead.

4.3 Heavy metal content in plants

Crop samples were also collected from the four rice soil types for plant analysis to determine heavy metal content, in order to

study correlation if any between soil and plant content. The results of the analyses of plant samples are presented in Table -5. The results obtained were analysed statistically as CRD.

4.3.1 Mean Cd content in rice plants

The Cd content of paddy straw were in the order of 2.44 ppm (Karappadam soils), 2.33 ppm (Kari soils), 1.77 ppm (Kayal soils) and 0.88 ppm (Trivandrum sandy loam soils).

The variation in Cd content of plants grown in the four different soil types were not found to be statistically significant.

4.3.2 Mean N₁ content in rice plants

The mean N₁ content in rice plants in Karappadam, Kayal, Kari and Trivandrum sandy loam soils were found to be 14.99, 2.99, 2.87 and 1.94 ppm respectively. The difference in the N₁ content among the four soil types was found to be statistically significant. The N₁ content of rice plants grown on Karappadam soils was significantly higher as compared to the plants grown on other soils. The other two types of soils were on par with reference to the N₁ content of rice plants grown on them.

Table - 5 Mean heavy metal content in rice plants grown on different rice soils

Sl No	Soil types	Heavy metal content in ppm		
		Cd	Ni	Pb
1	Karappadam	2.44	14.99	5.75
2	Kayal	1.77	22.99	10.03
3	Kari	2.33	2.87	4.44
4	Trivandrum sandy loam	0.88	1.94	6.22

4 3 3 Mean Pb content in rice plants

The mean Pb content in rice plants grown in KayaI soils was maximum (10 030 ppm), while it was the least in rice grown in KarI soils (4 440 ppm) The gradation of Pb content in the descending order was, KayaI soils (10 030 ppm), Tiruvadurum sandy loam (6 220 ppm), Karappadam soils (5 750 ppm), and KarI soils (4 440 ppm) The variation in the Pb content in the plants taken from the different soil types was found to be significant, when tested statistically

4 4 Comparison of different treatments in relation to heavy metal content in the soil of Permanent Manurial Trial with tall indica rice (1961-1985) (Table 6)

4 4 1 Soil Cadmium

The total Cd content was highest in the soil under treatment T₃ and the least in T₅ The total Cd content for the T₃ and T₅ were 0 99 and 0 49 ppm respectively The total Cd content of soils was in the order of T₃ (0 99 ppm), T₇ (0 81 ppm), T₁ (0 71 ppm), T₆ (0 66 ppm), T₈ (0 61 ppm) T₂ (0 56 ppm), T₄ (0 50 ppm) and T₅ (0 49 ppm) The total Cd content in the eight treatment combinations did not show any difference statistically

The DTPA extractable Cd content was highest in T₁ treatment (0.078 ppm) followed by T₇ (0.038 ppm), T₃ and T₅ (both 0.037 ppm), T₆ and T₄ (0.036 ppm each), T₈ (0.035 ppm) and T₂ (0.033 ppm). The DTPA extractable Cd also did not vary significantly among the treatments.

4.4.2 Soil nickel

The total Ni content was 59,560 ppm in T₁ treatment which was the highest, with a diminishing trend in treatments T₄, T₈, T₂, T₇, T₆, T₅, and T₃ giving corresponding values of 58,100, 57,100, 56,800, 55,100, 54,900, 54,000 and 53,600 ppm. In this case also the variation in total Ni among treatments was not found to be statistically significant.

The maximum extractable Ni content was associated with T₅ treatment (0.490 ppm), while the minimum amount was detected in the soil taken from T₆ (0.220 ppm). The other treatments T₁, T₇, T₃, T₈, T₂ and T₄ gave total Ni content in the diminishing order of 0.470, 0.440, 0.420, 0.340, 0.280 and 0.230 ppm. Among the different treatments, the soils from T₅, T₁, T₇ and T₃ were on par with reference to total Ni content, while T₁, T₃ and T₈ were also on par. Even though the treatments were statistically

Table - 6 Heavy metal status of the soil in the different treatments of permanent manurial trial with tall indica

Treat- ment No	Total Cd ppm	Extractable Cd ppm	Total Ni ppm	Extractable Ni ppm	Total Pb ppm	Extractable Pb ppm
T ₁	0.713	0.038	59.563	0.470	21.700	1.936
T ₂	0.563	0.033	56.750	0.280	23.050	2.163
T ₃	0.988	0.037	53.588	0.435	23.513	2.138
T ₄	0.496	0.036	58.100	0.227	23.513	2.424
T ₅	0.488	0.037	54.000	0.489	22.325	1.946
T ₆	0.663	0.036	59.925	0.218	23.275	2.556
T ₇	0.813	0.038	55.125	0.492	25.450	2.455
T ₈	0.614	0.035	57.075	0.341	19.710	2.464

significant, because of the number of treatments showing statistical parity were large, no single treatment could be isolated as superior over the other treatments

4 4 3 Soil lead

Total lead content varied in the diminishing order of 25 500, 23 500, 23 300, 23 300, 23 100, 22 200, 21 700 and 19 700 ppm corresponding to treatments T_7 , T_4 , T_6 , T_3 , T_2 , T_5 , T_1 and T_8 . The difference in the total soil Pb content among the different treatments were not found to be statistically significant

The DTPA extractable Pb content was highest in treatment T_6 (2 560 ppm) and the lowest in treatment T_1 (1 940 ppm). In the soils of other treatments the values were in the order of 2 460 ppm (T_8), 2 460 ppm (T_7), 2 430 ppm (T_4), 2 160 ppm (T_2), 2 140 ppm (T_3) and 1 950 ppm (T_5). In this case also the treatment difference was not significant in relation to extractable Pb content

4 5 Comparison of different treatments in relation to heavy metal content in the soil, plant and grain of permanent manurial trial with dwarf japonica rice (1973-1985) (Table 6)

4 5 1 Heavy metal content in soils

4 5 1 1 Cadmium

The mean total Cd content of soils from the eight treatments varied from 1 330 ppm (T₁) to 0 780 ppm (T₆) The other treatments T₄, T₃, T₈, T₅, T₇, and T₂ had a total Cd content of 1 180, 1 30, 1 080, 1 030, 0 950 and 0 850 ppm respectively Much significant variation was not evident in the mean values The variation in the total soil Cd in the different treatments were not found to be statistically significant

The extractable Cd content in soils of the eight different treatments, also did not show any statistical difference among them The maximum extractable Cd content was noted in T₁ (0 041 ppm) followed by T₈ (0 030 ppm), T₇ and T₃ (both 0 031 ppm), T₅ (0 028 ppm), T₂ (0 027 ppm), T₄ (0 026 ppm) and T₆ (0 025 ppm)

4 5 1 2 Nickel

The maximum total nickel content in soil was associated with T₃ (56 630 ppm) and the minimum amount was noted in T₇ (44 930 ppm) The total Ni content in relation to treatments 4, 2, 5, 6, 1 and 8 were in the decreasing order of 52 430, 52 350, 51 930, 51 750, 49 530 and 47 980 ppm respectively The variation in the total Ni content among all the treatments were statistically not significant

The extractable Ni content was also found to be statistically not significant among treatments with values ranging from 0.370 ppm (T_7) to 0.110 ppm (T_4). The soils from other plots (T_3 , T_8 , T_2 , T_5 , T_7 and T_6) contained extractable Ni in the order of 0.300, 0.270, 0.260, 0.260, 0.240 and 0.180 respectively.

4.5.1.3 Lead

Similar to soil Ni, the total Pb content in the soils of the different treatments also did not show any statistically significant difference among them. The maximum value was attributed to T_5 treatment (29.130 ppm) followed by 28.300 ppm (T_3), 27.780 ppm (T_8), 27.180 ppm (T_2), 27.150 ppm (T_7), 26.100 ppm (T_6), 24.730 ppm (T_4) and 24.630 ppm (T_7).

In contrast to the total Pb content in soils of the different treatments, the extractable Pb content was found to differ significantly. The values ranged between 2.320 ppm (T_2) and 0.800 ppm (T_7). The values for other treatments were 1.780 ppm (T_4), 1.730 ppm (T_3), 1.410 ppm (T_6), 1.310 ppm (T_8), 1.140 ppm (T_5) and 1.070 ppm (T_1). Treatments T_2 , T_4 and T_3 were on par statistically whereas T_3 , T_6 , T_8 and T_5 were also on par. Therefore any one

treatment could not be singled out as definitely superior to other treatments in the extractable lead content in the soil

4.5.2 Heavy metal content in plants (without grain)

4.5.2.1 Plant Cadmium (Rice plant without grain)

There was outstanding statistically significant variation in Cd content in the vegetative parts of rice plants grown under treatment T₁ (8.150 ppm). T₈ and T₆ were on par with values of 5.850 and 5.700 ppm respectively. Similarly T₆ and T₇ were also found to be on par (5.500 ppm for T₇). T₃ and T₄ were on par (5.150 ppm and 4.950 ppm), so also T₂ and T₅ were on par (4.150 ppm and 4.100 ppm).

4.5.2.2 Plant Nickel (without grain)

Even though statistically significant difference among treatments were observed, no treatments could be singled out as superior to other treatments. T₇, (6.850 ppm), T₃, (5.500 ppm), T₆ (5.000 ppm), T₅, (3.150 ppm) and T₂, (3.150 ppm) were on par statistically. T₄ and T₁ were inferior to other treatments in their Ni content (1.250 and 0.200 ppm). T₁ recorded the least Ni content.

4.5.2.3 Plant lead (without grain)

The mean Pb content in rice plants showed statistically significant variation between treatments. Treatments T₈ (24.900 ppm) and T₃ (23.350 ppm) were distinctly superior to other treatments. T₂ was found to follow these two treatments with a value of 17.500 ppm. Treatments T₅ (15.850 ppm), T₆ (15.500 ppm), T₄ (15.100 ppm) and T₇ (14.650 ppm) were found to be on par, but inferior to T₈, T₃ and T₂. The treatment T₇ gave the least value of 14.100 ppm.

Table 7 Heavy metal content in the soil, plant and grain in the different treatments of permanent manurial trial with dwarf japonica rice (n ppm)

Treatment No	Soil heavy metals						Plant heavy metals			Grain heavy metals		
	Cd		Ni		Pb		Cd	Ni	Pb	Cd	Ni	Pb
	Total	DTPA Extractable	Total	DTPA extractable	Total	DTPA extractable						
T ₁	1 325	0 041	42 525	0 366	27 150	1 072	8 150	0 200	14 650	3 280	0 150	10 090
T ₂	0 850	0 027	52 350	0 362	27 175	2 317	4 150	3 150	17 500	2 810	1 820	11 360
T ₃	1 125	0 031	56 625	0 299	28 300	1 731	5 150	5 500	23 350	3 020	3 200	14 380
T ₄	1 175	0 026	52 425	0 109	24 725	1 781	4 950	1 250	15 100	3 045	0 800	10 960
T ₅	1 025	0 028	51 925	0 258	29 125	1 142	4 100	3 750	15 950	2 590	1 960	10 900
T ₆	0 775	0 025	51 750	0 175	26 075	1 412	5,700	5 000	15 500	3 490	3 080	10 600
T ₇	0 950	0 031	44 920	0 240	24 625	0 803	5 500	6 850	14 100	3 290	3 810	8 980
T ₈	1 075	0 036	47 975	0 270	27 775	1 308	5 850	3 150	24 900	3 470	1 990	14 650

4 5 3 Heavy metal content in grain

4 5 3 1 Cd in rice grain

The analytical data showed that treatment No 6 was having the highest Cd content in grain (3 490 ppm), though it did not exhibit definite superiority over other treatments. Treatment T₇ was found to be on par with T₈, T₇ and T₁ which were having values of 3 470, 3 290 and 3 280 ppm Cd respectively. The mean Cd content in the grain showed a decreasing trend with respect to the other treatment in the order of T₄ (3 050 ppm), T₃ (3 020 ppm), T₂ (2 810 ppm) and T₅ (2 590 ppm). The variation in the Cd content among the treatments was found to be statistically significant.

