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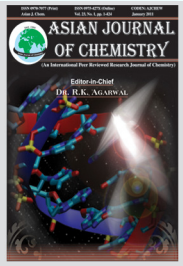

Accumulation of Heavy Metals in the Agricultural Soils Close to the Industrial Drains/Areas

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The present study is conducted to assess the accumulation of heavy metals in some selected urban and peri-urban agricultural areas in Faisalabad. The purpose of study is to investigate the extent of soil contamination in those areas which are either irrigated or not-irrigated by the industrial waste water but are either close to industrial sectors or industrial waste water drainages. All the soil samples were analyzed for different heavy metals including Cd, Cr, Cu, Ni, Hg, Pb, Mn and Zn by atomic absorption spectrophotometer. Mercury was determined by using cold vapour technique. All the soil samples were found within permissible ranges with respect to Pb, Mn and Zn. The level of mercury was found much higher than the permissible level in some samples. The higher levels of Ni and Pb were found in the soil samples collected from the surroundings of ghee mills.

Key Words: Soil pollution, Heavy metals, Toxic drains, Waste water, Industrial drains, Heavy metal pollutions.

INTRODUCTION

In medical usage, heavy metals are loosely defined[1]. The contamination of soil by metallic elements and their aerial deposition is likely to result in corresponding contamination of harvested crops and foods consumers' eat[2,3]. Some heavy metals are essential in trace amounts and play important role in plants and animals' nutrition, enzymatic reactions and metabolic processes[4]. Cadmium and several cadmium containing compounds are known as carcinogenic and can induce many type of cancers[5]. The adverse physiological effects commonly encountered due to high cadmium exposure include depressed growth rate, anemia and hypertension, damage to renal tubules and poor mineralization and bones[6]. Chromium compounds are highly toxic to plants and are detrimental to their growth and development. Although some crops are not affected by low Cr concentration[7]. Trivalent chromium in trace amounts influences sugar and lipid metabolism in humans and its deficiency is suspected to cause a disease called chromium deficiency[8]. In contrast, hexavalent chromium is very toxic and mutagenic when inhaled. Cr(VI) has not been established as a carcinogen when in solution, though it may cause allergic contact dermatitis[9]. The organ most affected by very high concentrations of copper in the soil is the root[10]. High concentrations of total copper in topsoils can result from the accumulation of fungicidal sprays[11]. Nickel has been considered to be an essential trace element for humans and animals health. It is present in body tissues even before birth. In living system, it is associated with DNA and RNA molecules and also a regulatory element for the various enzyme systems[12]. The phytotoxicity varies with the concentration of Ni in soil solution as well as with the plant species[13]. Mercury poisoning is a disease caused by exposure to mercury or its compounds. Toxic effects include damage to brain and kidneys and lungs[14]. Acrodynia (also known as "calomel disease," "erythredemic polyneuropathy," and "pink disease") is a type of mercury poisoning in children characterized by pain and pink discoloration of the hands and feet[15]. Lead poisoning in humans causes several damages in kidneys, brain, reproductive system, central nervous system and sometime cause death[16]. The body contains about 120 mg of lead which is mainly present in skeleton and in smaller amount in hair and blood[17]. It accumulates with age in bones, aorta, kidney, liver and spleen[18]. Manganese is an essential trace nutrient in all forms of life[19]. The human body contains about 10 mg of manganese, which is stored mainly in the liver and kidneys. In the human brain the manganese is bound to manganese metalloproteinase most notably glutamine synthetase in astrocytes[20]. Zinc is involved in numerous aspects of cellular metabolism. it is required for the catalytic activities of approximately 100 enzymes[21,22] and it plays a role in immune function[23,24], protein synthesis[24], wound healing[25],

DNA synthesis[22,24] and cell divisions[24] and is required for proper sense of taste and smell[26]. Although zinc is an essential requirement for good health, excess zinc can be harmful. Excessive absorption of zinc suppresses copper and iron absorption[27].

EXPERIMENTAL

The present study is conducted in those areas of Faisalabad which are either irrigated or not by industrial waste water but are close to the industrial drains in such a way that the waste water either passes through the fields or is directly pumped to the agricultural fields.

