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# Assessment of drain water receiving effluent from tanneries and its impact on soil and plants with particular emphasis on bioaccumulation of heavy metals

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***Abstract:*** *In the present study, impact of tannery and other industrial effluents on the physico-chemical characteristics of loamy drain water and their consequent impact on soil and plants irrigated with effluent have been studied. The study reveals most of the parameter pH,* $BOD_5$ *and COD at sampling station I was higher than station II. Waste water quality at both Stations I and II exceeded prescribed limits (BIS) for safe disposal of effluents into the surface water. Samples of soil and vegetables from the land irrigated with loamy drain water has been collected and analyzed for Cu, Zn, Ni, Cr, Pb and Cd. The different metals showed different enrichment factor for loamy drain water irrigated soil and are as follows: Cd 30% (max), Pb 26%, Zn 18%, Cr 5%, Cu 5%, Ni 2% (min). For plant samples collected at polluted sites are Ni 46% spinach (whole plant) (max), Zn 42% spinach (whole plant), Cr 39% spinach (whole plant), Cu 33% spinach (whole plant), Pb 20% potato tuber, Cd 20% potato tuber (min).The levels of Zn 145, Cu 5.25, and Ni 39.25 µg/g in spinach, Pb 29.25, Cr 38.25 and Cd 3.2 µg/g in potato tuber grown on polluted soil irrigated with contaminated drain water were found more than the reference value, which may create chronic health hazard problem to human and cattle through food chain in long run . Accumulation of toxic heavy metals may be build up in the agriculturally productive land where it is treated with contaminated effluent enrich with metals in turn bio-concentrated in the edible fodder/plants.*

***Key words :*** *Tannery effluents, Chemical composition, Heavy metal and enrichment*
*PDF file of full length paper is available with author*

## Introduction

About thirty numbers of tanneries and other industries are discharging their untreated and semi treated effluents into the loamy drain, a storm natural drain at Unnao, Uttar Pradesh, India. This contaminated drain water has been used for cultivation of cereals, vegetables and others economically important plants (Nath *et al*., 2005). Farmers are ignorant about the hidden toxicity of the heavily polluted discharges and their subsequent negative impacts. It has already created a major nuisance of foul odour at an area of about > 3 sq km and also contaminated the ground aquifer.

Tanneries, oil refineries and metal industries are causing depletion of surface and ground water quality (Raj *et al.,* 1996). The discharge of various sub processes of tanneries like bathing, pickling, tanning, dyeing and fat liquoring may cause water pollution severely. The pollution of a particular water body can always be link to an industry or sewage or agricultural run off (Subramanyam and Sambamurty, 2000; Sathwara *et al.,* 2007). Likewise, contamination of soil by the release of heavy metals as a result of industrial and anthropogenic activities is a threat to human health and ecosystem. Presence of heavy metals in soil is known to have potential toxic impact on environmental quality and on human health via ground water and surface water (Mishra and Pandey, 2005; Akinola and Ekiyoyo, 2006). More over concentration of heavy metals in soil may render soils non productive because of phytotoxicity and may cause bioaccumulation of heavy metals in human beings (Abdel-Sahab *et al.,* 1994; Memon *et al.,* 2001; Singh *et al.,* 2006).

The primary objectives of the present study are to assess the wastewater quality of loamy drain receiving effluent from tanneries and other industries and to study their impacts on soil and vegetables irrigated with this. The secondary objectives are to draw the attention of industries and to increase the awareness of public about the possible long term effect of health hazard of hidden toxicity.

## Materials and Methods

Water samples were drawn from two locations of loamy drain, Station I (confluence point between loamy drain and effluent channel) and Station II (500 m down stream) from the first location. Selected physico-chemical parameters were analyzed (APHA *et al.,* 1995). Upper productive soil (0 to 30 cm) and plant samples were collected randomly from polluted site. The sampling frequency was once in a month, during December 2000 to November 2001 to cover all the four seasons. Soil samples were freed from extraneous matter (stones, pebbles *etc*) and air-dried. After air-drying, the samples were ground and sieved through 2 mm sieve to ensure uniform particle size. The samples were analysed for pH, electrical conductivity, bulk density, porosity, organic matter, nitrite, nitrate, inorganic phosphate and chloride (Piper, 1942; Jackson, 1979) which have a bearing on the availability of heavy metals to the plants.

