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# Effect of long term fertilizer application on heavy metals accumulation under medium black calcareous soils

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## Abstract
A Long term fertilizer experiment was conducted at Sagadividi Farm, College of Agriculture, Junagadh Agricultural University, Junagadh to using Groundnut as test crop studing the status of available heavy metals (Fe, Mn, Zn, Cu, Pb, Cd, Cr and Ni) in soil (0-15 cm) after 32$^{nd}$, 36$^{th}$ and 40$^{th}$ years. All the heavy metals slightly increased with increase in levels of N fertilizer. The significantly highest Ni, Fe and Zn content in soil during 32$^{nd}$ years, Cr, Cd and Fe during 36$^{th}$ years and Zn, Cd and Cr during 40$^{th}$ years were observed with the application of 25 kg N ha$^{-1}$ in the form of urea over control. The DTPA extractable Fe, Mn, Zn, Cu, Pb, Cd, Cr and Ni contents in soil were significantly higher with application of 100 kg $P_2O_5$ ha$^{-1}$ through single super phosphate over control after 32$^{nd}$, 36$^{th}$ and 40$^{th}$ years. The DTPA extractable Fe, Mn, Zn, Cu, Pb, Cd, Cr and Ni contents slightly increased with increase in levels of $P_2O_5$ fertilizer. The accumulation of Cu, Mn, Zn, Fe, Cd, Cr, Ni and Pb in soil was 1.41, 8.00, 1.12, 8.93, 0.07, 0.15, 0.36 and 0.99 mg kg$^{-1}$ from their initial values of 0.96, 4.00, 0.20, 1.73, 0.02, 0.03, 0.06 and 0.33 mg kg$^{-1}$, respectively with fertilizer application after 40$^{th}$ years. These data clearly indicated that the accumulation of heavy metals in the soil was increased considerably with increase in the application of nitrogen and phosphatic fertilizer after 40$^{th}$ years over their initial value of soil.

**Keywords:** Groundnut, nitrogen, phosphorus, heavy metals status, black soil

## Introduction
Incorporation of fertilizers containing heavy metals is chief source of contamination in cultivated soils. Phosphatic fertilizers like single superphosphate derived from the rock phosphate are the chief source of heavy metals like cadmium and lead. The soil pollution by heavy metals resulting from phosphate fertilizer application has been a cause for concern in some countries (Alloway 1990) [1]. On an average, rock phosphate contains 11, 25, 188, 32, 10, and 239 mg kg$^{-1}$ of As, Cd, Cr, Cu, Pb and Zn, respectively (Mortvedt and Beaton 1995) [15]. The nitrogenous fertilizer may increase Cd concentrations in plants, even if the fertilizers do not contain significant levels of Cd (Waongstrand *et al*. 2007) [23]. In addition, Alloway (1995) [2] concluded that phosphate fertilizer application in agricultural lands can cause increased levels of Cd, As, Cr, and Pb in soil and dramatically decreased soil pH that cause desorption of heavy metals from the soil matrix. Manures and fertilizers contain not only major elements necessary for plant nutrition and growth but also trace metal as impurities. These metals can accumulate in the soil, be taken up by plants and passed on in the food chain to animals and human (Taylor and Percival 2001) [21]. Fertilizer applications may be able to influence Cd speciation and complexation which affects the Cd movement to plant roots as well as Cd uptake (Waongstrand *et al.* 2007) [23]. Based on interview with farmers and the information availability at different agricultural centres, the application of fertilizers in this area is more than crop requirements, which results in high concentration of heavy metal in the soil. The present study was carried out to assess the result of prolonged application of chemical fertilizer under LTFE with groundnut as test crop on status of heavy metals in soil (*vertic haplustepts*).