The sampling was done in the month of March 2008. Forty eight soil samples were collected from sixteen sites of Faisalabad in such away that three soil samples were collected from one site with the depth of 0-15, 15-30 and 30-45 cm (Table-1). The samples were collected in polythene bags with the complete labeling of temperature, date, humidity and weather conditions of the day.

The stones and gravels were removed from the soil samples. The soil samples were air dried in shade, ground with a wooden mortar and sieved through 2.0 and 0.5 mm nylon mesh size sieves. The samples were then tightly repacked in polythene bags and labeled again. The samples were preserved according to scientific method[28].

TABLE-1
CONCENTRATION OF Cd, Cr, Co, Cu, Mn, Ni, Pb, Zn AND Hg (mg/kg) IN THE SOIL SAMPLES COLLECTED FROM SELECTED AREAS OF FAISALABAD

S. No.	Sampling site	Sample No.	Depth (cm)	Cd	Cr	Cu	Mn	Ni	Pb	Zn	Hg
1	Khurrianwala (edge of the drain)	1-A	0-15	2.99	350	56.0	440	53.0	31.8	160	49.8
		1-B	15-30	1.95	340	60.0	410	53.0	28.9	200	25.8
		1-C	30-45	1.68	320	50.0	400	51.0	19.5	150	3.04
2	Khurrianwala (wheat field about ½ km away from drain)	2-A	0-15	0.37	400	30.0	265	40.0	17.2	70.0	3.04
		2-B	15-30	0.90	280	35.0	260	37.4	17.2	70.0	7.50
		2-C	30-45	0.11	270	33.0	251	38.4	17.2	60.0	7.50
3	Khurrianwala (edge of drain about 5 km away from sample No. 1)	3-A	0-15	1.68	440	80.0	420	52.9	23.0	130	7.50
		3-B	15-30	1.42	400	64.0	415	56.9	20.0	140	10.0
		3-C	30-45	1.42	340	40.0	360	43.2	20.0	90.0	10.0
4	Khurrianwala (wheat field beside the drain)	4-A	0-15	0.01	260	39.0	300	37.4	20.0	80.0	7.50
		4-B	15-30	0.01	310	35.0	320	43.2	17.2	80.0	10.0
		4-C	30-45	0.01	270	40.8	290	50.9	20.0	90.0	5.27
5	Satyana road industrial and domestic drain (edge of the drain)	5-A	0-15	3.25	270	60.0	350	52.9	20.0	110	10.0
		5-B	15-30	2.99	260	50.0	320	46.1	20.0	90.0	7.50
		5-C	30-45	3.51	250	43.0	300	40.3	20.0	70.0	5.27
6	Satyana road industrial and domestic drain (wheat field)	6-A	0-15	2.99	340	65.0	373	51.0	15.0	140	7.50
		6-B	15-30	2.45	320	50.0	400	76.0	25.0	110	7.50
		6-C	30-45	2.73	290	40.6	370	44.2	25.0	90.0	10.0
7	Mukkuana (edge of drain, coming out China Rice Mill)	7-A	0-15	3.25	300	50.0	335	48.0	17.2	90.0	7.50
		7-B	15-30	3.25	300	40.0	326	70.2	15.0	80.0	7.50
		7-C	30-45	2.73	340	39.0	350	57.7	26.0	90.0	7.50
8	Mukkuana (green chilly field irrigated by mill drain)	8-A	0-15	2.73	300	38.0	360	51.0	23.0	80.0	183
		8-B	15-30	3.78	270	1.30	355	43.2	32.0	70.0	136
		8-C	30-45	3.52	280	34.0	300	48.0	32.0	130	61.0
9	Surroundings of Kashmir Ghee Mill (Grassy field behind the mill)	9-A	0-15	3.25	350	70.0	430	36.9	32.0	130	47.64
		9-B	15-30	2.45	340	50.0	440	95.4	26.0	100	36.49
		9-C	30-45	2.99	350	60.0	460	55.8	21.0	90.0	14.2
10	Surroundings of Kashmir Ghee Mill (Behind the Mill)	10-A	0-15	3.25	290	110	300	1079	78.0	160	18.6
		10-B	15-30	3.51	310	100	352	671.7	60.6	155	14.2
		10-C	30-45	3.38	310	170	340	1129	69.6	170	11.9
11	Surroundings of Kashmir Ghee Mill (behind the Mill another corner)	11-A	0-15	2.45	300	65.0	390	63.8	29.0	100	11.9
		11-B	15-30	2.45	320	62.0	385	85.6	29.0	110	11.9
		11-C	30-45	2.73	340	52.0	425	56.7	26.0	90.0	11.9
12	Surroundings of Darja Awal Ghee Mill Sumandari Road (wheat field)	12-A	0-15	2.99	350	41.0	378	184.2	29.0	91.8	11.9
		12-B	15-30	2.45	320	39.0	425	50.2	26.0	82.7	10.0
		12-C	30-45	2.73	320	45.0	400	38.4	25.0	70.0	7.50
13	Surroundings of Darja Awal Ghee Mill Sumandari Road(wheat field in which mill waste water spills)	13-A	0-15	3.78	280	80.0	390	886.6	40.5	136	10.0
		13-B	15-30	2.99	300	43.0	290	210.4	31.8	98.0	10.0
		13-C	30-45	2.45	290	40.0	230	184.4	28.0	70.0	7.50
14	Surroundings of Darja Awal Ghee Mill Sumandari road (Chara field)	14-A	0-15	3.35	360	100	390	76.0	40.5	147	7.50
		14-B	15-30	3.35	350	41.0	400	51.0	31.8	82.0	7.50
		14-C	30-45	2.99	340	39.0	392	43.2	29.0	80.0	7.50
15	Chak No.79 J-B "jay-Pur" Dist. Faisalabad (field away from the industrial sector)	15-A	0-15	2.73	300	40.0	370	32.8	23.0	70.0	7.50
		15-B	15-30	2.45	310	35.6	371	32.8	20.0	67.8	7.50
		15-C	30-45	2.45	310	31.0	379	32.8	19.5	50.0	7.50
16	Chak No.73 G-B "Gaddian Bahatter" Dist. Faisalabad (Sugarcane field)	16-A	0-15	3.25	220	31.0	210	25.7	37.4	58.3	7.50
		16-B	15-30	4.56	330	43.0	297	37.6	37.6	126	5.23
		16-C	30-45	4.04	340	44.0	302	40.0	37.6	136	5.23

