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Bio-accumulation of Heavy Metals Present in Pulp and Paper Mill Effluents

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Bio-accumulation of Ni, Cr, Mn, Zn, Cu, Fe and Cd present in pulp and paper mill effluents by *Arachis hypogea* (groundnut) and *Lycopersicon esculentum* (tomato) plants were investigated by performing pot experiment. The plants were treated with different concentrations of the metals in the form of their metal nitrates, through soil. In each case the investigation period was six weeks. The order of accumulation was Mn > Cu > Fe > Zn > Ni > Cr > Cd. The doses of the wastes were taken 25, 50, 75 and 100 mL, respectively. Throughout the experiment fresh samples of the waste were utilized. Also the concentrations of these metals in wastes and plant sample were determined by ICP-AES technique.

Key Words: Bio accumulation, Heavy metals, ICP-AES analysis, Pot experiments, Metals uptake.

INTRODUCTION

Among the major industries in India, pulp and paper is one of the industries which contributes significantly to water pollution. The quantity of fresh water used in the production of 20 tonnes of paper is about 8000 m^3 per day[1]. Nearly 75 to 95% of fresh water used in the paper and pulp mill is discharged as effluents containing organic and inorganic pollutants and colouring material. Effluents are used for irrigation in dry land areas after treatment. These effluents not only contain nutrients that enhance the growth of crop plants but also have toxic materials that interfere with the soil ecosystem.

Land application of wastewater is a preferred alternative for its disposal since soil is believed to have a capacity for receiving and decomposing waste and pollutants[2], where organic materials are stabilized through the activity of microflora in the soil.

Transfer of potentially toxic metals from soil into the shoots of higher terrestial plants is typically low compared to those of micronutrients[3]. Therefore, those species that accumulate exceptionally large concentrations of heavy metals in their tissues have attracted scientists to a study of the evolutionary, ecological and physiological aspects involved in the process. Baker and Brooks[4], defined

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plant accumulating metals as hyper accumulator species. Hyper accumulation of metals has been found in temperate as well as in tropical regions throughout the plant kingdom, but is generally restricted to endemic species growing on mineralized soil and related rock types[4], while hyper accumulators have been used to identify mineralized rocks and ores. In order to develop phyto-remediation of the heavy metals, a new field of research is quickly evolving[5].

The increasing percentage of these metals in waste sewage[6] and the continuous use of these wastewaters for irrigation results in the enrichment of the top soil with these heavy metals[7].

To remove these metals from the soil several plant species have been used which can accumulate metals to a degree far in excess of normal physiological requirement[8, 9]. As an extension of this, we recommend the use of *Arachis hypogea* and *Lycopersicon esculentum* to remove metals from the soil through accumulation.

EXPERIMENTAL

Chemicals used were of AR grade. Stock solutions (1000 μg/mL) of Ni, Cr, Mn, Zn, Cu, Fe and Cd as their metal nitrates were prepared in double distilled water.

The *Arachis hypogea* and *Lycopersicon esculentum* plants were grown in plastic pots having dimension $30 \times 30 \times 30$ cm^3. The actual experimentation was started after fifteen days of transplantation of the plants at a new site.

Different doses (25, 50, 75, 100 mL) of metal nitrate solutions (500 mL pots) were provided to the plants; control plants were treated with equal volumes of distilled water. The soil of each system for a further duration was kept moist and left undisturbed.

After six weeks approximately 3 g of composite plant sample was taken in each case and placed in a clean test tube. The sample were dried in an oven at 105°C for overnight. The sample were then weighed and digested in 2 M HNO_3. The acid digests were taken in 100 mL of 6 N HCl, made to volume and filtered to remove any insoluble material. The extracts were analyzed for metals using atomic absorption spectrophotometer as per the corresponding wavelength of metals.

RESULTS AND DISCUSSION

Metals accumulated by *Arachis hypogea* and *Lycopersicon esculentum* at different concentrations in six weeks duration are given in Tables 1 and 2.

TABLE-1
METALS (μg/g) UPTAKE BY PLANTS AND SOIL SAMPLES

Plant name	Ni	Cr	Mn	Zn	Cu	Fe	Cd
Lycopersicon esculentum (Tomato)	28.80	1.10	72.16	7.16	86.2	12.20	ND
Arachis hypogea (Groundnut)	0.56	0.66	78.40	2.23	10.16	13.60	ND
Soil sample	ND	0.14	ND	1.68	0.33	7.00	0.003

ND: Not detected.

TABLE-2
BIO-ACCUMULATION OF METALS (μg/g DRY WT.) BY *LYCOPERSICON ESCULENTUM* AND *ARACHIS HYPOGEA* PLANTS AT DIFFERENT CONCENTRATIONS IN SIX WEEKS DURATION

Dose treatment (mL)	Ni	Cr	Mn	Zn	Cu	Fe	Cd
Lycopersicon esculentum (Tomato):							
25	0.26	ND	78.58	4.80	5.92	7.6	ND
50	0.56	0.16	78.80	5.61	9.10	8.2	ND
75	0.93	0.72	78.70	5.88	9.20	8.3	ND
100 mL	1.16	1.22	78.50	6.00	8.98	8.4	ND
Arachis hypogea (groundnut):							
25	2.38	0.12	72.15	4.60	5.80	7.20	ND
50	3.16	0.18	72.62	4.12	8.20	7.10	ND
75	3.42	0.21	73.00	5.20	7.82	7.92	ND
100 mL	3.72	0.27	72.92	7.10	8.16	8.20	ND

*Each value is the average of three determinations. Metal nitrates were used for six weeks.
ND: Not detected.