The potentially toxic elements- Fe, Mn, Zn, Cu, Pb, Ni, Cr and of Cd were analysed for soil and plant samples using atomic absorption spectrophotometer (Perkin Elmer 5000). Plant and soil samples were digested with $HNO_3$-$HClO_4$ mixture following the method of Piper (1942).

Reference soil and plant samples receiving pond water irrigation were also collected at a distance of 10 km from polluted site having similar soil profile and climate condition. This area is not devoid of any industry, nor has any major road intersection that may subsequently contribute to automobile pollution.

Metal enrichment factor (MEF) were calculated by following formula :

$$\text{MEF} = \frac{\text{Metal in soil or plant at contaminated site} - \text{Metal in soil or plant at uncontaminated site}}{\text{Total metal in soil}}$$

## Results and Discussion

**Water:** Annual average of pH, TSS, BOD, COD, chloride, sulfate and inorganic phosphate were 8.03 ± 0.43, 134.63 ± 18.77, 91.31 ± 22.0, 299.63 ± 58.29, 642.50 ± 198.43, 23.38 ± 8.27, 4.10 ± 1.02 mg/l at Station I and 7.56 ± 0.18, 119.50 ± 19.17, 77.75 ± 10.38, 273.85 ± 51.35, 571.88 ± 131.69, 17.53 ± 7.35 and 1.85 ± 0.26 mg/l at Station II respectively (Table 1).

All these chemical parameters showed higher concentrations at Station I than at Station II. This may be either due to the gravitational settling of pollutants along the drain or dilution cum self purification system of the natural loamy drain. TSS, $BOD_5$ and COD of loamy drain were much higher than their respective prescribed standard 100, 30 and 250 mg/l respectively for the final discharged of the tannery effluent into the inland surface water (IS: 2490, 1999) at both sampling points because of improper treatment of influent in the effluent treatment plant which results high chemical load in the discharged tannery effluents (Karagul *et al.*, 2005; Malaviya and Rathore, 2007).

Annual average metal concentrations of Cu, Zn, Ni, total Cr, Pb and Cd were 0.20 ± 0.08, 0.31 ± 0.10, 0.05 ± 0.01, 1.55 ± 0.09, 0.50 ± 0.06, 0.07 ± 0.03 at Station I and at Station II were 0.07 ± 0.04, 0.16 ± 0.08, 0.03 ± 0.01, 1.48 ± 0.10, 0.44 ± 0.07 and 0.05 ± 0.03 μg/l respectively (Table 1). Except Pb, our measured values of Cu, Zn, Ni, total Cr, Pb and Cd are lower than their prescribed standard 3.0, 5.0, 3.0, 2.0, 0.1 and 2.0 mg/l respectively for safe disposal of treated effluent into the inland surface water (IS: 2490, 1999). However, chromium concentrations approach the higher limit for disposal (Kannan *et al.*, 2005).

**Soils:** Annual average pH of polluted soil was 8.24 ± 0.19 and unpolluted soil 7.50 ± 0.13. Polluted soil become alkaline in nature due to the continuous receiving of tannery effluents. Annual average concentrations of chloride, sulphate and nitrate were 75.08 ± 24.92, 24.38 ± 11.38 and 0.46 ± 0.18 mg/l in polluted soil while 19.3 ± 4.58, 18.88 ± 9.97, 0.29 ± 0.08 mg/l respectively in unpolluted soil. Chloride and sulphate have significantly increased by factor of 3.9 and 1.3 and may be the cause of soil salinity within a short period of time (Table 2).