10 g of 2 mm sieved soil was taken in round bottom flask of 500 mL capacity. Added 30 mL of 50 % HCl and refluxed for 0.5 h on flame. Then cooled to room temperature and filtered by using Whattman No. 10 filter paper by applying negative pressure. Filtrate was collected in a 500 mL capacity beaker, labeled with sample number and residue was reentered into same flask and refluxed again for 0.5 h with 50 % HNO_3. It was again cooled at room temperature and filtered. The filtrate was added into the previous beaker in which HCl extract was added. The residue was again introduced into same round bottom flask and finally refluxed for 0.5 h with aqua-regia. It was filtered again and introduced into the previous beaker. The same process of extraction was applied to each sample. The volume of each extract, so obtained, was reduced to 10 mL under vacuum. It was diluted upto 100 mL with distilled water in 100 mL measuring flask.

All the metals in each sample were estimated with the help of atomic absorption spectrophotometer Perkin-Elemer Analyst-100 using aqua-regia extraction[29,30].

RESULTS AND DISCUSSION

Sample sites No. 2 and 4 were found within the permissible limits and all the other samples were found with higher concentration of cadmium than the permissible limit (Tables 1 and 2). In the top-soils (0-15 cm) the highest value (3.78 mg Kg^{-1}) of Cd was found in sample No. 13-A collected from the surroundings of Darja-Awal ghee mill (DAGM) on Sumundari road. This shows that cadmium may be used in the manufacturing process in some ghee mills. The highest value (4.56 mg Kg^{-1}) of cadmium in sub-soils (15-30 cm) and (4.04 mg Kg^{-1}) in sub soils (30-45 cm) was found in sample No. 16-B and 16-C, respectively, collected from a village named Gaddiya Bahater, 73 G.B. This village is miles away from the industrial sectors and its fields are irrigated by the canal water. The results were astonishing showing that some mills are discharging their effluents into the canals.

