



Determination of DTPA extractable heavy metals from sewage irrigated fields and plants

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ABSTRACT

The field experiments were conducted to evaluate the accumulation of heavy metals in soil and plant parts. The protocol based on DTPA (Diethylene triamine penta acetic acid) assisted extraction of heavy metal was used to find out the amount of different heavy metals. The relative level of accumulation of heavy metal was determined in response to sewage irrigation and ground water irrigation of soil and different crops. The amount of heavy metals like Cd, Cr, Cu and Ni was observed to higher level in case of sewage effluent irrigated soil than ground water. The Nickel, Cadmium, Chromium and Copper metal also varied on the depth, having higher amount of metals on upper surface than the lower layers of soil.

Keywords: Sewage, Heavy metal, Ground water, soil texture, Pollution, Sewage Irrigation, Maximum Permissible Limit.

Introduction

Over the last few decades, various developmental activities such as rapid industrialization, urbanization have drastic effect on environment. There has been continuous deterioration and degradation of agricultural land due to soil erosion, soil salinization¹ and pollution of water basically due to disposal of huge amount of sewage. Although raw sewage contains few agronomically important plant nutrients viz. Phosphorus (P), Nitrogen (N), Potassium (K), Zinc (Zn) and organic solids but it invariably contains potentially hazardous heavy metals such as Cadmium (Cd^{2+}), Lead (Pb^{2+}), Nickel (Ni^{2+}), Aluminium (Al^{3+}) etc.^{2,3} Heavy metals constitute an important group of environmental pollutants. Metal weighting more than 6.0 mg/m³ and atomic weight more than iron are called as heavy metals e.g. Zn(7.1), Chromium (Cr) (7.2), Ni(8.7), Cd(8.6), Cobalt Co(8.9), Pb(11.4).⁴ Heavy metals are the major environmental pollutants spread to the soil by sewage which is being used for irrigation. The possible injurious effect of

exposure of plants, animals and man to metals has generated as justifiable global concern. As metal pollutants are non-degradable and are also quite readily taken up by plants, they have tendency to enter into the food chain. The total consequences of ingestion of food contaminated either accidentally or naturally with heavy metals emphatically illustrated by documented incidence of "Itai-Itai" and "Minemata" disease in Japan which were occurred due to consumption of food having higher amount or concentration of Cd and Hg respectively. Heavy metals have been classified as the dreaded pollutants which have potential of eliciting human health via soil solid- soil solution plant roots- edible parts – animals continuum.⁵

The continuously increasing shortage of fresh water for irrigation,⁶ application of sewage on agricultural lands offers a promising alternative for fresh water irrigation. The uncontrolled use of sewage water for irrigation can result in accumulation of some potentially toxic metals in the soil⁷ and may affect plant growth adversely. These contaminants⁸ can be absorbed in higher quantities by crops and may enter the food chain through consumption of these crops by humans and Animals. The sewage contains lots of degraded organic materials which help in plant growth and higher crop yields.⁹ Sewage application although increases crop production but also results in accumulation of toxic substances into soil and plants. So, present study was done to evaluate the heavy metal impact of sewage irrigated soil and plants grown on this soil.

Material and Methods

All chemicals used were of analytical grade. To prepare 1 liter of DTPA extract solution, 13.1 ml TEA (Triethylamine), 1.967 gm of DTPA (Diethylene triamine penta acetic acid)

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and 1.47 gm of CaCl₂ (Calcium chloride) were dissolved in 1 liter of double distilled water. Solution was shaken for sufficient time to dissolve the DTPA completely. Addition of ~ 4 ml of 1N HCl (Hydrochloric acid) brought pH to 7.3. This solution is stable and can be used for months. The final solution contains 0.005 M DTPA, 0.1 M TEA, 0.01 M CaCl₂.H₂O in reagent. Seeds were purchased from Chaudhary Charan Singh Hisar Agricultural University (CCSHAU), Hisar and Krishi Gyan Kendra, Rohtak.

Procedure

Heavy metal contents in soil samples: 10 gm of soil was added to the flask and 20 ml of DTPA extracting solution was added to it. The mouth of flask was closed with tight stopper and shook the flask continuously for 2 hrs on automated shaker. The mixture was filtered through whatman filter paper (42 no.). The heavy metal contents in DTPA extract were determined on Atomic absorption spectroscopy using respective cathode lamps.