The porosity and organic matter percentage varied from 33.13 ± 7.74 and 11.28 ± 2.57 in polluted soil with comparison to 47.05 ± 4.52 and 16.15 ± 4.41 in unpolluted soil (Table 2). These two soil fertility parameters; porosity which retain enough water and air for plant growth and organic matter were markedly decreased due to the receiving of contaminated wastewater. Bulk density of the polluted soil has significantly increased and make the receiving soil jeopardize due to the low content of organic matter in the effluent. The bulk density of sandy soils and clay soils should not be more than 1.4 gm/cc and 1.2 gm/cc respectively for optimum crop growth (Kolay, 2000).

The heavy metals concentrations of Fe, Cu, Zn, Ni, Total Cr, Pb and Cd were 144.5 ± 10.54, 8.13 ± 1.46, 75.48 ± 8.05, 7.25 ± 0.90, 51.49 ± 4.72, 49.70 ± 10.17, 3.55 ± 0.62 in polluted soil and 14.91 ± 2.36, 5.13 ± 0.68, 63.83 ± 9.51, 0.65 ± 0.15, 0 0.12 ± 0.06, 2.15 ±1.24 and 0.27 ± 0.17 μg/l respectively in unpolluted soil. Polluted soil showed 447.7 (Cr) > 23.1(Pb) > 13.4

**Table 1 :** Assessment of water quality at Station I and Station II

| Parameter | Unit | Winter | | Summer | | Monsoon | | Post-monsoon | |
|---|---|---|---|---|---|---|---|---|---|
| | | Station-I | Station-II | Station-I | Station-II | Station-I | Station-II | Station-I | Station-II |
| pH | | 8.2 | 7.65 | 8.55 | 7.75 | 7.65 | 7.35 | 7.7 | 7.5 |
| Temperature | °C | 18.6 | 18.4 | 32.3 | 30.3 | 31.7 | 31.2 | 22.2 | 21.9 |
| $BOD_5$ | mg/l | 79.75 | 75.5 | 114.0 | 85.0 | 105.0 | 86.5 | 66.5 | 64.0 |
| COD | mg/l | 240.0 | 227.5 | 365.0 | 307.5 | 331.0 | 327.9 | 262.5 | 232.5 |
| Total solid | mg/l | 615.0 | 497.5 | 792.5 | 700.0 | 675.0 | 535.0 | 615.0 | 540.0 |
| TSS | mg/l | 122.5 | 105.0 | 161.0 | 144.0 | 135.0 | 125.5 | 120.0 | 103.5 |
| Chloride | mg/l | 590.0 | 542.5 | 925.0 | 675.0 | 595.0 | 672.5 | 460.0 | 397.5 |
| Sulphate | mg/l | 11.75 | 9.6 | 28.5 | 20.0 | 30.0 | 26.5 | 23.25 | 14.0 |
| Inorganic phosphate | mg/l | 2.8 | 1.6 | 4.5 | 2.2 | 3.9 | 1.7 | 5.2 | 1.9 |
| Cu | mg/l | 0.24 | 0.08 | 0.26 | 0.04 | 0.21 | 0.12 | 0.08 | 0.05 |
| Zn | mg/l | 0.4 | 0.12 | 0.38 | 0.28 | 0.30 | 0.12 | 0.17 | 0.13 |
| Ni | mg/l | 0.05 | 0.02 | 0.04 | 0.04 | 0.05 | 0.04 | 0.05 | 0.02 |
| Cr | mg/l | 1.48 | 1.42 | 1.68 | 1.62 | 1.55 | 1.42 | 1.48 | 1.45 |
| Pb | mg/l | 0.47 | 0.43 | 0.59 | 0.52 | 0.47 | 0.45 | 0.46 | 0.36 |
| Cd | mg/l | 0.08 | 0.05 | 0.09 | 0.08 | 0.07 | 0.04 | 0.03 | 0.02 |

n = 12

**Table 2:** Physico-chemical characteristics of unpolluted soil (without irrigation with industrial effluent) and polluted soil (irrigated with effluent)