4 5 3 2 Ni in rice grain

As revealed by the analysis of variance data, the average Ni content in rice grain did not show any significant variation. But it was noticed that the T₇ treatment ranked first with respect to Ni content in grains with a value of 3 810 ppm. This was followed by other treatments in the diminishing order of T₃ (3 200 ppm), T₆ (3 080 ppm), T₈ (1 990 ppm), T₅ (1 960 ppm), T₂ (1 820 ppm), T₄ (0 800 ppm) and T₁ (0 150 ppm).

4 5 3 3 Pb content in rice grain

The average Pb content in rice grain varied from a maximum value of 14 650 ppm (T₈) to a minimum of 8 980 ppm (T₇). But this

variation was not found to be statistically significant. The mean Pb content in the rice grain varied in the descending order with respect to the other treatment viz T₃ (14 380 ppm), T₂ (11 360 ppm), T₄ (10 960 ppm), T₅ (10 900 ppm), T₆ (10 600 ppm), T₁ (10 090 ppm) and T₇ (8 980 ppm)

4.6 Pot culture experiments with added cadmium

4.6.1 Rice (Table- 8)

4.6.1.1 Total cadmium content of soil after harvest

The results of the pot culture experiment with added Cd at the rate of 10 g (T₁), 20 g (T₂) and 30 g (T₃) Cd per hectare in the form of CdCl₂, and one control (T₄) without any added Cd, are presented in Table - 8. The crop was harvested after maturity, and uniform samples of soil, plant and grain were analysed.

The results showed that the maximum total Cd content was present in T₃ (1 388 ppm) followed by T₂ and T₁ (both 0 975 ppm). The control (T₄) registered the lowest value of 0 900 ppm Cd. The variation in Cd content of soil after harvest did not show any statistically significant difference.

4.6.1.2 DTPA extractable Cd content of soil

Maximum extractable Cd was detected in T₄ (control) with a value of 0 031 ppm. The mean values of other treatments were in the

Table 8 Cadmium content of soil, plant and grain
in the pot culture experiment with rice

Treatments	Total Cd in soil ppm	Extractable Cd in soil ppm	Total Cd in plant ppm	Total Cd in grain ppm
T ₁ (10 g Cd/ha)	0.975	0.025	5.65	3.5
T ₂ (20 g Cd/ha)	0.975	0.027	5.85	3.3
T ₃ (30 g Cd/ha)	1.388	0.026	5.60	3.0
T ₄ (Control)	0.900	0.031	6.35	4.65

decreasing order of T₂ (0.027 ppm), T₃ (0.026 ppm) and T₁ (0.025 ppm). Here also the values did not differ significantly among them.

4.6.1.3 Cd content in straw

The maximum mean Cd content was noted in T₄ (6.350 ppm) followed by T₂ (5.850 ppm), T₁ (5.650 ppm) and T₃ (5.600 ppm). The difference in the Cd content of straw among the four treatments was not found to be statistically significant.

4.6.1.4 Cadmium content in grain

Here also T₄ registered the highest Cd content of 4.650 ppm. The grain Cd content in T₁ was 3.500 ppm followed by T₂ (3.300 ppm) and T₃ (3.000 ppm). Even though difference in grain Cd content among the Cd added treatments was not statistically significant, the difference between treated plots and control was found to be significant.

4.6.2 Amaranthus (Table 9)

4.6.2.1 Total Cd content in soil after harvest

The total Cd content in soils after harvest was in the order of T₃ (2.000 ppm), T₂ (1.400 ppm), T₁ (1.290 ppm) and T₄ (1.100 ppm). Treatment T₃ was statistically superior in Cd content over other treatments. Treatments T₂, T₁ and T₄ were statistically on par.

4.6.2.2 DTPA extractable Cd content of soil

The extractable Cd content in the soil was found to be highest

Table - 9 Cadmium content of soil and plant in the
pot culture experiment with Amaranthus

Treatments	Total Cd in soil ppm	Extractable Cd in soil ppm	Plant Cd ppm
T ₁ (10 g Cd/ha)	1 288	0 033	6 55
T ₂ (20 g Cd/ha)	1 400	0 035	14 38
T ₃ (30 g Cd/ha)	2 000	0 033	10 50
T ₄ (Control)	1 100	0 030	15 95

in T_2 (0.035 ppm), followed T_3 (0.033 ppm), T_1 (0.033) and T_4 (0.030 ppm). There was no statistically significant variation among treatments.

4.6.2.3 Plant Cadmium

Even though plants from the control pot (T_4) contained the maximum amount of Cadmium (15.950 ppm), the difference in Cd content among all the treatments were not statistically significant. The plant Cd content in T_2 , T_3 and T_1 were in the order of 14.350, 10.500 and 6.550 ppm.

4.6.3 Guinea grass (Table 10)

4.6.3.1 Total Cd content in soil

The maximum soil Cd content was noticed in T_1 Treatment (1.775 ppm), followed by T_3 (1.587 ppm), T_2 (1.463 ppm) and T_4 (1.387 ppm). The treatment difference was not found to be statistically significant.

4.6.3.2 DTPA extractable Cd in soil

The maximum extractable Cd was found to be associated with T_2 (0.039 ppm). This was followed by T_1 (0.035 ppm), T_3 (0.032 ppm) and T_4 (0.031 ppm).

4.6.3.3 Plant Cadmium

The highest Cd content was associated with T_3 (14.400 ppm) followed by T_1 (8.850 ppm), T_2 (8.400 ppm) and T_4 (7.730 ppm).

Table - 10 Cadmium content of soil and plant in the
pot culture experiment with guinea grass

Treatments	Total Cd in soil ppm	Extractable Cd in soil ppm	Plant Cd ppm
T ₁ (10 g Cd/ha)	1 778	0 035	8 850
T ₂ (20 g Cd/ha)	1 463	0 039	8 400
T ₃ (30 g Cd/ha)	1 588	0 032	14 400
T ₄ (Control)	1 388	0 032	7 225

In this case also the treatment difference was not found to be statistically significant

4 7 Correlation coefficients between fertilizer nutrients applied nutrient content in soil, soil heavy metals and plant heavy metals

4 7 1 Correlation coefficients associated with soil total Cd

A negative correlation was observed between the total Cd content of the soil and applied fertilizer N, ($r = -0.0126$) The correlation between total soil Cd and applied P and also applied K fertilizers were found to be positive, the latter being significant ($r = 0.0580$ and 0.2736^*) Soil total Cd was found to be positively and significantly correlated with plant Cd ($r = 0.2268^*$) Total Cd showed a positive correlation with Soil N ($r = 0.2198^*$) A negative and significant correlation ($r = -0.3144^*$) was observed between total Cd content in soil and the soil available P In the case of soil potassium the correlation was positive and significant with total Cd in soil ($r = 0.2796^*$)

4 7 2 Correlation coefficients associated with soil total N₁

The correlation coefficient values between total N₁ content in soil and applied fertilizer N, P, K, plant N₁, soil N, soil P and soil K were found to be positive The corresponding r values were 0.0992, 0.8524^{*}, 0.3445^{*}, 0.1788, 0.3525^{*}, 0.1487 and 0.2226^{*}

4 7 3 Correlation coefficients associated with soil total Pb

The correlation between soil total Pb and applied N, applied P and applied K were found to be negative ($r = 0.0397$, -0.1545 and -0.2187^*) The plant Pb content was found to be positively and significantly correlated to soil total Pb ($r = 0.3077^*$) The soil Pb was found to have a negative correlation with soil N and soil K ($r = -0.0018$ and -0.0892) But the correlation was positive in the case of soil P with an r value of 0.0228

4 7 4 Correlation coefficient associated with extractable Cd

The extractable Cd was found to be positively correlated to applied N, plant Cd and soil P, the last only being significant ($r = 0.1178$, 0.0172 , and 0.2173^*) A negative correlation was observed between extractable Cd and applied P, applied K, soil N and soil K ($r = -0.0086$, -0.0201 , -0.1377 and -0.1302)

4 7 5 Correlation coefficients associated with extractable Ni

The extractable Ni in soil was negatively correlated to applied N ($r = -0.0530$) while the r values were positive in the case of applied P ($r = 0.0879$) and positive and significant with applied K ($r = 0.3169^*$) the correlation between extractable Ni and plant Ni gave a positive and significant value ($r = 0.4132^*$) The extractable Ni was positively and significantly correlated to

Correlation coefficients between fertilizer nutrients applied nutrient content in soil soil heavy metals and plant heavy metals

	Total Cd in soil	Total Ni in soil	Total Pb in soil	Ex Cd in soil	Ex Ni in soil	Ex Pb in soil	Ferti lizer N applied	Ferti lizer P applied	Ferti lizer K applied	Cd in plant	Ni in plant	Pb in plant	N in soil	P ₂ O ₅ in soil	K ₂ O in soil
Total Cd in soil	1 000	0 3757	0 3745	0 3071*	0 48 2*	0 4914*	0 0126	0 0580	0 2736*	0 2268*	0 2915*	0 0981	0 2198*	0 3144*	0 2706
Total Ni in soil		1 000	0 3393*	0 1726	0 1945*	0 3497*	0 0992	0 8524	0 3445*	0 8854*	0 1788	0 1555	0 3525*	0 1487	0 2226*
Total Pb in soil			1 000	0 0683*	0 1958*	0 3081*	0 0997	0 1545	0 2187*	0 3100*	0 1177	0 3077*	0 0018	0 228	0 0892
Ex Cd in soil				1 000	0 2885*	0 2087	0 1178	0 0086	0 0201	0 172	0 2657*	0 675	0 1377	0 2173	0 0692
Ex Ni in soil					1 000	0 247 *	0 0530	0 0879	0 3169*	0 1318	0 4132	0 0338	0 2 35*	0 4295	0 3079*
Ex Pb in soil						1 000	0 1008	0 0125	0 2227*	0 0878	0 1578	0 0045	0 1090	0 1004	0 1459*
Fertilizer N applied							1 000	0 7435+	0 7740*	0 4595*	0 0928	0 3810*	0 0432	0 2567*	0 0089
Fertilizer P applied								1 000	0 6392	0 6675*	0 1583	0 2350*	0 2175	0 0253	0 01 4
Fertilizer K applied									1 000	0 5528*	0 516*	0 3778*	0 1274	0 0606	0 1248
Cd in plant										1 000	0 2238*	0 1631*	0 1078	0 0340	0 0258
Ni in plant											1 000	0 2635*	0 0458	0 1052	0 0991
Pb in plant												1 000	0 2211*	0 0916	0 0333
N in soil													1 000	0 2979*	0 1829
P ₂ O ₅ in soil														1 000	0 0327
K ₂ O in soil															1 000

+ Significant at 5 level (0 185)

soil N and soil K ($r = 0.2335^*$ and 0.3079^*), while the correlation was significantly negative with soil P ($r = 0.4295^*$)

4.7.6 Correlation coefficients associated with extractable Pb

The soil extractable Pb was positively correlated to applied N, P, K, plant Pb, soil P, and soil K ($r = 0.1008$, 0.0125 , 0.2227^* , 0.0045 , 0.1004 and 0.1459^*) But the correlation was significantly positive only in the case of applied K, and soil K. In contrast to the above the extractable Pb yielded a negative correlation with soil N ($r = 0.1090$), though the value was not statistically significant.

