J. Appl. Environ. Biol. Sci., **1(10)464-469, 2011**

ISSN: 2090-4215
Journal of Applied Environmental and Biological Sciences
www.textroad.com

Cr, Pb and Hg Contamination on Agricultural Soil and Paddy Grain after Irrigation Using Metropolitan Sewage Effluent

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ABSTRACT

The degree of heavy metal (Cr, Pb and Hg) contamination in the paddy fields utilizing the sewage effluent of Kolkata metropolitan city, near East Kolkata Wetland, India, along with the irrigation water and paddy grains were investigated in 2010 and 2011. The nutrient concentration, pH and electrical conductivity status during the sowing time was also monitored. Though the pH of the irrigation water was found suitable in all instances but the electrical conductivity values were observed to be inappropriate in 4 sites. Hg was found beyond the permissible limit in the water used for irrigation as well as paddy soils of all the study sites. Evaluation of enrichment ratio revealed alarming Hg contamination in two sites out of six sites studied. Enrichment ratio values of Pb were moderately high in four sites exhibiting polluting effect. The geo-accumulation index calculated was found to support similar observations. Cr in water and soil samples was found within the threshold limit, but in the paddy grain it was found beyond the maximum allowable limit. Hg and Pb, however, were found below detection level in all the rice samples. Pollution load index was estimated in all the sites and it varied from 0.860 to 1.827. Virtually no polluting activity was found in the samples obtained from control stations situated far away from the effluent source, where irrigation is primarily done using groundwater.

Keywords: Heavy metal contamination; Enrichment ratio; Geo-accumulation index; pollution load index; Boro rice cultivation; dry season.

INTRODUCTION

Environmental pollution of agricultural fields as a result of heavy metal toxicity has begun to cause a world-wide concern. The untreated but nutrient rich sewage waters from various metropolitan cities are effectively used for the irrigation purpose. This acts as a cheap and cost effective natural treatment to get reed of polluted waters without any investment as such, before it enters the river system [1]. Rapid urbanization and industrialization, with improper environmental planning often lead to discharge of unwanted substances into natural water bodies [2]. These effluents from the unregulated industrial units like tanneries, battery production houses may pose considerable threat to the natural purifying systems [3].

Mobilization of heavy metals in the environment due to industrial activities is of serious concern due to the toxicity exhibited by these metals in human and other forms of life [4]. The heavy metals cannot be degraded biologically and they get deposited in the agricultural soil and eventually get concentrated in the plant tissues and fish bodies [5]. Human beings are exposed to severe risk of heavy metal pollution due to intake of foods grown on polluted soils. Heavy metals like Lead (Pb), Chromium (Cr) and mercury (Hg) can pose risks to human health and ecosystem [6]. The contamination of heavy metals like Pb, Cr and Hg in the agricultural soil and eventually in the paddy crops has been reported from various parts of the world. Almost a decade ago, Jung and Thorton [7] detected heavy metals incorporation in paddy soils and grains due to mining activity in Korea. Similar observations were made by Simmons et al. [8] in Thailand, Liu et al [9] in the Zhengzhou City, China and Tsukada et al [10] in Aomori, Japan.

Previously Mitra and Gupta [11] conducted a similar study on the effect of sewage water used for irrigation in the same geographical realm as that of our study site, but the emphasis was on the soil of vegetable cultivation. In this paper we have carried out a comprehensive study of the toxic heavy metals like Cr, Pb and Hg in the canal water used for irrigation, agricultural soil and paddy grain. Apart from the inspection of heavy metals, pH, electrical conductivity and nutrient availability in the canal water and that in the paddy field were also examined separately.

MATERIALS AND METHODS

Study site

The present study site comprises the paddy fields around East Kolkata Wetland (EKW), lying between latitudes 20° 25′ to 22° 35′ North and longitudes 88° 20′ to 88° 35′ East, in West Bengal state, India. It has been designated as a

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Ramsar site on August 19, 2002. It processes the city's waste—both garbage and sewage through two major canals, Dry weather flow (DWF) and Storm weather flow (SWF) which meets Kulti (Bidyadhari) river. The paddy fields in this zone harvests rice twice a year. During monsoon it utilizes the rain water, whereas the 'Boro' rice cultivation is generally carried out using the easily available sewage effluent.