At different dose treatment on *Arachis hypogea* and *Lycopersicon esculentum*, the metal concentration will be increased with increasing dose treatment, *i.e.*, Ni, Cr, Zn, Fe respectively. But Mn and Cu concentrations will be increased as well as decreased. Cadmium will not be detected in both plants.

Therefore Ni, Cr, Mn, Zn, Cu, Fe are tolerated by more plant species than cadmium. This finding is in agreement with the fact that cadmium is more toxic than other metals[10]. There exists direct evidence of interference caused by cadmium in the metabolic system[11]. At low concentration the orders of accumulation of metals in *Arachis hypogea* and *Lycopersicon esculentum* are Mn > Fe > Cu > Zn > Ni > Cr > Cd and Mn > Fe > Cu > Zn > Ni and Cd respectively.

The lowest accumulation of cadmium in *Arachis hypogea* with respect to 25, 50, 75, 100 mL concentrations may be attributed to the reason that cadmium is converted into its methylated compounds in the soil by the reaction of microorganism present in the soil[12], which may inhibit accumulation in plants. In the plant *Lycopersicon esculentum* the lowest accumulations of Cr and Cd have been found with respect to all the doses of concentration. It is also indicated that these metals are converted into these methylated compounds in the soil.

From the studies of accumulation of Ni, Cr, Mn, Zn, Cu, Fe, it has been found that accumulation of all the metals is more or less constant and in the increasing order except chromium in *Lycopersicon* at 25 mL dose. The soil used has high

pH and high calcium concentration. It has been observed that high pH favours the accumulation of metals like Pb[13] and high concentration of calcium lowers the accumulation of cadmium[14].

A large number of parameters are involved in the accumulation of metals by different plants[15]. On the basis of our result it can be concluded that growing of *Arachis hypogea* and *Lycopersicon esculentum* plants in the soil irrigated by sewage and industrial wasteswater like pulp and paper mill effuents enriched with Ni, Cr, Mn, Zn, Cu, Fe, Cd, may help remove the metals from the soil through bio-accumulation.

For comparison, the concentrations of metals in pulp and paper mill effluents, nearby plants and their amended soils, are being given in Table-3. Cr was not detected in all the samples. The concentration of Fe, Zn and Cu was found to be higher in comparison to other metals.

TABLE-3
CONCENTRATION OF METALS (ppm) IN PULP AND PAPER MILL EFFLUENTS, NEARBY PLANTS AND THEIR EMENDED SOILS

No. of sample	Ni	Cr	Mn	Zn	Cu	Fe	Cd
1	2.00	ND	0.29	0.46	0.38	40.0	0.45
2	1.22	ND	0.22	0.38	0.36	32.0	0.41
3	0.96	ND	0.11	0.26	0.21	22.2	0.27
4	1.96	ND	0.82	0.77	0.48	88.0	0.57
5	0.62	ND	0.22	0.22	0.23	28.7	0.18
6	1.42	ND	0.73	1.21	0.42	50.0	1.1
7	0.42	ND	ND	2.46	0.99	158.0	0.032
8	0.70	ND	ND	2.22	1.18	160.0	0.046
9	0.02	ND	0.81	25.2	118	86.2	3.00
10	0.04	ND	0.68	18.7	0.92	118.0	9.00
11	0.02	ND	0.93	14.2	112	124.0	2.60

ND: Not detected.

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REFERENCES

1. C.A. Shastri, V. Kothanclaraman and K.M. Abbo, *Indian J. Environ. Hlth.*, **19**, 346 (1977).
2. J.C. Young, G.N. Dermott and D. Jenkin, *J. Water Poll. Cont. Fed.*, **53**, 1253 (1981).
3. D.C. Adriano, Trace Elements in the Terrestrial Environment, Springer-Verlag, New York-Berlin-Heidelberg-Tokyo (1986).
4. A.J.M. Baker and R.R. Brooks, *Biorecovery*, **1**, 81 (1989).
5. W.W. Wenzel, D. Salt, R.S. Smith and D.C. Adriano, Phytoremediation: A plant microbe based remediation system, in: D.C. Adriano and J.M. Ballog (Eds.), Bioaccumulation of Soil, SSSA Monographs (1998).
6. W.E. Larson, J.R. Gilley and D.R. Linden, *Conservations*, **2**, 68 (1975).
7. Anderson and K.O.Nelson. *Ambio*, **1**, 176 (1973).
8. G.T. Goodman, C.T.R. Piteran and R.P. Gemmel, in: R. Hutnik and G. Davis (Eds.), Ecology and Reclamation of Devasted Land, Gordon and Breach, London, Vol. 11, p. 149 (1963).
9. M.O. Humphries and A.D. Bradshaw, in: M.J. Wright and S.A. Ferrari (Eds.), Plant Adaptation to Mineral Stress in Problem Soils, Cornell Univ. Exp. Stn., Ithacu, p. 95 (1997).
10. B.L. Vallee and D.D. Ulmer, *Ann. Rev. Biochem. Ann. Biochem.*, **41**, 91 (1972).
11. T. Takenchi, Environmental Metal Mercury Contamination Science, Pub. Inc. Arhar. Mich., p. 272 (1972).
12. Jenson and A.G. Jernelov, *Nature*, **233**, 257 (1969).
13. J. Narayana and S. Parveez, Treatment of Paper Mill Effluent Using Water Hyacinth, *Eichhornia crassipes* (2000).
14. P. Dhevagi, G. Rajannan and G. Oblisami, Effect of Paper Mill Effluent on Soil Microflora of Maize (2000).
15. R.S. Sindhu and R. Sharma, Bioaccumulation of Lead, Cadmium and Mercury by *Galium tricorne* (1999).

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