4.7.7 Correlation coefficient associated with fertilizer nitrogen, phosphorus and potassium

Applied nitrogen fertilizers were found to have positive relationships between plant Cd, plant Ni and plant Pb ($r = 0.4595^*$, 0.0928 , and 0.3870^*) The correlations were significantly positive in the case of Cd and Pb only.

The correlation coefficient values for fertilizer phosphorus and plant Cd, plant Ni and plant Pb were all positive but significant only in the first and last cases ($r = 0.6675^*$, 0.1503 and 0.2350^*)

Fertilizer potassium was found to be positively and significantly correlated to plant Cd, plant Ni and plant Pb ($r = 0.5528^*$, 0.3516^* , 0.3778^*)

DISCUSSION

DISCUSSION

The salient findings of the investigation on the heavy metal content of four major rice growing soils of Kerala and also on the possible accumulation of the heavy metals in the soils under different treatments of two permanent manurial trials are discussed in this chapter. Sixteen each of soil, plant and grain samples from one permanent manurial trial with dwarf japonica rice and pot culture experiments with one grain crop (rice) one fodder crop (guinea grass) and one leafy vegetable (amaranthus) were also studied and the results from the analysis of soils, plant and grain samples are discussed. The major contributory factor involving the inflow of heavy metals in soils viz fertilizers have been analysed and the contribution to the addition and consequent accumulation of heavy metals in the soil is also discussed. In the absence of similar works in the state and elsewhere, thorough discussion and comparisons proved to be difficult.

5.1 Heavy metal content in common fertilizers

Eight commonly used fertilizers viz Factamphos, Ammonium sulphate, 17 17 17 complex, Super phosphate, Mussoorie phosphate, imported Rock phosphate, Muriate of potash and Urea were subjected to analysis with reference to their Cd, Ni and Pb content. The results showed that these fertilizers differed significantly among them in the heavy metal content.

5.1.1 Cadmium content in fertilizers

Factamphos was found to contain the highest amount of Cd (7.160 ppm) as compared to other fertilizers. Ammonium sulphate contained the least quantity of the metal (0.658 ppm). The Cd content of three fertilizers viz Factamphos, 17 17 17 complex and Super phosphate were definitely higher than that contained in other fertilizers. Factamphos and 17 17 17 complex use phosphoric acid as a component in the manufacture while super phosphate is manufactured by treating rock phosphate with sulphuric acid. Therefore it is natural that heavy metals like Cd contained in the crude natural rock phosphate becomes more soluble and transferred to the phosphoric acid manufactured from them. O. Gunnarsson (1983) has reported that 80-90% of Cd is transformed from rock phosphate to super phosphate at the time of manufacture. Similarly acid treatment of Rock phosphate, for example in the manufacture of

Super phosphate, makes the insoluble or sparingly soluble heavy metals, more soluble. The Cd content in the other fertilizers were in the diminishing order of Mussoorie rock phosphate, Muriate of potash, imported Rock phosphate and Ammonium sulphate. The value obtained for Mussoorie phosphate (1 873 ppm) was found to agree more or less with the test value (2 000 ppm) (No 8684 No 2720/dt 23-4-1983 of shri Ram test house, Delhi). It is interesting to note that the imported Rock phosphate contains less Cd than the Indian Mussoorie rock phosphate. This shows that the source of raw material is an important factor influencing the content of heavy metals in fertilizers. According to Mortvedt et al (1981) the Cd content of rock phosphate varies from 3 to 15 ppm in Florida, upto 130 ppm in United States and 4 to 109 ppm in Australia.

5.1.2 Nickel Content in fertilizers

Mussoorie rock phosphate had the highest mean Ni content (45 190 ppm) whereas Ammonium sulphate contained the least Ni (0 730 ppm). The Ni content of Mussoorie phosphate was found to be very much higher than that contained in all other fertilizers investigated. The value obtained is in conformity with the test value (45 ppm) quoted in the test certificate provided by (No 8686/ Mo 2722 dated 23-4 1983) Sri Ram test house, Delhi. The other fertilizers viz Factamphos, Super phosphate, 17 17 17 complex and

imported Rock phosphate did not have any significant variation among them with reference to their Ni content. The relative abundance of the element is variable according to the source of the natural mineral deposits. Mortvedt et al. (1981) has reported that reagent grade Diammonium phosphate contained 1 100 ppm, Idaho phosphate 64 000 ppm and North Carolina phosphate 38 000 ppm Ni. The data shows that the highest quantity of Ni is present in Mussoorie rock phosphate as compared to imported rock phosphate.

5.1.3 Lead content in fertilizers

As in the case of Nickel, Pb content also was significantly higher in Mussoorie rock phosphate (8 030 ppm). This value is also found to be in conformity with a test certificate in which the Pb content in Mussoorie phosphate is noted as 8 000 ppm (Test certificate No 8686/Mo/2722 dt 23.4.1983 of Sriram test house, Delhi). In the present analysis the maximum content was noted in Urea (0 280 ppm).

5.2 Heavy metal content of four different rice soils

Thirty Nos of soil samples from Karappadam and 36 Nos each from Kayal and Kari soils of Kuttanad and 12 sandy loam soils of Trivandrum District were analysed for the total as well as DTPA extractable Cd, Ni and Pb. The percentage of available heavy metals in relation to their total content in soils were also worked out.

The results obtained are discussed in the following section

5 2 1 1 Total Cd content in different soil types

The mean total Cd content in soils was found to be in the order of Karappadam soils (2 270 ppm), Kayal soils (1 680 ppm), Karı soils (0 920 ppm) and Trivandrum sandy loam soils (0 370 ppm) Karappadam soils is water logged for a lesser period as compared to Kayal and Karı soils where acidity is higher (PH 4 4 and 3 6 respectively) and therefore solubility and consequent leaching of elements is much higher Hence, naturally the retention of cations will be much more in Karappadam soils than in Karı and Kayal soils Trivandrum sandy loam soils being sandy in nature (with clay content of 5 8%) the exchange complex will naturally be less (CCC 4 2 meq/100 g) so that lesser amount of cations are retained by these soils Lund et al (1981) reported that the Cd concentration in soil derived from shale parent material was 7 500 ppm and in soils formed from sandstone and basalt, 0 84 ppm According to Gunnarsson (1983) the natural content of Cd in soils varies from 0 100 to more than 1 000 ppm in Sweden Mulla et al (1980) reported that the Cd content was 1 ppm after 36 years of P fertilization against a control of 0 07 ppm Since the soils studied were different in nature in their origin, the difference in their Cd content is natural Since the values presently obtained

is not much greater, than those observed by the above authors, and since only soils with more than 3 00 ppm Cd is considered to be polluted, it can be said that continuous fertilizer application has not built up Cd levels to any hazardous extent

5 2 1 2 DTPA extractable Cd in different soil types

Kari and Kayal soils yielded the highest amount of DTPA extractable Cd (0 026 ppm and 0 024 ppm) These soils were statistically on par The higher acidity of these soils might have contributed to the higher extractability of Cd in these soils as compared to Karappadam soils The lower value of extractable Cd (0 013 ppm) in Karappadam soils may be attributed to its inherent physico chemical properties The Trivandrum sandy loam soils yielded only 0 011 ppm DTPA extractable Cd, which was the lowest This lowest value has to be viewed in the light of its lowest total Cd content (0 37 ppm) and lowest CEC (4 43 to 6 10 meq/100 g) The rate of application of phosphatic fertilizers also affect the extractable Cd content in soil In an experiment by Mortvedt and Giordano (1983) it was found that 0 IN HCl extractable Cd was increased from 0 050 ppm with no P to 0 150 ppm with higher rate of application According to Gunnarsson (1985) loamy soils with low clay content and low CEC produce high concentration of Cd and increasing pH also reduces Cd content

5 2 2 1 Total Ni content in different soil types

The total Ni content of Kayal and Karappadam soils were statistically superior to Kari soils and Trivandrum sandy loam soils. The maximum total Ni was observed in Kayal soils (53 160 ppm) followed by Karappadam soils (48 720 ppm). The trend is more or less same as in the case of Cd. The least total Ni content (14 020 ppm) was observed in Trivandrum sandy loam soil while it was higher than this (30 270 ppm) in Kari soils. The reason stated for the variation of total Cd content in the four soil types can be attributed to the dynamics of each heavy metal in relation to the pH of the soil. As per estimations done by Rasheed et al (1981) in Mississippi river bank the total Ni in soil varied from 8 000 to 53 ppm in sewage irrigated fields.

5 2 2 2 DTPA extractable Ni

The DTPA extractable Ni was in the order of Kayal (1 280 ppm), Karappadam (1 240 ppm), Trivandrum sandy loam (0 680 ppm) and Kari soil (0 610 ppm). The trend of DTPA extractable Ni is similar to that of total Ni in the case of Kayal and Karappadam soils. Much differences was noticed between Kari and Trivandrum sandy soils with reference to DTPA extractable Ni. It was stated by Lucia et al (1982) that there is least mobility of metals in non acid mineral soils with relatively high pH, CEC and exchangeable base

content and the order of mobility was Cu Zn Ni Cd But the behaviour of the element cannot be explained with reference to the physico chemical property of the soils as in the other case Gunnarsson (1983) also opined that very little is known about Ni to explain its agricultural significance The extractable amount of Ni was 0.39 to 6.4 ppm as per the works by Rashid et al (1981) in sewage irrigated fields

5.2.3.1 Total Pb content in different soil types

The total Pb was maximum in Kari soils (17 500 ppm) and is lowest in Trivandrum sandy loam soils (5 970 ppm) The variation in the total Pb content was in the order of Kari soils Kayal soils Karappadam soils & Trivandrum sandy loam soils Kari soils are highly rich in organic matter (15.910%) and the sandy loam soils are having a low value (0.727%) Vegetation has got a tendency to absorb and accumulate the Pb from the atmosphere and soil Turner et al (1985) reported that the falling Pb was retained by organic floor (75%) and mineral soil (25%) This is why large scale planting of trees is advocated in metropolitan cities which are exposed to large scale automobile exhaust fumes containing TEL (Tetra ethyl lead) The highest Pb content in Kari soils may be due to the fact that these soils were originated from forest vegetation which has got mixed with mineral soil due to some geological

upheaval occurred long ago. Preer et al (1980) has reported that leafy vegetables grown near highways with heavy traffic contain high amount of Pb. This shows that the plants have a tendency to accumulate lead. Rolfe (1973) is seen to have stated that Pb is a normal soil constituent and it varies from 1 to 200 ppm in the soil. In the light of this observation it is safe to assume that the Pb content of soils presently investigated are only normal.