## Materials and Methods
The Junagadh city is situated at 21.5$^o$ N latitude and 70.5$^o$ E longitudes with altitude of 60 meters above the mean sea level on the Western side at the foothills of mountain Girnar in South Saurashtra agro-climatic zone of Gujarat state. A Long term fertilizer experiment was conducted at Sagadividi Farm, College of Agriculture, Junagadh Agricultural University, Junagadh. This residual soil has basaltic trap parent material. Morphologically the profiles of

these soils have A-C horizon characteristics and having moderate sub angular blocky structure. The experimental soils are plastic, sticky and hard in consistency. The colour of the soil varies from dark gray to light gray. Taxonomically, the soil is classified as *haplustepts*. The soil is calcareous in nature, slightly alkaline (pH 7.9) in reaction and clayey in texture. There is no problem of salinity and organic carbon contain is around 0.55% and clay in nature. From fertility point of view, available nitrogen and phosphorus are low and high in available potassium status. Status of all the heavy metals at initial stage of the experiment were 0.96, 4.00, 0.20, 1.73, 0.02, 0.03, 0.06, and 0.33 ppm of Cu, Mn, Zn, Fe, Cd, Cr, Ni and Pb, respectively. The treatments were tested in factorial randomized block design replicated three times. After harvesting of groundnut crop, the soil samples were drawn periodically at the interval of initial (1978), 32$^{nd}$ (2006-07), 36$^{th}$ (2010-11) and 40$^{th}$ (2014-15) years from the depth of 0-15 cm. Nitrogen and phosphorus fertilizers were applied as per the treatment in the form of Urea and SSP in previously opened furrows, The 50 % nitrogen was given as basal dose and 50 % nitrogen given at 21 DAS of groundnut crop through urea fertilizer. The entire quantity of phosphorus fertilizer as per treatment was given as basal dose using Single Super Phosphate as source. The DTPA extractable elements like Fe, Mn, Zn, Cu, Pb, Cd, Cr and Ni were determined with the help of atomic absorption spectrophotometer (Lindsay and Norvell 1978) [12].

## Result and Discussion

### *Effect of nitrogen levelss*

The concentration of all the heavy metals (Fe, Mn, Zn, Cu, Pb, Cd, Cr and Ni) in soil after different years of the experiment is shown on Table 1 and Table 2 .The data revealed that application of nitrogen from 0 to 25 kg ha$^{-1}$ increased the amount of DTPA extractable all the heavy metals compare to initial (1978) status of heavy metals in soil. (Fig.1 and Fig. 2). Significantly highest available Fe content in soil was recorded through application of nitrogen 25 kg ha$^{-1}$ in 32$^{nd}$ and 36$^{th}$ year. Significantly highest available Zn (1.08 mg kg$^{-1}$) content in soil was recorded through application of nitrogen 25 kg ha$^{-1}$ in 32$^{nd}$ year. The results in table-2 revealed the effect of long term fertilizer application on DTPA extractable Cd and Cr content in soil at different years. Significantly highest available Cd content in soil was recorded through application of nitrogen 25 kg ha$^{-1}$ in 36$^{nd}$ and 40$^{th}$ years compare to control. Significantly highest available Cr in 32$^{nd}$, 34$^{th}$ and 40$^{th}$ year. The maximum concentration of Ni in soil was recorded with levels of 25kg N ha$^{-1}$ in 32$^{nd}$ year.