| Parameter | Unit | Winter | | Summer | | Monsoon | | Post-monsoon | |
|---|---|---|---|---|---|---|---|---|---|
| | | Un-polluted | Polluted | Un-polluted | Polluted | Un-polluted | Polluted | Un-polluted | Polluted |
| pH | | 7.65 | 8.51 | 7.55 | 8.28 | 7.45 | 8.24 | 7.35 | 8.63 |
| Bulk density | gm/cc | 1.12 | 1.53 | 1.1 | 1.48 | 1.13 | 1.39 | 1 | 1.45 |
| Porosity | % | 41.9 | 33.8 | 52.4 | 36.3 | 45.2 | 22.2 | 48.7 | 40.2 |
| Conductivity | m mho | 0.96 | 7.6 | 0.52 | 3.1 | 0.95 | 7.8 | 0.98 | 4.2 |
| Chloride | mg/g | 25.6 | 84.5 | 18.5 | 78.1 | 14.6 | 39.8 | 18.5 | 97.9 |
| Inorganic phosphate | mg/g | 0.49 | 0.73 | 0.35 | 0.58 | 0.48 | 0.42 | 0.26 | 0.7 |
| Sulphur | mg/g | 27 | 31 | 10.5 | 15 | 10 | 14.5 | 28 | 37 |
| Ammonia | mg/g | 0.32 | 0.54 | 0.39 | 0.72 | 0.19 | 0.91 | 0.11 | 0.89 |
| Nitrite | mg/g | 0.28 | 0.42 | 0.54 | 0.72 | 0.57 | 0.72 | 0.18 | 0.31 |
| Nitrate | mg/g | 0.28 | 0.42 | 0.36 | 0.72 | 0.34 | 0.39 | 0.18 | 0.31 |
| Organic matter | % | 20.9 | 14.9 | 10.7 | 9.3 | 18.2 | 9.6 | 14.8 | 11.3 |
| K | mg/g | 20 | 50 | 8 | 34 | 20 | 42 | 31 | 43 |
| Iron | μg/g | 16.75 | 155 | 15.2 | 130 | 11.5 | 145 | 16.2 | 148 |
| Copper | μg/g | 5.8 | 9.4 | 5.1 | 7.8 | 4.2 | 6.2 | 5.4 | 9.1 |
| Zinc | μg/g | 72.75 | 82.2 | 60.4 | 67 | 52 | 70.2 | 70.15 | 82.5 |
| Nickel | μg/g | 0.72 | 7.9 | 0.82 | 6.2 | 0.57 | 6.8 | 0.48 | 8.1 |
| Chromium | μg/g | 0.12 | 53.25 | 0.09 | 46.5 | 0.05 | 49 | 0.2 | 57.21 |
| Lead | μg/g | 0.4 | 56.6 | 2.8 | 39.5 | 2.2 | 42.6 | 3.2 | 60.1 |
| Cadmium | μg/g | 0.2 | 4.3 | 0.11 | 2.9 | 0.5 | 3.2 | 0.25 | 3.8 |