5.2.3.2 DTPA extractable Pb in soil

The maximum amount of DTPA extractable Pb was in Kari soils (8.140 ppm) and the minimum in Trivandrum sandy loam (0.5000 ppm). The trend was in the order of Kari soils > Karappadam soils (1.620 ppm) > Kayal soils (1.110 ppm) > and the Trivandrum loamy soils. The DTPA extractable Pb content is seen related to the high total Pb content in the Kari soils. These soils are acidic having very low pH values as compared to other soils studied. The Trivandrum sandy loam soils contained the least amount of extractable Pb. As discussed in the case of other heavy metals, the lowest amount of this fraction in the last soil may be due to its very low content of exchange complex and the consequent low CEC. According to John (1972) soil properties particularly soil pH, extractable Al etc are related to Pb availability. Gunnarsson (1973) also revealed that Pb is strongly fixed in some soils. The content of DTPA

extractable Pb differed significantly between Karappadam and Kayal soils. The extractability of Pb from Karappadam soils was found to be much greater than that of Kayal soils. This may be due to the oxidised condition prevailing in Karappadam soils as compared to Kayal soils which remain submerged for longer periods of the year.

5.2.4 Percentage extractable to total heavy metals in different soils

The exchangeability of the three heavy metals from the four soil types was studied and was found to differ from soil to soil. The percentage of extractable to total Cd was found to be 0.62 in Karappadam soils, 1.43 in Kayal soils, 2.83 in Kari soils and 2.96 in Trivandrum sandy loam soils. The percentage of extractability decreased in the order of Trivandrum sandy loam soils > Kari soils > Kayal soils > Karappadam soils.

The trend in the extractability of Ni showed a different pattern. It was in the decreasing order of Karappadam soils (2.56%), Kayal soils (2.40%), Kari soils (2.03%) and Trivandrum sandy loam soils (0.48%).

In the case of Pb the trend of extractability was in the decreasing order of Kari soils (46.38%) > Karappadam soils (17.44%), > Trivandrum sandy loam soils (8.38%) > Kayal soils (6.55%). In view of the diverge characteristics of the soil studied viz amount

of exchange complex, redox potential, pH, abundance of microflora, period of inundation, total content and chemical nature of heavy metal present etc the behaviour and extractability of such metals in these soils cannot be satisfactorily explained Reddy and Patrick (1977) has pointed out that redox potential and pH affect both solubility and uptake of heavy metals in flooded soils and by altering these parameters we can manipulate the behaviour of some heavy metals But with regard to Kerala soils, literature to support or refute the present findings could not be located

5.3 Heavy metals in plants

The result of analysis of 114 plant samples collected from the four rice soils in relation to their Cd, Ni and Pb content are discussed below

5.3.1 Cadmium content in plants

The Cd content of rice plants without grain, collected from the four rice soils investigated, ranged between 2.400 ppm in the plants from Karappadam soils to 0.880 ppm in the plants of Trivandrum sandy loam soils There was no statistically significant variation in the Cd content among the rice plants grown on the four soil types investigated

Ito and Imura (1976) has reported that the metal will cause

growth disorders in rice when the content in the straw exceeds 20 ppm and in brown rice 2 ppm. But according to Gunnarsson (1983) a 10 ppm level is toxic. By adding 5 ppm Cd in soil, McLean (1976) found that the Cd content in lettuce was 10.360 ppm and in tobacco leaves it was 11.570 ppm. In a survey of plants grown in Los Angeles Lund et al (1981) found that the Cd content in plants varied as Swisschard (0.6 to 72.0 ppm), Radish tubers (0.1 to 14 ppm) pepper fruit (0.01 to 4.7 ppm) and pepper leaf (0.4 to 52 ppm) therefore it can be positively inferred that Cd is not at all present in toxic levels in the rice plant grown in any of the soils investigated. It may also be worthwhile to notice that yield reduction was noticed in lettuce when the leaves contain 118 to 147 ppm Cd and in wheat 36 to 43 ppm (Mitchell et al 1978). In a trial conducted by Reuss et al⁽¹⁹⁷⁸⁾ it was found that the use of concentrated superphosphate containing 174 ppm resulted in plant Cd levels of 2.4, 3.4, 6.3, 0.9 and 0.5 ppm for radish roots, radish top, lettuce, pea seeds and pea foliage respectively. Giordano et al (1975) reported that the corn forage grown by applying municipal waste was found to contain 0.7 to 5.3 ppm Cd. The Cd levels in the paddy straw presently observed, cannot be declared as high, in view of the work by the above authors.

5 3 2 Nickel content in plants

The Ni content in plants varied from 14 990 ppm in Karappadam soils to 1 940 ppm in the plants grown in Trivandrum sandy loam soils. The higher content of Ni in the Kayal soils (53 158 ppm), Karappadam (48 717 ppm) and Kari soils (30 265 ppm) may be attributed to the presence of large quantities of serpentine derived soils such as chlorite whose chemical composition varies to a great extent. Toxic elements like Ni is reported to occur in large quantities in mafic chlorites (Bear 1971). Probably this might be the reason why large amount of Ni happened to occur in the rice plants grown in these soils. The values obtained are higher when compared to the works by Rashid et al (1981) in which the Ni content in sewage irrigated soil was 0.41 to 4.7 ppm. According to Giordano et al (1975) the Ni in corn forage grown by applying municipal waste was 2.6 to 6.9 ppm. No literature was available to compare the present values to determine whether the plant content was above toxic level.

5 3 3 Lead content in plants

The Pb content of rice plants grown in the four soil types varied from 10.03 ppm in Kayal soils to 5.75 ppm in Karappadam soils. This difference was statistically significant, i.e., soil type is a deciding factor in the Pb content of the crops. Crops

grown on soils derived from acid igneous rock can appreciably exceed the normal content of 1 000 ppm in dry matter, which may give rise to chronic ailment in animal and human (Bear 1965) But this factor does not pose a health problem due to the fact that, upto a certain level Pb excretion keep pace with ingestion, so that retention is negligible In sheep no Pb is retained if less than 3 mg per kg body weight is ingested (Underwood 1971) There is also reports that Pb is harmful when the dry matter contain 150 ppm Pb (Baumhardt and Welch, 1972) In the sewage irrigated Rhodes grass the Pb content was found to be 0.08 to 1.2 ppm (Rashid 1982) But in another work it was reported that by application of 500 ppm Pb the content of Pb in oats increased to 20 ppm whereas the control registered 11 ppm and in lettuce it reached 54 ppm (John 1972)

5.4 Comparison of different treatments in relation to heavy metal content in the permanent manurial expt. with tall indica rice (1961 - 1985)

The soils from eight treatments with four replications of a PMF being carried out for 25 years with the same treatments were analysed to find out the accumulation of heavy metals if any due to the combination with fertilizers, and chemical fertilizers alone Only green leaves cattle manure, ammonium sulphate, super phosphate and muriate of potash were used in different combinations in the trial Vegetation has got a tendency for bio cycling and

consequently any element whether essential or not are indiscriminately taken up and accumulated by plant tissue, especially in the leaves and are returned to the arable part of the soil. Therefore the application of green matter or farmyard manure is most likely to induce accumulation of elements including heavy metals in the soil due to continuous application of such organic manure. Similarly the continuous application of super phosphate which is an acid treated natural mineral (apatite) containing Cd and other heavy metals as impurities are theoretically expected to add and accumulate such heavy metals in soils. But such an accumulation will be controlled by the plant uptake and consequent removal, leaching, percolation etc. The present investigation was aimed at establishing whether any accumulation of toxic heavy metals is possible through the continuous application of organic matter, chemical fertilizers or a combination of both.

5.4.1.1 Total soil cadmium

The maximum amount of total Cd of 0.990 ppm was observed in T₃ (cattle manure and green leaves at the rate of 4410 kg per ha each) and the least value was obtained in T₅ with a value of 0.490 ppm (cattle manure 4410 kg/ha + Ammonium Sulphate 110 kg/ha). It is interesting to note that the plots which received only manures of organic origin has registered the maximum content of total Cd. The next highest concentration was obtained in T₇ (0.810 ppm). This

treatment also incorporates equal quantities of farmyard manure and green manure (2205 kg each) along with ammonium sulphate, super phosphate and muriate of potash in the same dose as in T₅. The treatment number T₁ with cattle manure alone at 8820 kg/ha and T₂ with green leaves at 8820 kg/ha have registered a total Cd content of 0.710 and 0.560 ppm respectively. The treatment with farmyard manure alone (8820 kg/ha) happened to stand 3rd in rank with reference to the total Cd content in soil. This was followed by T₆ wherein green manure @4410 kg/ha along with Ammonium sulphate @110 kg/ha superphosphate @137 kg/ha and Mussoorie phosphate @36 kg/ha are involved. In view of the results obtained in relation to various treatments no definite conclusion can be drawn as to which combination contribute towards the accumulation of Cd in soils. However the Cd content was higher in treatments receiving green manure, green manure + farmyard manure and farmyard manure + inorganic fertilizers except in T₅. The treatment combinations did not differ statistically among them. The Cd levels in any of the treatments cannot be said to be in toxic levels since only soils having a total Cd content of 3 ppm is said to be polluted (Gunnarsson 1983).

5.4.1.2 DTPA extractable Cd in soils

The extractable Cd content varied between 0.078 ppm in T₁ to 0.033 ppm in T₂. The difference in the DTPA extractable Cd was not

statistically significant among treatments. However T₁ comprising green manure alone gave the maximum DTPA extractable Cd while T₂ with farmyard manure alone gave the minimum amount of this fraction. The results reveal that none of the treatment combinations could significantly influence the extractable Cd in soil. The Cd retention depends not only on aqueous chemistry of Cd and surface chemistry of adsorbant, but also the chemistry of synthetic which complexing agents can play an important part in determining the fate of metal in the soil water-plant environment (Chubin and Street 1981).

5.4.2.1 Total Nickel in soils

Total Ni in soil ranged between 59.56 ppm in T₁ to 53.6 ppm in T₃. There was no statistically significant variation between treatments in the total Ni content among the various treatment combinations. It is evident from the results that any treatment could influence the accumulation of Ni in soils, i.e. total Ni content of soil is independent of the input of fertilizers in any form. Thus it is safe to assume that a stable equilibrium exist in the soil with reference to the retention of the metal.