Sampling stations

Six sites were chosen (Fig 1) for the collection of water, soil and paddy grain samples namely Kantatola (North) (22º 30′ 48.6″, 88º 30′ 9.2″) (SS1), Karaidanga (22º 30′32.2″, 88º 31′32.6″) (SS2), Kulbaria (22º 33′15.9″, 88º 30′ 4.3″) (SS3), Narayanpur (22º 29′48.7″, 88º 34′32.1″) (SS4), Babupara (22º 30′30.4″, 88º 29′ 58″) (SS5)and Ghoshpur (22º 30′57.1″, 88º 39′49.3″) (SS6). Two control stations were selected namely Bali (22º 9′48.6″, 88º 47′53.9″) (CS1) and Jharkhali (22º 1′38.2″, 88º 41′20.3″) (CS2), situated far away from the effluent source and exclusively irrigated with ground water. Sampling in all the stations were done in two consecutive years of 2010 and 2011.

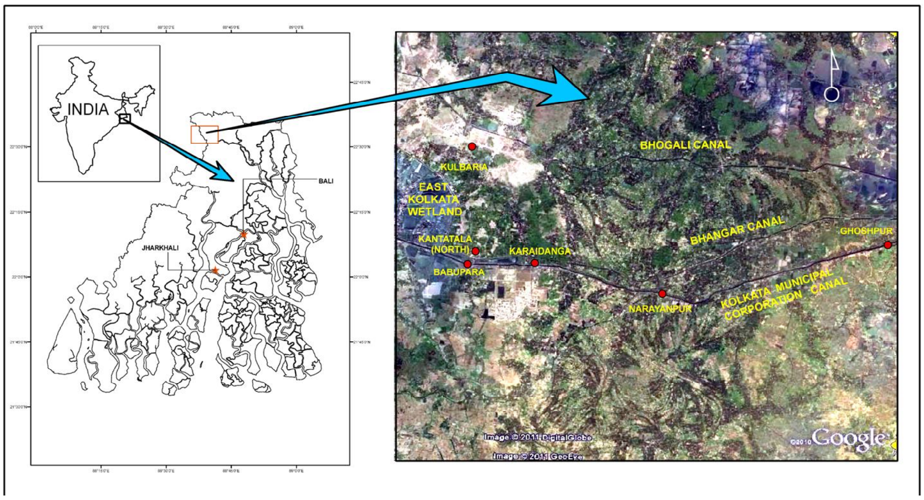

Fig 1 Study site showing the sampling and control stations

Sampling procedure

Water samples were collected from the mouth of the irrigation canals and from the agricultural field. A total of 5 grab water samples were collected from each site and stored in washed plastic containers. The samples were preserved with 4 ml concentrated nitric acid and stored in freezer at about 4^oC so as to prevent adsorption and precipitation of metals. The stored samples were sent back and processed in laboratory within 24 hours of sampling. Random soil samples were collected from the surface level (0-20 cm) at various points of each agricultural site in which rice cultivation is done. Paddy grain samples were also collected in the same fashion at the time of harvesting. In each site 10 random samples of ~ 1 gm paddy grain were collected.

Analysis

pH, conductivity and temperature of water used for irrigation were measured on spot with the help of a Multikit, WTW Multi 340i Set (made in Germany) using the probe WTW Tetracon 325 (for water surface temperature & conductivity) and WTW Sentix 41-3 (for pH). Heavy metals Cr, Pb and Hg of soil and water samples along with dissolved inorganic nitrate (DIN), dissolved inorganic phosphate (DIP) and potassium content in water samples were analyzed [12]. Additionally Fe in soil samples was measured in each site in order to investigate the Enrichment ratio. The available NPK of the soils were analyzed following the standard methods [13]. The heavy metal concentration of the paddy grains were measured following the methods of Schumacher et al [14]. The heavy metals of water samples were determined by Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES. Model no. ICAP6300DUO (THERMO)) and that of soil and paddy grains were analyzed by Atomic Absorption Spectrophotometer (model no. AA50 –VARIAN). A minimum of 5 replicate samples in case of all parameters were analyzed. The two-year mean values along with the standard deviations were considered in tabulating all the data presented below.