Digestion of plant material for analysis: 0.5 gm of the dried and grinded sample was digested with di-acid (mixture of nitric acid and perchloric acid (4:1)) on hot plate till get a clear solution. The volume of mixture was made to 25 ml with addition of double distilled H₂O, filtered and stored in washed plastic bottles. The heavy metals Cd, Ni, Cr, Cu, Zn, Pb were determined by AAS (Atomic absorption spectrophotometer).

Collection of Sewage water samples: The water was collected from different outlets near main sewage disposal sites of Rohtak in clean plastic bottles. Concentrated nitric acid (5ml) was added to the bottle at the time of collection of sample to avoid adsorption of heavy metals on walls of bottle and to preserve it. Samples were also collected without addition of acid in storage bottles. These unacidified samples were used for the estimation of EC, pH within two day of sample collection. Heavy metals were estimated as such after filtering and digesting of 100 ml of sample with diacid digestion. pH was determined on Systronics digital pH meter. EC was determined for filtered sample with help of conductivity bridge (USDA). Heavy metals were determined by AAS.

Collection of plant and soil samples: Soil samples from both sewage irrigated and tube well irrigated fields were collected from 2 depths i.e. 0-15 cm and 15-30 cm depths in polyethene bags. Plant samples were collected from the same site from where soil samples were collected. Plant samples were washed with running tap water first to remove adhering soil particles followed by acidified de-ionized water and then with double distilled water. Excess water was removed by gentle shaking and pressing against filter paper. Washed samples were air dried, and kept in paper bages in oven at 65°C to get accurate weight. After that different plant samples were separated and graded samples were stored in small paper bags for analysis.

Results

Heavy metal content of sewage effluent and its accumulation in soil and plant parts: The physico-chemical characteristics of sewage water in table 1 indicate that heavy metal content were within permissible limits acceptable for

CPCB (Central Pollution Control Board) water quality guidelines.

Zinc, lead, nickel,¹⁰ chromium, copper and cadmium were 238, 595, 195, 183, 67.4 and 6.5 ug/lit respectively. Concentration of these heavy metals in sewage irrigated soil was more that the tube well irrigated soil and it is in increased amount in surface horizon more than the sub surface soil samples. The mean Zinc concentration was 7.9, copper 6.9, lead 9.7, nickel 1.28, chromium 0.29, cadmium 0.59 mg/kg in sewage irrigated soil samples (0-15 cm) respectively (table 3). The mean contents of these metals decreased with increasing depth. Comparatively lesser amount of these metals in sub-surface soil was due to reduced mobility of metals to lower horizon (table 3, 4).

Table 1. Average Heavy Metal Content of Sewage Water (µg /litre)

| Metal | Observed | Permissible limit ⁶ |
|----------|----------|--------------------------------|
| Cadmium | 6.5 | 10 |
| Chromium | 183 | 100 |
| Nickel | 195 | 200 |
| Lead | 595 | 500 |
| Copper | 67.4 | 200 |
| Zinc | 238 | 2000 |

Table 2 Heavy metal content of soil irrigated with tubewell water (mgkg⁻¹)

| Heavy metal | Depth 0-15 (cm.) | Depth 15-30(cm.) |
|-------------|------------------|------------------|
| Copper | 3.05± 0.011 | 2.60±0.040 |
| Zinc | 4.13±0.002 | 3.51±0.001 |
| Lead | 2.80±0.01 | 1.68±0.031 |
| Cadmium | 0.25±0.001 | 0.13±0.010 |
| Chromium | 0.16±0.002 | 0.10±0.003 |
| Nickel | 1.00±0.004 | 0.85±0.001 |

SD ± of 10 samples

Table 3 Heavy metal content of sewage irrigated soil (mgkg⁻¹ dry soil)

| Heavy metal | Depth 0-15 (cm.) | Depth 15-30(cm.) |
|-------------|------------------|------------------|
| Copper | 6.99± 0.059 | 5.62± 0.045 |
| Zinc | 7.94± 0.062 | 6.44± 0.034 |
| Lead | 9.77± 0.073 | 8.28± 0.046 |
| Cadmium | 0.58 ±0.045 | 0.46± 0.036 |
| Chromium | 0.29±0.012 | 0.06± 0.002 |
| Nickel | 1.28±0.014 | 1.20± 0.01 |