5.4.2.2 DTPA extractable Nickel

As in the case of total Ni, no single treatment could be isolated as a contributor to the extractability of Ni. The

extractable Ni in the various treatments ranged between 0.490 ppm in T₅ to 0.220 ppm in T₆.

5.4.3.1 Total Lead in soils

The total lead in different treatments varied from 25.500 ppm to 19.700 ppm in treatment T₇ and T₈ respectively. The effect of treatments on the accumulation of Pb in soils was not found to be statistically significant. Total Pb content in the different treatments might be controlled by several factors such as leaching, impurities in fertilizer material, plant uptake and cationic equilibrium in soils.

5.4.3.2 DTPA extractable Lead

The DTPA extractable Pb was also not found to differ significantly among various treatments. The maximum value of 2.560 ppm was obtained in T₆ and the minimum value (1.940 ppm) was observed in T₁. This shows that the extractable Pb content in soil is not influenced by the application of organic manures and/or chemical fertilizers.

5.5 Comparison of different treatment in relation to heavy metal content in soil, plant and grain in a permanent manual trial involving dwarf japonica rice

5.5.1 Soil content of heavy metals

5 5 1 1 Total soil Cadmium

The mean total Cd content varied from 1 330 ppm (T_1) to 0 780 ppm (T_6). The T_1 consisted of application of cattle manure @18000 kg/ha to give 90 kg N/ha, while T_6 consisted of 9000 kg green leaves, 225 kg of ammonium sulphate, 281 kg of super phosphate and 75 kg of MOP to give a fertilizer dose of 90 45 45 kg of N, P_2O_5 and K_2O per hectare. The other treatments except T_2 and T_3 (T_2 - 18000 kg of green leaves and T_3 - 9000 kg each of cattle manure and green leaves) all other treatments were combinations of cattle/green manure and chemical fertilizers. The most outstanding observation is that the total soil Cd content was found to be much higher in the experiment as compared to the old permanent manurial trial discussed earlier. This is because of the higher dose of organic manure and fertilizers used in the trial with a high yielding variety. However the soil Cd content was found to be far less than the safe limit of 3 ppm and plant toxic limit of 10 ppm (Gunnarsson 1984). Since the difference in total Cd content among treatment was not statistically significant, a discussion about the merits of each treatment is not warranted.

5 5 1 2 DTPA extractable Cadmium

This fraction of cadmium also was highest in T_1 (0 040 ppm) and lowest in T_6 (0 025 ppm). The trend is similar as in total soil

Cd content Since there was no statistically significant difference in extractable Cd among treatments and also in the absence of literature a discussion on this aspect is not undertaken McLean (1976) has reported that extractable Cd increased with higher amount of soil organic matter

5 5 2 1 Total soil Nickel

The total soil Ni varied from 56 625 ppm in T₃ to 44 920 ppm in T₇ Unlike total Cd the highest amount of total Ni was observed in the treatment receiving cattle manure and green leaves alone at 9000 kg each per hectare But the similarity between the Cd and Ni content of soil is that the maximum amount was noticed in plots treated with organic manure alone The difference between treatments in Ni content was not statistically significant Therefore it can be concluded that there is no credible relationship between the type and combination of fertilizer material added and the total Ni content of the soil

5 5 2 2 DTPA extractable Nickel

This fraction of Ni was highest in T₇ (0 366 ppm) receiving 18000 kg cattle manure per hectare The least amount of extractable Ni (0 109 ppm) was noticed in T₄ receiving ammonium sulphate alone as the source of N The different treatment did not vary among them in their content of extractable Ni

5 5 3 1 Total soil Lead

Content of total Pb was found to be the maximum in T₅ (29 125 ppm) while the least amount was noticed in T₇ (24 625 ppm) The treatment difference was not found to be statistically significant This trend is similar to that shown by the other two metals viz Cd and Ni

5 5 3 2 DTPA extractable Lead

The values varied from 2 317 ppm in T₂ to 0 803 ppm in T₇ Treatment T₂ was found to be statistically superior to all other treatment This treatment consisted of green leaves only, at 18000 kg per hectare This is an indication that organic matter even if used alone can influence the extractability of lead from soil i e Pb becomes readily available from the humus

5 5 4 1 Cadmium content in straw

The Cd content in straw was found to vary from 8 150 ppm (T₁) to 4 100 ppm (T₅) The variation in the Cd content among the treatments was found to be statistically significant Treatment T₁ receiving cattle manure alone at 18000 kg/ha gave the highest Cd content in straw The next highest Cd content was noticed in T₈ receiving chemical fertilizers alone (ammonium sulphate 450 kg, Super phosphate 281 kg and MOP 75 kg per hectare) The result

indicate that organic matter alone or chemical fertilizers alone can enhance the cadmium content in straw. But definite superiority was shown by the treatment receiving cattle manure alone over the other treatments. It was reported that as a result of 36 years of phosphorus fertilization, the concentration of Cd in Swiss chard was 1.6 ppm (Mulla et al 1980).

5.5.4.2 Nickel in straw

The highest Ni content (6.850 ppm) was observed in T₇ while the least amount (0.200 ppm) was associated with T₁. Giordano et al (1975) found that Ni in forage and grain ranged from 2.600 to 6.900 ppm with the application of municipal waste. Here, treatment difference with reference to Ni content in the straw was found to be statistically significant. But because of statistical parity among several treatments no treatment can be singled out as superior over others. It is also to be noted that while the Cd content in straw in T₁ was greatest, its Ni content was the least. This may be due to some antagonistic effect between the two elements. Cd might have taken up in preference to Ni by rice. Deviprasad and Deviprasad (1982) while carrying out some investigation on algae have found some interaction between Cd and Ni.

5 5 4 3 Lead in straw

The maximum content of Pb in straw was obtained from T₈ (24 900 ppm) and the least Pb content was present in the straw from T₇ (14 100 ppm). T₈ and T₃ (23 350 ppm) were distinctly superior to the other treatment in the lead content in straw. Many of the other treatments were found to be on par statistically. The results showed that plots receiving chemical fertilizers alone and organic manures alone (9000 kg each of cattle manure and green leaves) had influenced the Pb content in straw, i.e., both inorganic fertilizer alone or organic manure alone could enhance the Pb content in straw as compared to combination of organic manures and chemical fertilizers. Since many of the treatments were significant and on par with each other a definite conclusion could not be drawn about the availability of Pb to the plant in relation to treatments. Turner et al (1985) reported that the falling Pb will be retained by organic floor (75%) and by mineral soil (25%) and hence organic matter can influence the Pb content.

5 5 5 Heavy metal content in grain

Sixteen grain samples from 8 treatments were analysed for their heavy metal contents and whole grains were used for analysis. Since the husk of the rice grain is rich in ash, the heavy metals must be present in higher concentration in the unhusked grain. Higher

values of heavy metals obtained in the present study might be due to the analysis of whole grain, including the husk. If the grains were husked, polished and then analysed, probably much lower values would have been obtained.

5.5.5.1 Cadmium content in grain

The maximum amount of Cd was obtained in T₆ (3.490 ppm) while the least amount (2.590 ppm) was present in grains obtained from T₅. The difference in Cd content in grain from the different treatments was found to be statistically significant. Because many of the treatments were on par statistically, no treatment could be singled out as superior to other treatments. Therefore a discussion and conclusion on the treatment effect on Cd content in the grain is difficult. The values obtained are little higher when compared to a trial conducted by Mortvedt et al (1981) with diammonium phosphate containing Cd in which Cd in wheat grain was found to increase from 0.028 to 0.086 ppm. But in a survey work conducted by Lund et al (1981) at Los Angeles, the pepper fruit was found to contain 0.01 to 4.7 ppm^{Cd}. The content of Cd in Barley was 5.2 ppm when it was grown in fields fertilized with sludge for seven years (Vlamis 1985). Takijima et al (1973) reported that unpolished rice contained Cd from 0.02 to 1.82 ppm in a location near Kuzuryu river where the Cd content in soil was 0.2 to 10.4 ppm which has no relation with Cd

content in rice. In a field receiving phosphatic fertilizer for 36 years it was noticed that the Swiss chard grain contained a Cd level of 1.6 ppm (Mulla et al 1980). Hence it can be presumed that there will be variation in the content of Cd with respect to different crops and with the same crop there will be differences according to location.

5.5.2 Nickel content in grain

The Ni content in the grain varied from 3.810 ppm (T_7) to 0.150 ppm in T_1 . It was found that the variation in the Ni content between treatments were not significant. In an experiment conducted by Mortvedt et al (1981) with the application of Diammonium phosphate containing Ni, it was found that the Ni in grain varied from 0.08 to 0.22 ppm. The Rhodes grass when grown with sewage irrigation was found to contain 0.410 to 4.700 ppm Ni (Rashid et al 1981). The Nickel content in corn grain was found varying from 0.200 ppm to 1.200 ppm when the crop was grown with Municipal Waste (Giordano et al 1975). Therefore the slightly higher values obtained in the present study can be attributed to the different soil and climatic conditions prevailing in this region.

5.5.3 Lead content in grain

Maximum amount of Pb was present in T_8 (14.650 ppm) while it was present in the lowest quantity in T_7 (8.980 ppm). The

treatments did not vary significantly with reference to the Pb content in grain. John (1972) has reported that the Pb content in oats root was increased from 11 000 ppm in the control to 20 000 ppm by addition of 500 ppm Pb in soil. In tree foliage the Pb content was 4 000 ppm in a work conducted by Turner et al. (1985). In the absence of literature pertaining to our region the veracity of the figures obtained in the present study could not be checked.

5.6 Pot culture experiment with added Cadmium

The results obtained in a pot culture experiment with added Cd involving a grain crop (rice), a fodder crop (guinea grass) and a leafy vegetable (Amaranthus) in a CRD design, are discussed here. Apart from control, soils were treated with fertilizers having added Cd at 10 g, 20 g and 30 g per hectare which were far below a level which can make any impact on the crop or soil. The dose was fixed taking into consideration of the quantity of Cd which is annually added to the soil through fertilizers.

5.6.1 Rice

There was no statistically significant variation in the total and DTPA extractable Cd in the soil after the harvest of the rice crop. But strangely, maximum DTPA extractable Cd was obtained in the control plot (T₄). A similar phenomenon has been reported by Poletschny (1982) in which Cd was greatest in the control plot.

when he tried to study the Cd accumulation by potatoes, winter wheat and sugar beet using P fertilizers containing Cd as Cd source

The variation in Cd content in straw also did not show any statistically significant difference between treatments even though T₄ (Control) registered the maximum content of Cd (6.35 ppm)

As in the case of straw, in grain also the maximum content of Cd (4.65 ppm) was obtained in the control plot (T₄) But the treatment difference was not statistically significant

5.6.2 Amaranthus

The maximum total cadmium content in soil after harvest was obtained in T₃ (2.000 ppm) and the least in T₄ (1.100 ppm) Treatment T₃ happened to be statistically superior to other treatments

DTPA extractable Cd in the soil after harvest did not vary significantly

Amaranthus plant from the control pot contained the maximum amount of Cd (15.950 ppm) But plant content of Cd among the four treatments did not vary significantly

Amaranthus being a short duration crop it might have taken up the native Cd present in the potting mixture of the control pot, while in the other treatments fertilizer added Cd was probably

undergoing fixation or interaction with other elements. This might be the reason why the amaranthus from the control pot happened to contain the highest amount of Cd. The accumulation of Cd was more in amaranthus considering other crops. Preer et al (1980) has found that leafy and root vegetables accumulated Cd than fruity vegetables. It was also reported by Gunnarsson (1983) that the Cd content was found varying in barley (24 ng), rye (16 ng), carrot (273 ng), lettuce (1000 ng) and spinach (2143 ng).