Computation of pollution indices

Enrichment Ratio (ER) [15] was analyzed according to the expression ER = $(C_n/Fe)_{sample}/(C_n/Fe)_{background}$, where C_n stands for concentration of the metal 'n'. The background value denotes the world surface rock average [16]. Pollution load index (PLI) of each site has been calculated using the formulae PLI = $(CF_1 \times CF_2 \times \ldots\ldots\ldots \times CF_n)^{1/n}$, where CF stands for contamination factor of each metal studied [17]. The geo-accumulation index (I_{geo}) was evaluated according to the expression $I_{geo} = \log_2[C_n/1.5B_n]$, where C_n represents concentration of metal 'n', and B_n denotes its geochemical background value [18].

RESULTS AND DISCUSSION

Table 1 shows the electrical conductivity, pH, water temperature, nutrient availability and heavy metal concentration in the water samples collected from the respective irrigation canals carrying water to the agricultural fields. The mean concentrations of Cr and Pb (mg l^{-1}) in the irrigation canals were well below the maximum permissible limit (MPL) of 2.0 mg l^{-1} and 1.0 mg l^{-1} respectively as per the standards posed by Central Pollution Control Board (CPCB) of India. The Cr concentrations varied from 0.003±0.001 to 0.074±0.01 mg l^{-1}. In site SS3, it was found below detection level. The Pb concentrations varied from 0.004±0.001 to 0.01±0.005 mg l^{-1}. Hg concentrations were found to have a much higher value than the MPL of 0.01 mg l^{-1} (CPCB), with a maximum value of 0.98 mg l^{-1} in SS4. 4 out of 6 stations were having high Hg level (beyond MPL) in canal water used for irrigation. The hierarchy of heavy metals in SS1, SS2 and SS3 followed the trend Hg>Pb>Cr, and in SS4, SS5 and SS6 it was found Hg>Cr>Pb. The pH of irrigation water should usually be within the range of 6.5 to 8.0 [19]. These levels enhance the solubility of most micronutrients and avoid a steady increase in the pH of the growing medium. This pH range also optimizes the solubility of nutrients in concentrated fertilizer stock solutions. The pH values in all the stations were well with in the limit and ranged between 6.79±0.10 to 7.90±0.09. The electrical conductivity values were beyond permissible range [19] in SS3 and SS4 and found absolutely unsuitable in SS5 and SS6. Irrigation of fields having high EC values inhibit plant growth due to two prime reasons, firstly it trims down the ability of the plant to take up water due to the osmotic effect and secondly it blocks the transpiration activity [20]. The nutrient availability on the other hand was found suitable from all perspectives. The NO_3-N concentrations in 5 out of 6 stations were in the 'slight to moderate' range (5-30 mg l^{-1}) as prescribed by FAO [19]. In the site SS4, it was marginally beyond the threshold of >30 mg l^{-1}. The PO_4-P concentrations ranged from 0.076±0.03 to 1.23±0.21 mg l^{-1}, which lied with in the usual range of 0-2 mg l^{-1}. The potassium ion content surpassed the usual range of 0-2 mg l^{-1} in all the sites, but the maximum allowable limit of K+ is 210 ppm [19] which is not crossed in any of the sites. The potassium ion content varied from 11.56±1.46 to 48.2±0.91 mg l^{-1}.

Table 1 Mean ± S.D of EC, pH, nutrients and metal concentration (mg/l) in the water samples of irrigation canals