### *Effect of phosphorus levels*

The concentration of all the heavy metals (Fe, Mn, Zn, Cu, Pb, Cd, Cr and Ni) in soil after different years of the experiment is shown on Table 1 and Table 2 .The data revealed that application of phosphorus from 0 to 100 kg ha$^{-1}$ increased the amount of DTPA extractable all the heavy metals compare to initial (1978) status of heavy metals in soil. (Fig. 1 and Fig. 2). Significantly higher Fe content in soil was recorded through application of 100 kg $P_2O_5$ ha$^{-1}$ over control. Selvi *et al.* (2002) [19] reported that continuous application of NPK increase the available Fe content in surface soil after 25 years. These results are also in agreement with those obtained by Yogananda *et al.* (2004) [24] and Chaudhary. Phosphorus application from 0 to 100 kg ha$^{-1}$ increased the available Mn content in soil at each interval period. Similar results were obtained by Singh *et al.* (2010) [20] who reported that the highest Mn content was recorded in plots receiving 100% NPK+FYM in soil. Significantly highest available Cu content was observed with application of 100 kg $P_2O_5$ ha$^{-1}$ in all the years overall control. Bowszys *et al.* (2005) [4] reported that long term fertilizer application improved Cu content in soil. However present result is also agreement with those obtained by Sahu and Mandal (2004) [18], Liu *et al.* (2005) [13], Gayatri and Mathur (2007) [8] and Liu *et al.* (2007) [14]. Significantly highest amount of available Zn was recorded with the levels of 100 kg $P_2O_5$ ha$^{-1}$ from the 32$^{nd}$ (1.626 mg kg$^{-1}$), 36$^{nd}$ (1.639 mg kg$^{-1}$) and 40$^{nd}$ (1.618 mg kg$^{-1}$) years respectively. These results are in conformity with those obtained by Chitdeshwari and Krishnasamy (2001) [7], Ghosh *et al.* (2001) [9], Ogunwole and Ogunleye (2004) [16] and Jalali and Moharami (2010) [10]. Over the control higher Pb content in soil was found 21.80% in 32$^{nd}$ year, 22.33% in 36$^{th}$ year and 92.93% in 40$^{th}$ year with the application of 100 kg $P_2O_5$ ha$^{-1}$. These results are in line with Oyedele *et al.* (2006) [17] who observed that the Pb contents in the soil increased significantly with the addition of the fertilizer by about 14-60% over the control. Uprety *et al.* (2009) [22], was also observed higher Pb content in soil with SSP fertilizer application. Significantly highest available Cd and Cr content in soil were recorded through application of 100 kg $P_2O_5$ ha$^{-1}$ all the years compare to 0 kg $P_2O_5$ ha$^{-1}$ and initial status of soil. Karpova and Potatueva (2003) [11] reported that prolonged application of a liquid fertilizer is based on super-phosphoric acid led to increase in Cd content. Atafar *et al.* (2010) [3] observed higher Cd concentrations in cultivated soils with single super phosphate application. Application of 100 kg $P_2O_5$ ha$^{-1}$ significantly increased available Ni content in soil at all the years. Chang and Page (2000) [5] observed that the accumulation of heavy metals were significantly higher in cropland with over time.

Based on the results summarized above it has been concluded that the application of nitrogen and phosphorus fertilizers leads to accumulation of all the heavy metals in the soil were increased considerably with increase in the rate of application of nitrogen and phosphorus fertilizer after 40$^{th}$ years over their initial values. Though the accumulation of these heavy metals in soil has not reached toxic levels even after 40$^{th}$ years, the rate of increase necessitates close monitoring the production systems involving fertilizers application in order to sustain them.

**Table 1:** Effect of long term fertilizer application on DTPA extractable heavy metal (Fe, Mn, Zn and Cu) content in soil during different years.