5.6.3 Guinea grass

The total and DTPA extractable Cd in the soil after harvest of guinea grass did not vary significantly among the four treatments.

The highest Cadmium content in the plant was associated with T₃ (14 400 ppm) in which maximum Cd was added. The added Cd might have been taken up by the plant in a short time before any fixation takes place, to put up fast vegetative growth. Page et al (1972) has explained that leaves are capable of accumulating excess Cd from solution concentration. Guinea grass being a fodder, it is cut down before the grain formation and so the vegetative parts are predominantly consists of leaves and hence it was having a higher Cd content. However, there was no statistically significant difference between treatments in influencing the plant Cd concentration.

5 71 Correlation coefficients between fertilizer nutrients applied, nutrient content in soil, soil heavy metals and plant heavy metals

5 711 Correlation coefficients associated with soil total cadmium

The total Cd concentration in soil was found to be negatively correlated with extractable Cd ($r = 0.3071^*$). This shows that when extractability of Cd in soil decreases, the total Cd content in soil remains comparatively higher. This may be due to several factors such as the amount of exchange complex, cationic balance, organic complexing, microbial activity etc, which determine the extractability of cadmium. Moreover due to higher uptake of cadmium by plants the extractable portion of Cd in a soil at any time may be much less. The findings by Koreak and Fanning (1985) established that high Fe and Mn oxides gave lower DTPA extractable value.

Applied fertilizer nitrogen also was found to have a negative correlation with the total soil Cd ($r = -0.0126$). But the correlation was not found to be statistically significant. Giordano and Mortvedt (1976) suggested that N fertilization may increase the mobility of heavy metal and will enhance uptake by increased growth of plant. This phenomenon will lead to the depletion of the total Cd content in soil. Therefore it is safe to assume that application of nitrogenous fertilizers do not help the accumulation of Cd in soil. This fact is corroborated by the low Cd content in the nitrogenous fertilizers investigated.

Applied phosphorus (through fertilizers) was found to positively influence the total Cd in soil. But its influence was not statistically significant. The works by Mortvedt et al (1981) also revealed that the addition of P fertilizers will increase the Cd content in soil even though the change was not significant. From this it is evident that application of phosphatic fertilizers do not result in significant accumulation of Cd in soil.

The correlation between soil total Cd and applied as well as soil K were found to be positive and significant ($r = 0.2736^*$ and $r = 0.2796^*$). Since K enrichment of the soils is related to the application of several fertilizers, their mixtures and complexes and also through solubilization of minerals, all of which contain Cd in different concentration, it is possible that K sources may increase the total Cd reverse in the soil. Soil N was also found to be positively and significantly correlated with total Cd in soil.

Interestingly soil available P was found to be negatively correlated to the total Cd content in the soil. Since the availability of P is related to several factors especially pH of the soil, this negative relationship cannot be satisfactorily explained. Most of the soils analysed were highly acidic in nature too.

The total soil Cd content was found to be positively and

significantly correlated with the Cd content in plants i.e., higher the Cd content in soil higher is the plant Cd content. In other words the Cd content is decided by the total Cd present in the soil. The findings of Anderson et al (1981) endorse this fact by revealing that there is positive significant correlation exists between plant Cd and the soil fraction of Cd. Takayama et al (1973) reported that heavy metal content in rice largely related to the content of paddy soil in 0.1N HCl soluble form as well as in total content.

5.7.1.2 Correlation coefficients associated with soil total Nickel

Total Ni in soil was found to be positively and significantly correlated with extractable Ni ($r = 0.1945^*$). This shows that as the total Ni content in soil increases extractability of the element also increases. The application of nitrogenous, phosphatic and potassic fertilizers were found to increase the total Ni content of the soils. The element might have been introduced into the soil as impurities present in fertilizers. But the correlation was significant only with reference to phosphatic and potassic fertilizers. The total soil Ni was found to be correlated to its content in plant as in the case of Cd, but the r value was not significant, i.e., total Ni in soil influences its content in plant also. Total Ni in soil was also found to be positively and

significantly correlated to soil N and soil K, but the correlation value though positive, was not significant in the case of soil available P. This shows that sources and input of these nutrients may be related to its presence in the soil.

5 7 1 3 Correlation coefficients associated with total Lead content in soil

The total Pb content in soil showed an almost opposite trend as compared to Cd and Ni. It was negatively correlated to its exchangeable form ($r = -0.455$) and applied K (0.2187^*). This shows that the application of fertilizers do not result in an accumulation of Pb in soil. Probably it is more amenable to removal from soil by vegetation. This theory is further strengthened by the fact that the total Pb content in soil was positively and significantly correlated to its content in plant ($r = 0.3077^*$). The total Pb content in soil was negatively but not significantly correlated with soil N and K, but its relation with soil P was positive at the same time not significant. The results show that the total Pb content at any time is not associated with the soil N and K content of soil. But its positive relation with phosphorus is an indication that the source of soil phosphorus has some relation to the lead accumulation. But the theory that the soil Pb has bearing on plant Pb is vindicated by the works of Baunhardt et al (1972) and John et al (1972) in lettuce and oats respectively with added Pb.

5.7.14 Correlation coefficients associated with DTPA extractable Cd, Ni and Pb

No substantial results which could be compared to any acknowledged work has come out from the comparisons between the extractable heavy metals and factors like applied N, plant Cd soil P etc. Since the extractability behaviour of these heavy metals depends upon several soil, climatic and other factors no specific conclusion could be drawn. In general, extractable Cd was found to be positively correlated to applied N, plant Cd and soil P, the last only being significant. This is in conformity with the works of Anderson (1981) who has stated that there was rectilinear positive relationship between added P and extractable Cd, and between grain Cd and other Cd fractions in soil. This was endorsed by Takijima (1973) by stating that heavy metal concentration in rice was related to 0.1N HCl soluble form of heavy metals.

But in the case of Nickel positive correlation of this fraction was observed in the case of applied P and K. As in the case of Cd, extractable Ni and Pb are found to positively influence their content in plants. Extractable Pb was also found to be positively correlated with applied N, P and K, soil P and K, while the relationship was negative in the case of soil N.

6.15 Correlation coefficients associated with Fertilizer N, P and K

As evidenced from the correlation studies, applied nitrogenous

fertilizers were found to be correlated with plant Cd ($r = 0.4595^*$), plant Ni ($r = 0.0928$) and plant Pb ($r = 0.3810^*$). But this relationship was not significant in the case of Ni. In other words nitrogenous fertilizers tend to increase the heavy metal content in plants. Nitrogen tends to increase the heavy metal content in an indirect way by promoting the growth of plants and thereby creating extra ability for absorption.

Applied phosphatic fertilizers also showed the same trend with r values of 0.6675^* for Cd, 0.1503 for Ni and 0.2350^* for Pb. It was reported that rate of increase in soil Cd levels caused by normal P fertilization range from 0.33 to 1.1% annually (Anderson 1981) and so the relation between Cd and P are justified. Mortvedt (1979) also suggested increased Cd content in plants with the use of increased P fertilizers containing Cd.

The correlation between applied potassic fertilizers and the Cd, Ni and Pb content of plants were invariably positive and significant ($r = 0.5528^*$, 0.3516 and 0.3778^* respectively).

In general, it can be concluded that the continuous use of chemical fertilizers tend to increase the heavy metal content of plant but certainly not at a rapid pace.

SUMMARY

SUMMARY

Some concern about the possible health hazards through fertilizer borne heavy metals especially Cd was being raised recently from certain quarters. The present investigation was meant to gain some information in this regard which may be helpful in removing the common man's fears or in warning him about the health hazards that may arise through unscrupulous fertilizer use. The salient results obtained in the study are presented below.

1) There was statistically significant variation among the different fertilizers in their heavy metal content. Factamphos contained the maximum amount of Cd while Ammonium sulphate gave the least, 17 17 17 complex followed by Super phosphate ranked second and third in Cd content.

In the case of N₁, Mussoorie phosphate ranked first in N₁ content closely followed by Factamphos and Superphosphate. As in the case of Cd, the least N₁ content was obtained in Ammonium sulphate.

Mussoorie rock phosphate stood first in lead content also, while the maximum amount was noted in Urea. The Mussoorie rock phosphate was statistically on par with super phosphate which in turn was on par with Factamphos which again happened to be on par with Ammonium sulphate.

2) The mean total Cd content in the four rice soil types ranged between 0.370 ppm and 2.270 ppm with the greatest content in

Karappadam soils Kayal soils contained 1 680 ppm and in Kari soils it was 0 920 ppm with the least content in Trivandrum sandy loam soils (0 370 ppm) All the soil types studied varied significantly among themselves in total Cd content

Kari soils yielded the maximum amount of DTPA extractable Cd (0 026 ppm) followed by Kayal soils (0 024 ppm), Karappadam soils contained only about half of the amount present in Kari soils Kari and Kayal soils were statistically on par in the DTPA extractable Cd

3) Total Ni content among the four soil types studied varied between 14 020 ppm to 53 160 ppm with the minimum in Trivandrum sandy loam soils and maximum in Kayal soils The total Ni content of Kayal and Karappadam soils were significantly higher as compared to Kari and Trivandrum sandy loam soils The maximum content of 53 160 ppm was closely followed by that present in Karappadam soils (48 720 ppm)

The DTPA extractable Ni was also in the same trend shown by total Ni the maximum value of 1 280 ppm of Kayal soils is closely followed by that of Karappadam soils (1 240 ppm)

4) The total Pb content of Kari and Kayal soils were significantly higher than that contained in Karappadam and Trivandrum sandy loam soils The maximum of 17 560 ppm was found in Kari soils and the maximum of 5 970 ppm in Trivandrum sandy loam The total Pb

content of Kaya1 soils and Karappadam soils were 14 770 ppm and 9 310 ppm respectively

As in the case of total Pb, the DTPA extractable Pb was also maximum in Kari soils (8 140 ppm), and least in Trivandrum sandy loam soils (0 500 ppm) Karappadam and Kaya1 soils recorded 1 620 and 1 110 ppm of this fraction of Pb respectively All the soils were significantly different from each other in DTPA extractable Pb

5) the percentage of DTPA extractable to total Cd was highest in the Trivandrum sandy loam soils (2 96%) followed by Kari soils (2 83%) Kaya1 soils (1 43/) and Karappadam soils (0 62%)

The percentage of DTPA extractable to total Ni was in the order of Karappadam soils (2 56%), Kaya1 soils 2 40%) Kari soils (2 03/) and Trivandrum sandy loam soils (0 48%) The first three soils did not show appreciable difference among them in the extractability of this metal

Wide variation was noted among the four soil types investigated in the extractability of Pb The percentage of this fraction of Pb was in the order of Kari soils (46 38%), Karappadam soils (27 44/) and Trivandrum sandy loam soils (8 38%) and Kari soils (6 55%)

6) Mean Cd content of rice straw at harvest was in the order of Karappadam soils (2 440 00m), Kari soils (2 330 ppm), Kaya1 soils (1 770 ppm) and Trivandrum sandy loam soils (0 880 ppm) The Cd content of plants grown in the four soil types did not vary significantly

7) The mean Ni content in rice plants in Karappadam, Kayal, Kari and Trivandrum sandy loam soils were 14 990, 2 870 and 1 940 ppm respectively. The values for total Ni in the plants from Karappadam soils were significantly higher than the rice plants grown on other soils.