Sampling sites	SS1	SS2	SS3	SS4	SS5	SS6
EC(µS/cm)	1567±113	1117±216	1891±24	2180±123	1653±101	6950±256
pH	7.90±0.09	7.18±0.05	7.18±0.06	7.09±0.02	6.79±0.10	7.49±0.05
Temp °C	35.4±0.81	35.5±0.46	34.9±1.24	22.4±0.87	24.0±0.42	22.2±1.44
N (mg/l)	11.44±2.32	20.32±1.93	19.01±2.56	30.4±3.42	22.7±0.56	14.6±1.62
P (mg/l)	1.23±0.21	0.095±0.01	0.076±0.03	0.23±0.02	0.27±0.01	0.13±0.01
K (mg/l)	16.7±1.55	19.26±2.16	11.56±1.46	15.4±1.33	14.0±0.59	48.2±0.91
Cr (mg/l)	0.003±0.001	0.005±0.002	BDL	0.39±0.09	0.074±0.01	0.021±0.008
Pb (mg/l)	0.01±0.005	0.01±0.004	0.01±0.005	0.006±0.003	0.006±0.002	0.004±0.001
Hg (mg/l)	0.0075±0.002	0.0038±0.001	0.05±0.01	0.098±0.03	0.018±0.005	0.096±0.03

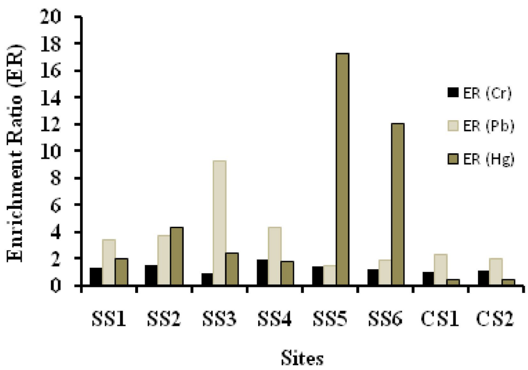

Fig 2 Enrichment ratios (ER) of heavy metals in study sites (SS) and control stations (CS)

Table 2 displays the same parameters as that of Table 1 in water samples collected from agricultural field. The analysis in agricultural field water was carried out with an intention to see whether there happens to be any dissipation in concentration in the pathway from the canal mouth to the agricultural fields. The heavy metal concentration in every site was found below than that observed in the respective canals. The range of Cr and Pb concentrations reduced to 0.002±0.001 to 0.014±0.007 and 0.004±0.001 to 0.0075±0.006 mg l^{-1} respectively. An overall decrease in the Hg concentration was also observed but even then it was beyond the threshold value. The pH values in this water were also found within the threshold, only in site SS5 it was 8.65±0.07, which is not fit for irrigation purpose. The electrical conductivity values increased by a huge margin in all the sites, possibly due to enhanced rate of evapo-transpiration in the fields leading to intolerable values like 4700±219 and 7550±541 µS/cm in SS5 and SS6. The nutrient concentration almost remained the same as that found in the canal water, with no noticeable depleting or increasing trend.

Table 2 Mean ± S.D of EC, pH, nutrients and metal concentration (mg/l) in the water samples collected from the paddy fields

Sampling sites	SS1	SS2	SS3	SS4	SS5	SS6
EC(µS/cm)	1706±223	1760±116	2700±149	2790±334	4700±219	7550±541
pH	7.30±0.06	7.93±0.09	7.50±0.19	7.54±0.01	8.65±0.07	7.87±0.01
Temp °C	35.6±0.71	36.5±0.55	35.6±0.49	30.5±1.46	30.2±0.78	30.4±0.63
N (mg/l)	28.9±0.29	12.75±1.26	25.13±0.49	19.09±0.97	8.89±1.23	6.27±1.73
P (mg/l)	0.11±0.03	0.34±0.11	0.087±0.02	2.06±0.09	0.64±0.24	0.71±0.15
K (mg/l)	11.82±1.95	17.98±2.22	9.25±4.23	16.22±1.47	16.61±1.32	30.33±1.29
Cr (mg/l)	BDL	0.003±0.001	0.003±0.001	0.014±0.007	0.002±0.001	0.002±0.001
Pb (mg/l)	0.005±0.003	0.0075±0.004	0.0075±0.006	0.006±0.003	0.004±0.001	0.004±0.002
Hg (mg/l)	0.01±0.003	0.0125±0.004	0.015±0.006	0.022±0.009	0.04±0.007	0.014±0.006