n = 8

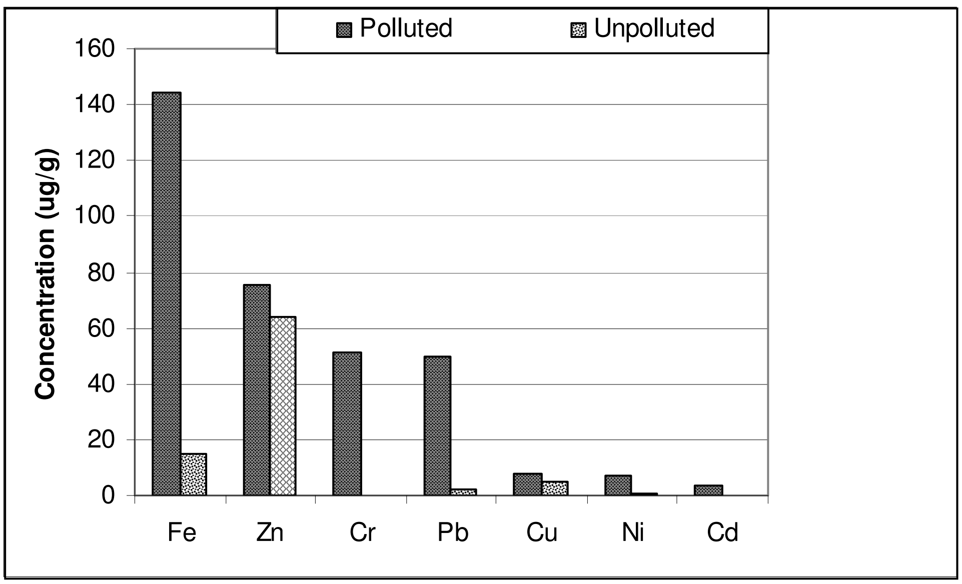


**Fig. 1:** Average heavy metal content in polluted and unpolluted soil

(Cd) > 11.2 (Ni)> 9.7 (Fe) >1.6 (Cu) > 1.2 (Zn) times higher toxic metal level than unpolluted soil. Obliviously, such build up of metal in soil irrigated with industrial effluent may be the source of bioaccumulation in cultivated crops grown on this land which not only affect the yield/ hectare but also fare chance to pass on to food web (Nath *et al*., 2005; Hooda, 2007) (Fig. 1).

**Seasonal variation of pollutants:** All the parameters (water and soil) varied significantly season to season. The highest concentrations of TSS, $BOD_5$, COD, chloride and metals in waste water were observed in the summer season. In the soil; porosity, inorganic matter and metals were generally found higher in summers. Seasonal variation is because of lean period and substantial evaporation due to extreme hot condition of the environment while the lowest concentration was observed either during monsoon or post monsoon season. It might be due to the heavy rain fall and dilution of the pollutants. The continuous discharge of tannery effluents into the impounded water body makes the water body completely unsuitable for any intended use. Furthermore, the adjoining residential areas (3 sq km) are badly affected by foul odour from stagnant tannery waste (Malaviya and Rathore, 2007).

**Table - 3:** Concentration (µg/g) of heavy metal in different plants grown on polluted soil

| Plant name | Part analyzed | Fe | Zn | Pb | Cr | Ni | Cu | Cd |
|---|---|---|---|---|---|---|---|---|
| *Spinacia oleracea* (Spinach) | Whole plant | 300 ±7.25 | 145 ±5.65 | 19.35 ±1.95 | 10.45 ±1.54 | 39.25 ±3.45 | 25.26 ± 2.24 | 2.85 ±.96 |
| *Solanum tuberosum* (Potato) | Tuber | 156.25 ±9.12 | 46.22 ±3.56 | 29.25 ±2.65 | 38.25 ±2.32 | 16.25 ±2.21 | 15.65 ±1.68 | 3.2±.98 |
| | Shoot | 135.24 ± 3.23 | 35.25 ±2.26 | 21.32 ± 1.92 | 22.35 ±2.12 | 12.25 ± 1.92 | 11.34 ± 1.25 | 2.1 ±0.86 |
| *Solanum melongena* (Brinjal) | Root | 142.62 ±2.52 | 25.32 ±1.52 | 15.26 ±1.24 | 16.35 ±1.65 | 12.45 ±1.25 | 11.32 ±1.15 | 1.2±0.85 |
| | Shoot | 135.24± 3.45 | 21.35± 1.62 | 12.25 ±1.65 | 12.56 ± 1.32 | 10.35 ± 1.15 | 9.25± 1.08 | 0.98 ± 0.85 |
| | Fruit | 95.25 ±2.65 | 15.35 ±1.24 | 8.52 ±1.21 | 7.65± 1.16 | 6.32 ±1.05 | 5.32 ± 1.08 | 0.69 ± 0.65 |
| Soil | | 114.08 2.24 | 62.22 ± 1.45 | 37.93± .65 | 42.57± .50 | 5.75± 1.08 | 7.15±1.21 | 4.65± 0.98 |