SD ± of 10 samples

Discussion

Environmental pollution is an undesirable change in atmosphere, hydrosphere and lithosphere. Advanced industrialization process have provided comforts to human beings on one hand but also resulted in indiscriminate release of gases and liquids which pollute environment of biological system. As there is shortage of water and unequal, abnormal rate of precipitation forced farmers to use waste water to irrigate vegetable fields. Second reason for this is very good

in agricultural fields without any hazard. Nevertheless, long term usage of effluent may ultimately leads to accumulation of amount in soils and vegetation grown upon this type of soil.¹¹

The present findings confirm presence of higher concentration of heavy metals in soil irrigated with sewage water as compared to canal water.¹² Accumulation in soil is affected by cation exchange capacity, pH and texture.¹³ With increasing depth there is decreasing availability of heavy metals in same way as in the surface layer $Pb > Zn > Cu > Ni > Cd > Cr$. The accumulation of metals may be

Table 4 Heavy metal content in different plant parts cultivated in tubewell irrigated fields (mg/kg dry wt.)

| Plant | Parts | Zinc | Copper | Lead | Cadmium | Chromium | Nickel |
|--------------|--------|-------|--------|-------|---------|----------|--------|
| Brinjal | Root | 22.5 | 5.5 | 4.40 | 2.60 | 0.69 | 1.03 |
| | Stem | 20.1 | 2.8 | 4.10 | 3.31 | 0.75 | 1.0 |
| | Fruit | 29.8 | 13.2 | 1.24 | 0.16 | 1.61 | 1.60 |
| Spinach | Root | 11.5 | 4.5 | 4.67 | 0.56 | 0.11 | 3.89 |
| | Leaves | 18.10 | 2.7 | 12.01 | 0.28 | 0.17 | 2.53 |
| Cabbage | Root | 17.84 | 6.0 | 5.5 | 4.35 | 0.06 | 3.14 |
| | Shoot | 10.5 | 5.7 | 5.3 | 4.10 | 0.09 | 2.95 |
| | Fruit | 25.3 | 5.8 | 3.8 | 3.87 | 0.11 | 2.92 |
| Cauli flower | Root | 21.8 | 5.1 | 4.6 | 3.17 | 0.44 | 2.19 |
| | Shoot | 17.4 | 4.9 | 4.7 | 3.00 | 0.30 | 2.55 |
| | Curd | 9.5 | 3.8 | 4.0 | 3.50 | 0.63 | 2.86 |
| Bottle Gourd | Root | 12.3 | 4.7 | 2.61 | 9.78 | 0.98 | 2.73 |
| | Stem | 7.5 | 6.1 | 1.48 | 9.65 | 0.71 | 2.64 |
| | Fruit | 13.4 | 5.2 | 3.65 | 9.21 | 0.50 | 2.00 |
| Coriander | Root | 31.8 | 12.8 | 5.71 | 3.11 | 1.1 | 2.64 |
| | Stem | 26.7 | 8.5 | 6.30 | 3.67 | 0.6 | 2.95 |
| | Leaves | 33.9 | 10.7 | 4.88 | 2.49 | 0.85 | 1.39 |
| Mustard | Root | 30.5 | 6.17 | 4.15 | 4.99 | 0.11 | 3.54 |
| | Stem | 25.7 | 9.33 | 5.32 | 2.26 | 0.16 | 4.43 |
| | Fruit | 38.9 | 12.14 | 2.73 | 1.97 | 0.08 | 2.29 |
| Sorghum | Root | 40.6 | 5.1 | 6.77 | 4.31 | 0.31 | 3.38 |
| | Stem | 48.7 | 3.8 | 7.81 | 2.64 | 0.36 | 4.46 |
| | Leaves | 12.3 | 210.1 | 87.4 | 15.42 | 115.4 | 77.5 |
| Barseem | Root | 21.6 | 3.1 | 2.66 | 1.98 | 0.17 | 4.87 |
| | Shoot | 18.7 | 3.0 | 2.62 | 2.87 | 0.19 | 3.34 |
| | Leaves | 13.5 | 2.6 | 1.39 | 2.70 | 0.09 | 3.21 |

yield of crops as sewage contains large number of organic material and some inorganic elements essential for plant growth. But along with these it also contains non essential heavy metals which if present beyond permissible limits could be transferred to various organisms via food chain in ecosystem.

Although sewage effluents contain heavy metals appropriate treatment or dilution can make them worth using

due to higher level in sewage water as reported earlier.