8) The mean Pb content in the rice plants grown on Kayal soils was maximum (10 030 ppm), while lowest value was obtained with reference to Kari soils (4 440 ppm). Trivandrum sandy loam soils and Karappadam soils recorded a mean Pb content of 6 220 ppm and 5 700 ppm respectively. The difference among the rice plants grown on the four soil types was found to be statistically significant.

9) (i) In the PMT with tall indica variety which was running continuously for 25 years, treatment receiving only organic manures recorded the maximum amount of total Cd of 0 990 ppm (T₃). The least value is obtained in the treatment T₅ receiving cattle manure at 4410 kg per hectare + Ammonium sulphate 110 kg per ha. The different treatment combinations did not differ statistically among them in total Cd content. The Cd content of soil in any treatment cannot be said to be present in toxic levels since only soils having 3 ppm and above of Cd is considered polluted.

DTPA extractable Cd content was found to be maximum in T₇ receiving farmyard manure alone (0 078 ppm). The treatment difference was not statistically significant in relation to DTPA extractable Cd.

(11) Total N₁ in soils did not vary significantly among treatments. However, total N₁ was highest in T₇ (59 560 ppm) and minimum in T₃ (53 600 ppm).

DTPA extractable N₁ also did not show any statistically significant difference among treatments. The extractable N₁ varied between 0 490 ppm in T₅ to 0 220 ppm in T₆.

(12) The total soil Pb varied from 25 500 ppm in T₇ to 19 700 ppm in T₈. The effect of treatments on the total soil Pb was not found to be statistically significant.

The variation in the DTPA extractable Pb also did not show any statistical significance. The values ranged from 2 560 ppm (T₆) to 1 940 ppm (T₇).

10) (1) The results of soil analysis from the eight treatments in a trial with dwarf japonica rice (13th year) showed that the mean total Cd content in the soil varied from 1 330 ppm (T₇) to 0 780 ppm (T₆). As in the case of the other permanent manurial experiment, the treatment consisted of manures of organic origin only gave the maximum amount of Cd. The total Cd content of this trial with dwarf japonica was much higher as compared to the old PMT with tall indica because of the higher levels of fertilizers and manures used. Here also the Cd content in the soil was far less than that

is required to pollute the soil. The treatment difference in the total Cd content was also not found to be statistically significant.

The DTPA extractable fraction of Cd was also highest in treatment T_1 (0.410 ppm) and lowest in T_6 (0.025 ppm). The treatment difference was not statistically significant with reference to extractable Cd.

(ii) The total Ni varied from ^{44.920 (T_7) to} 56.625 ppm in T_7 . Here also the treatment consists of organic manures only. The difference between treatments was not statistically significant.

The DTPA extractable Ni was maximum in T_1 (0.366 ppm) and the least amount was observed in T_4 (0.109 ppm). In this case also the T_1 was receiving 18000 kg cattle manure alone per ha. The treatments did not vary significantly among them.

(iii) In the case of total soil Pb the variation was not significant among treatments. The total Pb content was maximum in T_5 (29.125 ppm) whereas the least amount was noticed in T_7 (24.625 ppm). The trend is same as in the case of Cd and Ni.

The values for DTPA extractable Pb varied from ^{0.803 ppm in T_7 to} 2.317 ppm in T_2 . Treatment T_2 was statistically superior to all other treatments (Treatment receiving green leaves only, at 18000 kg/ha).

(iv) Cadmium content in straw varied from 8 150 ppm in T₁ to 4 100 ppm in T₅. Treatment receiving cattle manure only gave the highest Cd content in straw. The next highest Cd content was noticed in T₈ receiving Ammonium sulphate, Super phosphate and MOP at 450 kg, 281 kg, and 75 kg/ha respectively. T₁ showed significantly definite superiority over other treatments.

(v) The highest Ni content in straw was observed in T₇ (6 850 ppm) while the least amount of 0 200 ppm was obtained in T₁. The treatment difference in Ni content in straw was found to be statistically significant. Because of statistical parity among treatments, no treatment could be singled out as definitely superior over others.

(vi) The maximum content of Pb in straw was obtained in T₈ (24 900 ppm) while the least content was present in the treatment T₇ (14 100 ppm). Treatments T₈ and T₃ were distinctly superior to other treatments in the Pb content of straw. Plots receiving chemical fertilizers alone and organic manures alone seem to influence the Pb content in straw.

(vii) The maximum content of Pb in grain was noticed in T₆ (3 490 ppm). The least amount of Cd in grain was found in treatment T₅ (2 590 ppm). Even though the Cd content in grain from different treatments was found to be statistically significant, no treatment could be singled out as definitely superior to others.

(vii) The Ni content in grain varied from 3 870 ppm in T_7 to 0 150 in T_1 . The variation in the Ni content among the treatments was not found to be statistically significant.

(ix) The maximum amount of Pb in grain was found in T_8 (14 650 ppm). The minimum quantity was present in T_7 (8 980 ppm). The treatment difference was not significant with reference to Pb.

11) In the pot culture experiment with rice there was no statistically significant variation in the total as well as DTPA extractable Cd in the soil after harvest among treatments with added Cd at 10, 20, 30 and 0 g Cd/ha.

The treatment difference in the Cd content in straw also did not show any statistically significant difference among treatments.

The same trend was observed with grains as in the case of straw.

12) The maximum total Cd content in soil after harvest was seen in T_3 (2 000 ppm) and the least value of 1 100 ppm in T_4 , in the case of Amaranthus. The treatment T_3 was found to be statistically superior over other treatments.

The DTPA extractable Cd in the soil after the harvest of amaranthus did not show any statistically significant difference among treatments.

13) In guinea grass both total and DTPA extractable Cd in soil did not vary significantly among treatments. The highest Cd content in plant parts was noticed in T₃ (14 400 ppm)

14) Considerable variation was shown among the grain, leafy vegetable and fodder crop in their uptake and accumulation of heavy metals

15) Applied fertilizer N did not show any significant correlation with soil total cadmium

16) Applied P was found to be positively correlated with Cd in soil

17) The correlation between soil total Cd and applied as well as soil K were found to be positive and significant

18) Soil available P was found to be negatively correlated with the total Cd content in soil

19) The soil total Cd content was positively and significantly correlated to plant Cd content

20) The extractable Cd was found to be positively correlated to applied N, plant Cd and soil P. This relationship was significant only in the case of soil P

21) The DTPA extractable N₁ showed a positive relationship with applied P and K

22) Extractable Pb was also found to be positively correlated with applied N, P and K and soil P and K

23) Applied N fertilizers were found to be positively and significantly correlated with plant Cd content, and plant Pb content

24) Applied P fertilizers also showed exactly the above trend

25) The correlation between applied K fertilizers and the plant Cd, Ni and Pb content were consistently positive and significant

The present study has revealed that ammonium sulphate, urea and MOP contained comparatively much less heavy metal content. Generally phosphatic fertilizers, especially those manufactured with phosphoric acid as a component contained higher levels^{of} heavy metals especially Cd.

Accumulation of heavy metals in appreciable levels to cause any alarm, was not found to occur due to continuous fertilizer application. But both organic manures and chemical fertilizers or their combinations were found to increase the soil and plant heavy metal content slightly, though not significantly.

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APPENDIX

Appendix - 1

Abstract of analysis of variance table on Cd
content in different fertilizers

Source	DF	MSS	F
Treatments	7	69.62	31.19*
Error	<u>31</u>	2.23	
Total	38		

*Significant at 5% level

Appendix - 2

Abstract of analysis of variance table on
Ni content in different fertilizers

Source	DF	MSS	F
Treatments	7	1252.76	99.66*
Error	<u>31</u>	12.57	
Total	38		

*Significant at 5% level

Appendix - 3

Abstract of analysis of variance table on

Pb content in different fertilizers

Source	DF	MSS	F
Treatments	7	48.67	19.65*
Error	<u>31</u>	2.48	
Total	38		

*Significant at 5% level

Appendix - 4

Abstract of analysis of variance table on total

Cd content in four different types of soil

Source	DF	MSS	F
Treatment	3	19.13	40.94*
Error	<u>110</u>	0.47	
Total	113		

*Significant at 5% level

Appendix - 5

Abstract of analysis of variance table on DTPA extractable

Cd content in four different types of soil

Source	DF	MSS	F
Treatment	3	0.0117	4.38*
Error	<u>110</u>	0.0269	
Total	113		

*Significant at 5% level

Appendix - 6

Abstract of analysis of variance table on total N₁

content in four different types of soil

Source	DF	MSS	F
Treatment	3	5199.76	19.67*
Error	<u>110</u>	264.32	
Total	113		

*Significant at 5% level

Appendix - 7

Abstract of analysis of variance table on DTPA extractable

Ni content in four different types of soil

Source	DF	MSS	F
Treatment	3	7.69	44.14*
Error	<u>110</u>	0.17	
Total	113		

*Significant at 5% level

Appendix 8

Abstract of analysis of variance table on total Pb

content in four different types of soils

Source	DF	MSS	F
Treatment	3	302.79	3.94*
Error	<u>110</u>	76.89	
Total	113		

*Significant at 5% level

Appendix - 9

Abstract of analysis of variance table on DTPA extractable

Pb content in four different types of soils

Source	DF	MSS	F
Treatment	3	20.17	32.28*
Error	<u>110</u>	0.62	
Total	113		

*Significant at 5% level

Appendix - 10

Abstract of analysis of variance table on Cd content

in plant samples

Source	DF	MSS	F
Treatment	3	7.69	2.25NS
Error	<u>110</u>	1.46	
Total	113		

NS Not significant

Appendix - 11

Abstract of analysis of variance table on Ni content
in plant samples

Source	DF	MSS	F
Treatments	3	1610 17	15 23*
Error	<u>110</u>	105 73	
Total	113		

*Significant at 5% level

Appendix - 12

Abstract of analysis of variance table on Pb
content in plant samples

Source	DF	MSS	F
Treatments	3	664 10	3 7836*
Error	<u>110</u>	175 56	
Total	113		

*Significant at 5% level

Appendix - 13

Abstract of analysis of variance table on total Cd content
of soil in the permanent manurial experiment with tall indica rice