n=9

**Table - 4:** Concentration (µg/g) of heavy metal in different plant grown at control site

| Plant name | Part analyzed | Fe | Zn | Pb | Cr | Ni | Cu | Cd |
|---|---|---|---|---|---|---|---|---|
| *Spinacia oleracea* | Whole plant | 35.25 ± 3.24 | 1.4 ± 0.65 | 0.098± 0.12 | 0.12± 0.11 | 8.55± 1.45 | 5.25 ± 1.21 | 0.052 ± .008 |
| *Solanum tuberosum* | Tuber | 26.52± 2.16 | 1.5± 0.85 | 0.12± 0.11 | 0.14± 0.12 | 7.25± 1.32 | 5.12± 1.45 | 0.098± 0.32 |
| | Shoot | 24.32± 2.12 | 1.2± 0.65 | 0.095± 0.12 | 0.11± 0.14 | 6.15± 1.45 | 3.2± 1.65 | 0.042± .003 |
| *Solanum melongena* | Root | 22.65± 2.05 | 1.3± 0.95 | 0.056± 0.11 | 0.095± 0.11 | 4.25± 1.25 | 3.1± 1.45 | 0.012± .006 |
| | Shoot | 18.52± 1.98 | 1.15± 0.75 | BDL | 0.085± 0.12 | 3.24± 0.75 | 2.5± 0.94 | BDL |
| | Fruit | 15.26± 1.58 | 1.05± 0.11 | BDL | 0.05± 0.32 | 2.65± 0.58 | 2.2± 0.98 | BDL |
| Soil | …….. | 10.87± 1.24 | 1.94± 0.12 | 0.18± 0.12 | 0.21±0.12 | 4.25±0.65 | 4.25±0.14 | 0.14±0.65 |