According to International Agricultural Soil Standards (Table-2), not a single sample was found within permissible limit with respect to chromium. All the samples have concentration more than 200 mg Kg^{-1} (Table-2). The higher concentration of chromium in soils sample No. 1, 2, 3 and 4 show that chromium can also be mobilized under basic conditions through the soil to the plants (As the pH test was also applied). The highest level of 440 mg Kg^{-1} in sample No. 3-A (at the edge of the drain) and other higher levels of 400 mg Kg^{-1} in sample No. 2-A (wheat field close to the drain but not irrigated by that) and 350 mg Kg^{-1} in sample No. 1-A (at the edge of the drain) and sample No. 9-A, 12-A and14-B (surroundings of DAGM), sites require serious attention.

Sample No. 10-A and 10-C (surroundings of Kashmir ghee mill) for copper (Cu) were found higher than permissible limit (Table-1). It is the property of copper that when it ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions.

According to International Agricultural Soil Standards (Table-2) not even a single soil sample was found within the permissible limit with respect to nickel. The unexpectedly higher concentrations of nickel in the sample No. 10, 12 and 13 were found which were collected from the surrounding area of ghee mills. Such a high level of nickel concentrations in these soil samples may be due to the excessive use of nickel as catalyst in the manufacturing process of the ghee.

All the soil samples were found to higher values of mercury than the permissible limit (1 mg Kg^{-1}). The higher values (183, 136 and 61 mg Kg^{-1}) in sample No. 8 (Table-1) may be due to the excessive use of pesticides and insecticides being used at that particular field, because later on, soil samples from the center of drain, which was irrigating this field, were also analyzed for mercury but normal levels of mercury were found in them. Urea samples were also analyzed for mercury which had been applied to that field but the results were negative. So it was concluded that only pesticides and insecticides are responsible for such a higher concentration of mercury at that particular field.

Lead, manganese and zinc were found within the permissible limits (Table-2) in all the soil samples. The comparatively

TABLE-2
RANGES AND AVERAGE VALUES OF Cd, Cr, Co, Cu, Mn, Zn, Pb, Ni AND Hg (mg/kg) EXTRACTED BY AQUA-REGIA. IN SOIL SAMPLES COLLECTED FROM SELECTED AREAS OF FAISALABAD

Metals	Top soil (0-15 cm)	Sub soil (15-30 cm)	Sub soil (30-45 cm)	Permissible limits (mg/kg) [Ref. 31]
Cadmium	0.01-3.78 (2.64)	0.01-4.56 (2.56)	0.01-4.04 (2.47)	1
Chromium	220-440 (319.38)	260-400 (316.25)	250-350 (310)	100
Copper	30 -110 (59.69)	1.3-100 (46.8)	31-170 (50.09)	100
Manganese	210-440 (356.31)	260-440 (360.38)	230-460 (346.81)	500
Nickel	25.7-1079.3 (173.2)	32.8-671.7 (103.79)	32.8-1129.13 (122.12)	20
Lead	15 -78 (29.78)	15 –60.6 (27.38)	17.2-69.6 (27.21)	500
Zinc	58.3-160 (109.57)	67.8-200 (103.84)	50-170 (95.38)	250
Mercury	3.04-183.6 (24.89)	5.24-136.8 (19.66)	3.04-61 (11.42)	1

higher values of lead in sample No. 10, 13 and 14 (collected from the surroundings of the ghee mills) show that lead may be used during processing in ghee mills.

Conclusion

The concentration of mercury, one hundred and eight two times higher than the permissible limits, in a farmer's vegetable garden require a serious attention and further opens paths for research. As the pesticides and insecticides were possibly found responsible for particular mercury contamination. All the soil samples were found within the permissible limits with respect to Mn, Zn and Pb. The extremely higher concentration of Ni and comparatively higher value of Pb in the soil samples collected from the surroundings of ghee mills show that these elements may be utilized in the manufac-turing process of ghee and are discharged without treatment into the environment. The drains are polluting the soils both directly and indirectly, pesticides and insecticides are also respon-sible for the soil pollution and ghee mills are adding nickel and lead to soil.

Recommendation

• Waste water from industries should be disposed off after suitable treatment. For this purpose a rule should be passed by government that big industrial sectors should establish their own waste water treatment plants and small industries should be grouped to establish combined waste water treatment plants. Any violation in this regard should be strictly dealt with.

• The drains should be under ground so that the farmers can't pump the waste water to their fields or the guidelines should be developed for the reuse of waste water.

• Drain channels should be lined to prevent the seepage of waste water from drains to the fields which are close to the drains.

• Those factories which dispose their waste water to the canals should be strictly dealt with.