| Treatments | Fe ( mg kg$^{-1}$) | | | Mn ( mg kg$^{-1}$) | | | Zn( mg kg$^{-1}$) | | | Cu ( mg kg$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 32$^{nd}$ | 36$^{th}$ | 40$^{th}$ | 32$^{nd}$ | 36$^{th}$ | 40$^{th}$ | 32$^{nd}$ | 36$^{th}$ | 40$^{th}$ | 32$^{nd}$ | 36$^{th}$ | 40$^{th}$ |
| **Nitrogen ( N kg ha$^{-1}$)** | | | | | | | | | | | | |
| 0 | 4.48 | 6.07 | 8.79 | 6.50 | 7.05 | 7.73 | 0.87 | 0.92 | 0.88 | 1.18 | 1.17 | 1.36 |
| 12.5 | 4.73 | 6.24 | 8.87 | 6.57 | 7.22 | 7.92 | 0.98 | 0.99 | 1.12 | 1.18 | 1.19 | 1.41 |
| 25 | 4.87 | 6.48 | 9.13 | 7.02 | 7.83 | 8.38 | 1.08 | 1.08 | 1.43 | 1.19 | 1.24 | 1.46 |
| S.Em.+ | 0.07 | 0.10 | 0.17 | 0.25 | 0.23 | 0.18 | 0.04 | 0.05 | 0.06 | 0.02 | 0.02 | 0.03 |
| C.D. (P=0.05) | 0.22 | 0.29 | NS | NS | NS | NS | 0.109 | NS | 0.16 | NS | NS | NS |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Phosphorus ( $P_2O_5$ kg $ha^{-1}$)** | | | | | | | | | | | | |
| 0 | 4.30 | 5.26 | 7.57 | 5.41 | 6.03 | 6.99 | 0.75 | 0.69 | 0.77 | 1.06 | 1.08 | 1.32 |
| 25 | 4.64 | 5.62 | 8.53 | 6.68 | 7.46 | 8.17 | 0.76 | 0.82 | 1.02 | 1.18 | 1.16 | 1.40 |
| 50 | 4.72 | 6.73 | 9.33 | 6.92 | 7.55 | 8.17 | 0.77 | 0.83 | 1.16 | 1.21 | 1.19 | 1.42 |
| 100 | 5.12 | 7.44 | 10.30 | 7.77 | 8.43 | 8.68 | 1.63 | 1.64 | 1.62 | 1.28 | 1.37 | 1.51 |
| S.Em.+ | 0.09 | 0.12 | 0.20 | 0.29 | 0.27 | 0.21 | 0.04 | 0.06 | 0.06 | 0.02 | 0.02 | 0.03 |
| C.D. (P=0.05) | 0.25 | 0.34 | 0.58 | 0.85 | 0.79 | 0.61 | 0.13 | 0.18 | 0.19 | 0.06 | 0.07 | 0.09 |
| **NxP Interaction** | | | | | | | | | | | | |
| S.Em.+ | 0.15 | 0.20 | 0.34 | 0.50 | 0.47 | 0.36 | 0.07 | 0.10 | 0.11 | 0.04 | 0.04 | 0.05 |
| C.D. (P=0.05) | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| C.V.% | 5.46 | 5.55 | 6.62 | 12.99 | 10.93 | 7.80 | 13.19 | 18.11 | 16.94 | 5.24 | 5.73 | 6.38 |
| Initial (1978) | 1.73 | | | 4.00 | | | 0.20 | | | 0.96 | | |

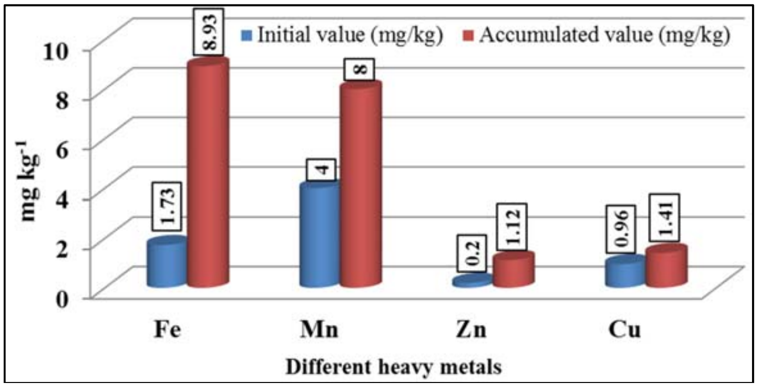


**Fig 1:** Accumulation of Fe, Mn, Zn and Cu (mg $kg^{-1}$) in soil at initial and after 40th year

**Table 2:** Effect of long term fertilizer application on DTPA extractable heavy metal (Pb, Cd, Cr and Ni) content in soil during different years.