n =9, BDL = Below Detection Limit

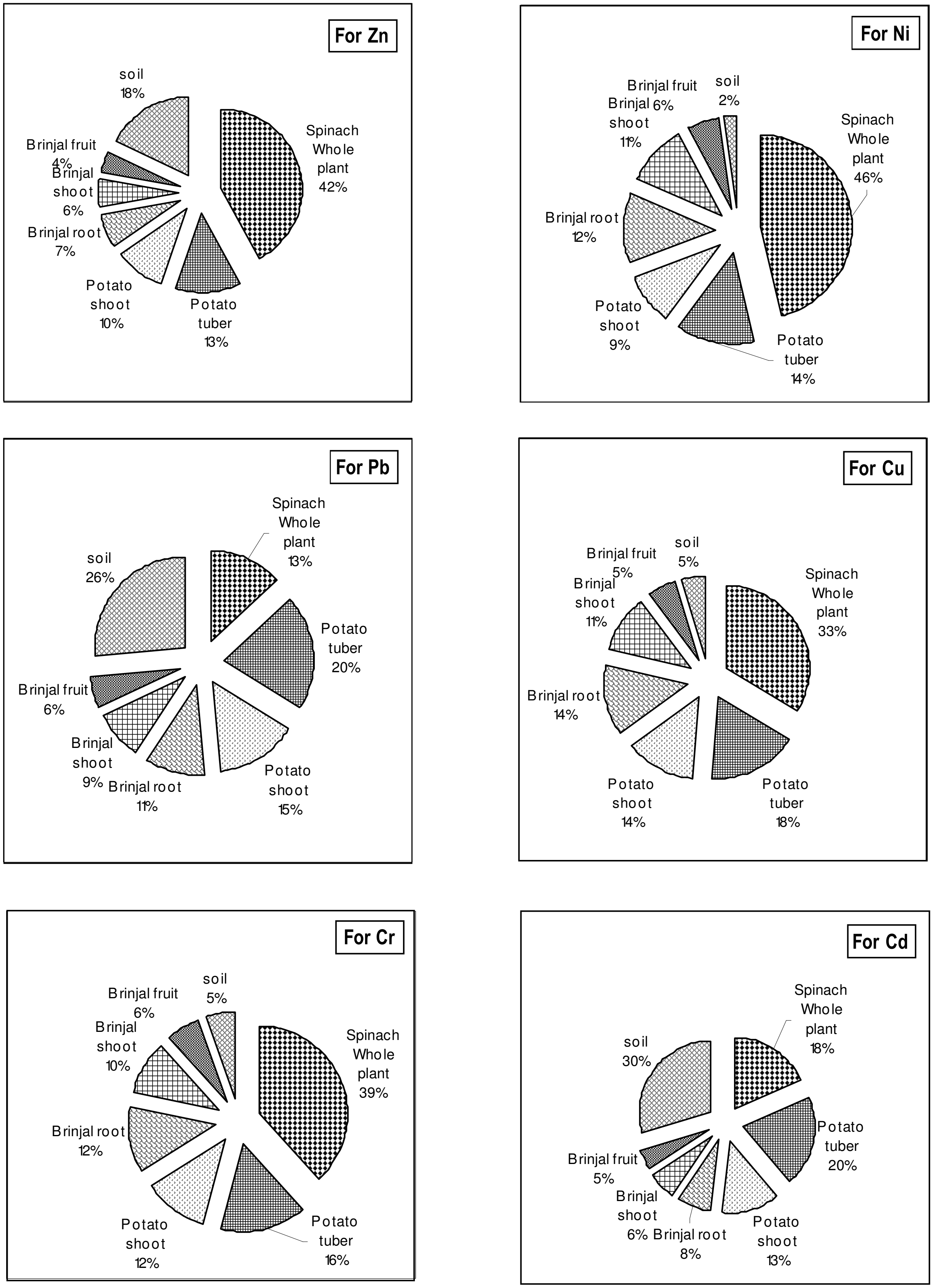


**Fig. 2:** Enrichment percentage (%) of heavy metals in different parts of vegetables and soil

**Plants:** The different metals showed different enrichment factor for polluted soil. Cd 30%(max.), Pb 26%, Zn 18%, Cr 5%, Cu 5%, Ni 2% (min.). Plant samples collected at polluted sites showed Ni 46% spinach (whole plant) (max.), Zn 42% spinach (whole plant), Cr 39% spinach (whole plant), Cu 33% spinach (whole plant), Pb 20% potato tuber, Cd 20% potato tuber (min.) . This results clearly shows that effluent containing loamy drain water enriches the soil metal content. The greater the build up of metal concentration; the greater the uptake, translocation and retention of metals in different plant tissues (Lee *et al.*, 2003; Greger and Lofstedt, 2004; Boularbah *et al.*, 2006)

The elevated levels of Zn 145 µg/g spinach (whole plant), Cr 38.25 µg/g potato tuber, Pb 29.25 µg/g potato tuber, Ni 39.25 µg/g spinach (whole plant), Cu 5.25 µg/g spinach (whole plant), Cd 3.2 µg/g potato tuber of metals were found in plants grown on polluted soil with compared to control values (Table 3, 4). There are several reports of high accumulation of cadmium in grains of rice, wheat and barley grown on soils irrigated with cadmium rich industrial effluents (Garcia *et al.,* 1981; Juwarkar and Sinde, 1986; Pandey, 2006). Consumption of cereal / grains having high Cd content for a long period (extending 2 to 3 decades) has been shown to cause the fatal disease referred to as 'ITAI ITAI' (Yamagata and Shigematsu, 1970).

As Pb has poor mobility in plants (Alloway, 1995), it largely remains accumulated in plant roots. Through bio-magnification, consumption of root vegetables adversely affects the synthesis of haem in the blood of human beings (Gallacher *et al.,* 1984).Therefore, daily intake of such plants that accumulate more toxic elements should be avoided for consumption. Especially, this is very important in the case of edible species particularly leafy vegetables (spinach) and root/ tuber vegetables (potato). Usually, the root values of heavy metals are one to two orders of magnitude higher than the shoot values. Whatever the amount accumulated by leafy and root/ tuber vegetables, there is a fare chance of direct entry into human diet (Kisku *et al*., 2000).

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