Source	DF	MSS	F
Replication	3	0,0259	0 2110
Treatment	7	0 1152	0 9392 NS
Error	<u>21</u>	0 1227	
Total	31		

NS Not significant

Appendix - 14

Abstract of analysis of variance table on the extractable Cd
content of soil in the permanent manurial experiment
with tall indica rice

Source	DF	MSS	F
Replication	3	0 000053	3 0736
Treatment	7	0 000010	0 0736 NS
Error	<u>21</u>	0 000017	
Total	31		

NS Not significant

Appendix 15

Abstract of analysis of variance table on the total N₁ content of soil in the permanent manual experiment tall indica rice

Source	DF	MSS	F
Replication	3	77 180	3 2591
Treatments	7	17 370	0 5820 NS
Error	<u>21</u>	29 818	
Total	31		

NS Not significant

Appendix - 16

Abstract of analysis of variance table on the extractable N₁ content of soil in the permanent manual experiment with tall indica rice

Source	DF	MSS	F
Replication	3	0 0261	4 7340
Treatment	7	0 0481	8 7067*
Error	<u>21</u>	0 0055	
Total	31		

*Significant at 5% level

Appendix 17

Abstract of analysis of variance table on the total Pb
content of soil in the permanent manurial experiment
with tall indica rice

Source	DF	MSS	F
Replication	3	32 9675	1 7372
Treatments	7	10 9303	0 5759 NS
Error	<u>21</u>	18 9774	
Total	31		

NS - Not significant

Appendix 18

Abstract of analysis of variance table on the extractable Pb
content of soil in the permanent manurial experiment
with tall indica rice

Source	DF	MSS	F
Replication	3	0 5470	2 0981
Treatments	7	0 2406	0 9827 NS
Error	<u>21</u>	0 2607	
Total	31		

Appendix - 19

Abstract of analysis of variance table on the total Cadmium content of soil in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	0.0306	0.3011
Treatments	7	0.0635	0.6251 NS
Error	<u>7</u>	0.1016	
Total	15		

NS Not significant

Appendix - 20

Abstract of analysis of variance table on the extractable Cadmium content of soil in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	0.00002	0.9456
Treatments	7	0.00005	2.8030 NS
Error	<u>7</u>	0.00002	
Total	15		

NS Not significant

Appendix -21

Abstract of analysis of variance table on the total Nickel content of soil in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	112 359	6 941
Treatments	7	24 318	1 502 NS
Error	<u>7</u>	16 188	
Total	15		

NS Not significant

Appendix - 22

Abstract of analysis of variance table on the extractable Ni content of the soil in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
REplication	1	0 0019	2 178
Treatments	7	0 0120	1 320 NS
Error	<u>7</u>	0 0090	
Total	15		

Appendix - 23

Abstract of analysis of variance table on the total Pb content of the soil in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	37 516	12 573
Treatments	7	5 255	1 761 NS
Error	<u>7</u>	2 0	
Total	15		

NS Not significant

Appendix - 24

Abstract of analysis of variance table on the extractable Pb content of the soil in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	0 0615	0 730
Treatments	7	0 463	5 487*
Error	<u>7</u>	0 0842	
Total	15		

*Significant at 5% level

Appendix -25

Abstract of analysis of variance table on the cadmium content of plants (without grain) in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	0 0057	0 334
Treatment	7	3 2470	190 527*
Error	<u>7</u>	1 7046	
Total	15		

*Significant at 5% level

Appendix - 26

Abstract of analysis of variance table on the nickel content of plants (without grain) in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	3 150	1 297
Treatments	7	9 612	3 959*
Error	7	2 428	
Total	15		

*Significant at 5% level

Appendix 27

Abstract of analysis of variance table on the lead content of plants (without grain) in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	5 406	12 331
Treatment	7	34 581	78 879*
Error	<u>7</u>	0 438	
Total	15		

*Significant at 5% level

Appendix - 28

Abstract of analysis of variance table on the cadmium content of grains in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	0 00006	
Treatments	7	0 2025	7 254*
Error	<u>7</u>	0 0279	
Total	15		

*Significant at 5% level

Appendix - 29

Abstract of analysis of variance table on the Nickel content of grains in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	0 4692	
Treatment	7	2 8392	NS
Error	<u>7</u>	1 0091	
Total	15		

NS Not significant

Appendix - 30

Abstract of analysis of variance table on the Lead content of grains in the permanent manurial experiment with dwarf japonica rice

Source	DF	MSS	F
Replication	1	0 0324	
Treatment	7	9 0102	NS
Error	<u>7</u>	2 1451	
Total	15		

NS Not significant

Appendix - 31

Abstract of analysis of variance table on the total Cd content of soil in the pot culture experiment with rice

Source	DF	MSS	F
Control Vs treated	1	0 136	0 567 NS
Treatments	2	0 226	0 949 NS
Error	<u>12</u>	0 238	
Total	15		

NS Not significant

Appendix - 32

Abstract of analysis of variance table on the extractable Cd content of soil in the pot culture experiment with rice

Source	DF	MSS	F
Control Vs treated	1	0 00006	4 472 NS
Treatments	2	0 00004	0 472 NS
Error	<u>12</u>	0 00001	
Total	15		

NS Not significant

Appendix - 33

Abstract of analysis of variance table on the Cadmium content of plant (without grain) in the pot culture experiment with rice

Source	DF	MSS	F
Control Vs treated	1	1 268	1 584 NS
Treatment	2	0 069	0 087 NS
Error	<u>12</u>	0 801	
Total	15		

NS Not significant

Appendix - 34

Abstract of analysis of variance table on the Cadmium content of grain in the pot culture experiment with rice

Source	DF	MSS	F
Control Vs treated	1	5 741	5 403*
Treatment	2	0 253	0 238
Error	<u>12</u>	1 062	
Total	15		

*Significant at 5% level

Appendix - 35

Abstract of analysis of variance table on the total Cd content of soil in the pot culture experiment with amaranthus

Source	DF	MSS	F
Control Vs treated	1	0.642	9.313*
Treatment	2	0.587	8.517**
Error	<u>12</u>	0.068	
Total	15		

*Significant at 5% level

**Significant at 1% level

Appendix - 36

Abstract of analysis of variance table on the extractable Cd content of soil in the pot culture experiment with amaranthus

Source	DF	MSS	F
Control Vs treated	1	0.00004	4.172 NS
Treatments	2	0.000005	0.552 NS
Error	<u>12</u>	0.000009	
Total	15		

NS Not significant

Appendix - 37

Abstract of analysis of variance table on the Cd content of plant in the pot culture experiment with Amaranthus

Source	DF	MSS	F
Control Vs treated	1	90 201	3 425 NS
Treatment	2	50 843	2 310 NS
Error	<u>12</u>	26 337	
Total	15		

NS Not significant

Appendix - 38

Abstract of analysis of variance take on the total Cadmium content of soil in the pot culture experiment with guinea grass

Source	DF	MSS	F
Control Vs treated	1	0 146	1 477 NS
Treatment	2	0 098	0 999 NS
Error	<u>12</u>	0 099	
Total	15		

NS Not significant

Appendix - 39

Abstract of analysis of variance table on the extractable Cd content of soil in the pot culture experiment with guinea grass

Source	DF	MSS	F
Control Vs treated	1	0 00004	1 692 NS
Treatment	2	0 00005	2 364 NS
Error	<u>12</u>		
Total	15		

NS Not significant

Appendix - 40

Abstract of analysis of variance table on the Cadmium content of plant in the pot culture experiment with guinea grass

Source	DF	MSS	F
Control Vs treated	1	32 177	2 134 NS
Treatment	2	44 669	2 962 NS
Error	<u>12</u>	15 081	
Total	15		

NS Not significant

**HEAVY METALS IN FERTILIZERS IN RELATION TO THEIR
ACCUMULATION IN SOILS DUE TO CONTINUOUS
FERTILIZER USE**

BY

SATHYAPRAKASAN S

ABSTRACT OF THE THESIS

**Submitted in partial fulfilment of the requirement
for the degree**

MASTER OF SCIENCE IN AGRICULTURE

Faculty of Agriculture

Kerala Agricultural University

**DEPARTMENT OF SOIL SCIENCE & AGRICULTURAL CHEMISTRY
COLLEGE OF AGRICULTURE
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ABSTRACT

The possible heavy metal pollution through continuous use of chemical fertilizers for the last several years has become a topic of grave concern in recent times. It is possible that such heavy metals if present in soil in sufficient quantities may enter the food chain and endanger animal and human life. The present study was taken up with a view to establishing whether the accumulation of heavy metals in soils and plants is appreciable so as to pose any health hazards.

With a view to achieve the above aim soils and rice plants grown in four major rice soils of Kerala which were receiving high doses of fertilizers for the last several years, and also eight common fertilizers used in these areas were collected and analysed for the heavy metal content with emphasis to cadmium. Soils from plots receiving organic manures, chemical fertilizers and a combination of both from one permanent manurial experiment with tallindica rice (25 years under same treatments) and soil, plant and grain from another permanent manurial experiment with dwarf Jeponica rice (13 years old) were collected and analysed for their heavy metal content. A pot culture with added cadmium alongwith fertilizers as per package of practices was

also conducted incorporating rice, amaranthus and guinea grass to study the plant to plant variation in the uptake and accumulation of heavy metals in their tissues

The result of the studies showed that the phosphatic fertilizers contained the highest amount of heavy metals and among the phosphatic fertilizers maximum amount of Cd was found in factomphos while Ni and Pb were highest in mussoorie rock phosphate

Among the four soil types investigated viz the Karappadam, Kayal, kari and Trivandrum sandy loam the highest content of total Cd Ni and Pb were observed in Karappadam, Kayal and Kari soils respectively The content of extractable Cd and Pb was highest in Kari soil while the extractable Ni was highest in Kayal soil

The mean Cd and Ni content of rice straw from Karapadam soil was found to be the highest where as the rice straw from Kayal soil registered the maximum content of Pb

The results obtained from the Permanent Menurial Experiemental trials revealed that the continuous use of organic matter alone or organic matter and chemical fertilizers in combination increased the heavy metal content in soils and plants

In the pot culture experiment with rice there was no significant variation in the total as well as the extractable Cd in the soil after harvest among treatments with 0 10 20 and 30 g Cd ha. The same trend was observed in the straw and grain as well. The Cd content in amaranthus also was not having significant variation among treatments. But in guinea grass the Cd content was significantly higher in the pot which received the highest dose of Cd viz 30 g ha. Since the doses viz 10, 20 and 30g Cd per hectare were fixed on the basis of annual addition through fertilizers the impact could be much less and therefore the results presently obtained cannot be said to be conclusive.

Correlation studies revealed that the soil total Cd was positively and significantly correlated to plant Cd content. The extractable Cd was also positively and significantly correlated to soil P. Applied N and P fertilizers were seen to significantly influence plant Cd content. The applied K fertilizers on the other hand were seen to positively enhance plant Cd, N₁ and Pb content.