| Treatments | Pb ( mg $kg^{-1}$) | | | Cd ( mg $kg^{-1}$) | | | Cr ( mg $kg^{-1}$) | | | Ni ( mg $kg^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 32nd | 36th | 40th | 32nd | 36th | 40th | 32nd | 36th | 40th | 32nd | 36th | 40th |
| **Nitrogen ( N kg $ha^{-1}$)** | | | | | | | | | | | | |
| 0 | 0.48 | 0.54 | 0.98 | 0.04 | 0.05 | 0.06 | 0.05 | 0.08 | 0.15 | 0.13 | 0.19 | 0.36 |
| 12.5 | 0.50 | 0.54 | 0.99 | 0.04 | 0.05 | 0.07 | 0.06 | 0.11 | 0.15 | 0.15 | 0.19 | 0.36 |
| 25 | 0.49 | 0.57 | 0.99 | 0.04 | 0.05 | 0.08 | 0.06 | 0.13 | 0.17 | 0.16 | 0.20 | 0.38 |
| S.Em.+ | 0.018 | 0.019 | 0.054 | 0.002 | 0.002 | 0.001 | 0.001 | 0.006 | 0.002 | 0.003 | 0.006 | 0.013 |
| C.D. (P=0.05) | NS | NS | NS | NS | 0.005 | 0.003 | NS | 0.016 | 0.007 | 0.008 | NS | NS |
| **Phosphorus ( $P_2O_5$ kg $ha^{-1}$)** | | | | | | | | | | | | |
| 0 | 0.45 | 0.50 | 0.72 | 0.03 | 0.04 | 0.06 | 0.04 | 0.08 | 0.13 | 0.13 | 0.17 | 0.34 |
| 25 | 0.45 | 0.51 | 0.89 | 0.04 | 0.05 | 0.07 | 0.05 | 0.10 | 0.14 | 0.13 | 0.18 | 0.34 |
| 50 | 0.51 | 0.57 | 0.94 | 0.04 | 0.05 | 0.07 | 0.06 | 0.13 | 0.17 | 0.15 | 0.19 | 0.36 |
| 100 | 0.55 | 0.61 | 1.39 | 0.04 | 0.06 | 0.08 | 0.07 | 0.13 | 0.18 | 0.17 | 0.22 | 0.43 |
| S.Em.+ | 0.020 | 0.022 | 0.062 | 0.002 | 0.002 | 0.001 | 0.001 | 0.006 | 0.003 | 0.003 | 0.007 | 0.015 |
| C.D. (P=0.05) | 0.060 | 0.063 | 0.183 | 0.007 | 0.006 | 0.003 | 0.003 | 0.019 | 0.008 | 0.009 | 0.021 | 0.044 |
| **NxP Interaction** | | | | | | | | | | | | |
| S.Em.+ | 0.035 | 0.037 | 0.108 | 0.004 | 0.004 | 0.002 | 0.002 | 0.011 | 0.005 | 0.005 | 0.012 | 0.026 |
| C.D. (P=0.05) | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| C.V.% | 12.43 | 11.83 | 18.95 | 17.98 | 13.32 | 4.30 | 5.54 | 17.74 | 5.34 | 6.16 | 11.30 | 16.54 |
| Initial (1978) | 0.33 | | | 0.02 | | | 0.03 | | | 0.06 | | |

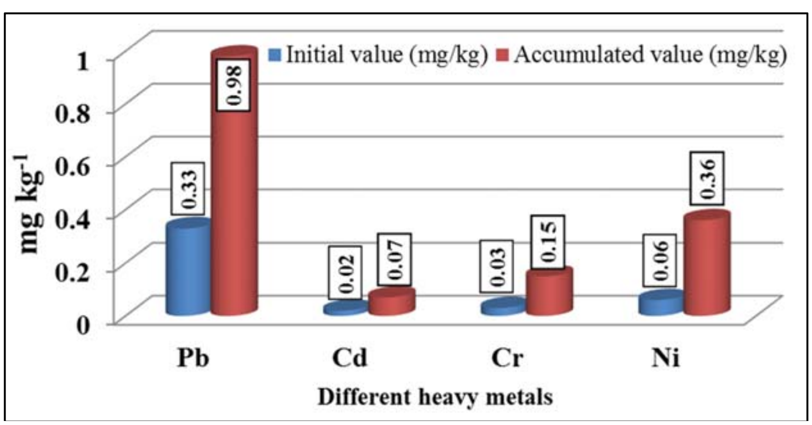


**Fig 2:** Accumulation of Pb, Cd, Cr and Ni (mg $kg^{-1}$) in soil at initial and after 40th year

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