As soil is the universal mother of all life forms, contaminated soil can modify nutritional value of food and fodder crops, their safety for living organism consumptions. Sewage effluent irrigation may considerably enhance availability of various heavy metal to plants. The heavy metal accumulation results obtained here resemble the earlier trends.^{14,15}

Table 5 Heavy metal content in different plant parts cultivated in sewage irrigated fields (mg/kg dry wt.)

| Plant | Parts | Copper | Zinc | Lead | Cadmium | Chromium | Nickel |
|--------------|--------|--------|-------|-------|---------|----------|--------|
| Cabbage | Root | 6.9 | 170 | 82.9 | 8.14 | 3.4 | 41.4 |
| | Shoot | 4.7 | 96 | 85.5 | 7.92 | 4.1 | 35.5 |
| | Curd | 11.4 | 220 | 94.1 | 7.23 | 6.8 | 50.2 |
| Cauli flower | Root | 5.9 | 188.5 | 60.0 | 3.25 | 176.2 | 148.7 |
| | Shoot | 5.0 | 124.1 | 78.2 | 12.6 | 157.4 | 197.4 |
| | Curd | 10.1 | 137.5 | 85.2 | 6.31 | 212.5 | 265.1 |
| Spinach | Root | 5.6 | 50.0 | 80.0 | 11.35 | 5.5 | 25.3 |
| | Stem | 13.5 | 225.0 | 108.0 | 12.22 | 3.9 | 37.9 |
| | Leaves | 15.5 | 340.1 | 34.6 | 15.11 | 7.3 | 48.7 |
| Tori | Root | 5.2 | 64.4 | 64.7 | 12.28 | 6.5 | 33.3 |
| | Stem | 7.7 | 32.6 | 86.3 | 7.75 | 4.9 | 74.6 |
| | Fruit | 8.4 | 54.7 | 97.2 | 12.28 | 6.6 | 11.4 |
| Brinjal | Root | 6.7 | 78.1 | 69.5 | 9.81 | 0.41 | 32.3 |
| | Stem | 5.6 | 22.4 | 77.2 | 7.18 | 0.65 | 27.9 |
| | Fruit | 6.9 | 20.6 | 72.4 | 6.50 | 0.23 | 16.2 |
| Capsicum | Root | 16.8 | 212.1 | 79.0 | 9.6 | 67.7 | 189.1 |
| | Stem | 42.4 | 366.4 | 95.4 | 8.4 | 16.7 | 72.3 |
| | Fruit | 58.3 | 415.0 | 88.0 | 9.8 | 20.5 | 88.3 |
| Coriander | Root | 29.2 | 464 | 84.3 | 15.4 | 26.4 | 21.3 |
| | Shoot | 13.3 | 379 | 115.0 | 12.5 | 4.6 | 42.0 |
| | Leaves | 32.1 | 480 | 96.1 | 13.2 | 2.5 | 31.5 |
| Mustard | Root | 10.5 | 170 | 21.5 | 12.82 | 2.4 | 35.2 |
| | Stem | 18.4 | 110 | 42.3 | 5.40 | 4.9 | 62.5 |
| | Fruit | 37.6 | 140 | 112.5 | 6.71 | 1.0 | 46.4 |
| Barseem | Root | 5.6 | 50.0 | 80.0 | 11.35 | 5.5 | 25.3 |
| | Shoot | 13.4 | 225 | 108.0 | 12.22 | 3.9 | 37.9 |

Among plant parts maximum concentration of heavy metal resides at roots followed by leaves and fruits. But few plants showed reverse pattern. Contents of heavy metals in all plants parts were within phytotoxic limit for these metals. Trace elements distribute mostly in roots with very little in shoot although distribution may change with some plants, species and with very high soil contents. Zn is the most bioavailable metals in polluted soils, absorption of Cu by plant roots are among lowest for essential elements. The metals accumulation in crop tissues are generally a function of metal concentration in soil and soil texture but the level of absorption differ according to crop species and tissue. Plants are one of the principal sinks of accumulated heavy metals and these contaminated edible portions acts as poison for human beings and other living organisms.^{16,17}

Conclusion

The sewage irrigated soil has accumulated higher concentration of heavy metals in upper layer of soil within permissible limit. Sewage water contains heavy metals in permissible limit except cadmium and chromium. Crop plants accumulated heavy metals in roots as well as in fruits. The concentration of heavy metals in tubewell irrigated soil and plants were much lower than the sewage irrigated fields.

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