REFERENCES

1. J.H. Duffus, *Pure Appl. Chem*., **74**, 793 (2002).
2. P.H. Roven, L.R. Berg and G.B. Johnson, Environment, Saunder College Publishing, Hartcourt Brace College Publishers, New York (1998).
3. M.B. McBridge, Environmental Chemistry of Soil, Oxford University Press, New York (1994).
4. H.A. Harper, V.W. Rodwell and P.A. Mayes, Drinking Water and Health, National academy press, Washington D.C., edn. 16, vol. 3, pp. 67-266 (1977).
5. National Toxicology, 11th Report on Carcinogens, Retrieved 21/04 (2008).
6. L. Friberge, M. Piscator, G.F. Nordberg and T. Kjellstorm, In Cadmium in the Environment, CRC Press Inc., Cleveland, Ohio (1974).
7. E.W.D. Huffman Jr. and H.W. Allaway, *J. Agric. Food Chem*., **21**, 982 (1973).
8. W. Mertz, *J. Nutr*, **123**, 626 (1993).
9. ATSDR. ToxFAQs: Chromium, Agency for Toxic Substances & Disease Registry, Centers for Disease Control and Prevention. http://www.atsdr.cdc.gov/tfacts7.html [Accessed 02/10/2007] (2001).
10. N.W. Lepp, Effects of Trace Metals on Plant Function, Applied Science Publishers, London. Ch. 4, vol. 1 (1981).
11. K.G. Tiller and R.H. Merry, in ed.: J.F. Loneragan, Copper in Soils and Plants, Academic Press, Sydney, Ch. 6 (1981).
12. I.M. Zai, N. Khan, M.J. Khan and R.A. Khattak, *J. Chem. Soc. Pak*., **23**, 23 (2001).
13. N. Mizuno, *Nature*, **912**, 1271 (1968).
14. J.C. Elifton, *J. Pediatr. Clin. North Am*., **54**, 237 (2007).
15. W.D. James, T.G. Berger and D.M. Elston, Andrews' Diseases of the Skin: Clinical Dermatology, Saunders, edn. 10, p. 134 (2006).
16. M.J. Ahmed and M. A. Mamun, *Talanta*, **55**, 43 (2001).
17. M. Younas, F. Shahzad, S. Afzal, M.I. and K. Ali, *Pak. J. Sci. Int*., **24**, 761 (1998).
18. J.E. Fergusson, The Heavy Elements Chemistry, Environmental Impact and Health effects. Pergamum Press, New York (1990).
19. Emsley and John, Manganese, Nature's Building Blocks: An A- Z Guide to the Elements, Oxford University Press, Oxford, UK, pp. 249-253 (2001).
20. A. Takeda, *Brain Res. Rev*., **41**, 79 (2003).
21. H.H. Sandstead, *J. Lab. Clin. Med*.., **124**, 322 (1994).
22. IMFNB, Institute of Medicine, Food and Nutrition Board, Dietary Reference Intake for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium and Zinc, National Academy press, Washington, DC (2001).
23. N.W. Solomons, *Nutr. Rev*., **56**, 27 (1998).
24. A.S. Prasad, *Proc. Ass. Am. Phys*., **11**, 39 (1995).
25. C.A. Heyneman, *J. Annals Pharmacother*., **30**, 186 (1996).
26. A.S. Prasad, F.W. Beck, S.M. Grabowski, J. Kplan and R.H. Mathog, *Proc. Ass. Am. Phys*., **109**, 68 (1997).
27. G.J. Fosmire, *Am. J. Clin. Nutr.*, **51**, 225 (1990).
28. K.G. Saeed and Muhammad Rafiq, Technical Guide for Chemical analysis of Soil and Water, Bulletin No. 14, Government of Pakistan Ministry of Food and Agriculture, Soil Survey of Pakistan, Lahore (1980).
29. B. Zarconas, M. McLaughlin and G. Cozen, *Environ. Geochem. Health*, **26**, 343 (2004).
30. Z. Zarconas, Bernhard, C. Ishak, M. McLaughlin and G. Cozen, *Environ. Geochem. Health*, **26**, 359 (2004).
31. B.J. Alloway, Heavy Metals in Soils, Blackie Glasgow London, John Wiley & Sons, Inc. New York (1990).