The soil analysis data (Table 3) show Cr and Pb concentration were well below the MPL of 300 mg/kg and 400 mg/kg respectively, with highest value of Cr concentration (105.2 mg/kg) in SS5 and Pb concentration (79.7 mg/kg) in SS3. The Hg concentrations in the soil samples of three stations were quite higher than the MPL of 1.0 mg/kg [21]. SS2, SS6 and SS5 have concentrations 1.68, 4.52 and 9.65 mg/kg respectively. SS5 had an alarming concentration, almost ten times greater than the maximum permissible limit. The hierarchy of heavy metals in terms of concentration followed the trend Cr>Pb>Hg in all the sites, only in SS3 it was Pb>Cr>Hg. Unlike the EC values of water the soil EC values were found within the threshold, and ranged between 0.337±0.07 to 0.930±0.22 mS/cm. A wide range of soil pH 4.5-8.2 is suitable for rice cultivation [22], which was fulfilled by the soils of every site. The soil was found enriched with nutrients (N, P, K). An average N: P: K ratio of 9:1:8 was observed in the agricultural sites.

Table 3: Mean ± S.D of EC, pH, nutrients and metal concentration (mg/kg) of soil samples from the agricultural land

Places	SS1	SS2	SS3	SS4	SS5	SS6	CS1	CS2
EC(mS/cm)	0.396±0.12	0.432±0.19	0.337±0.07	0.362±0.09	0.930±0.22	0.851±0.13	1.141±0.23	0.510±0.04
pH	7.26±0.21	7.81±0.11	6.92±0.05	7.77±0.06	7.57±0.12	6.7±0.16	5.43±0.03	5.41±0.08
N (mg/kg)	383.1±11.2	237.8±22.7	241.3±15.1	220.0±31.0	29.3±2.35	212.0±19.6	208.0±12.1	240.0±4.56
P (mg/kg)	40±2.53	27.6±4.57	19.6±5.99	65.0±1.26	8.7±4.66	19.1±3.49	29.3±7.55	16.8±4.29
K (mg/kg)	305±22.3	267.5±45.2	212.5±33.4	130±29.8	350±19.4	168±16.5	240.0±34.2	260.0±46.2
Cr (mg/kg)	65.9±8.5	76.4±4.9	40.2±6.7	83.0±21.5	105.2±11.8	61.5±2.2	55.6±5.27	62.3±14.3
Pb (mg/kg)	35.8±2.3	38.5±3.4	79.7±8.5	37.9±6.7	21.4±1.7	18.9±4.6	25.5±5.9	23.0±2.8
Hg (mg/kg)	0.79±0.09	1.68±0.28	0.76±0.11	0.58±0.07	9.65±0.24	4.52±0.35	0.19±0.07	0.21±0.04

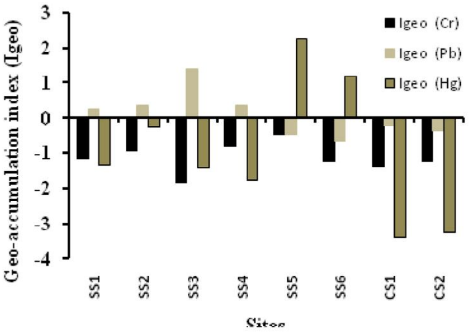

Fig 3 Geo-accumulation indices (I_{geo}) of heavy metals in study sites (SS) and control stations (CS)

Fe is considered as a normalization element while estimating the enrichment ratio, as it has a controlling influence on heavy metal distribution [23]. The more the ER values, the more is the polluting or enriching effect. ER values of Cr exhibits mild enrichment (>1) in all the stations except SS3, where a depleting trend (<1) is observed (Fig 2). Pb has shown fairly high (>3) ER values in 4 stations out of 6, SS3 marking the highest (9.269). The control stations have also showed a high ER value for Pb, which signifies, its enrichment cannot be ascertained due to canal effluent. The ER values of Hg revealed similar trends as that of Pb, but intense contamination (>10) was observed in SS5 and SS6. The pollution load index was evaluated in order to estimate the overall polluting activity in a particular area. Lower PLI values imply lesser anthropogenic effect and vice versa. The evaluated PLI values supported the maximum polluting activity in SS5 (1.827) and the least was observed in SS3 (0.860) (Fig 3). The geo-accumulation index (I_{geo}) scale consists of seven grades (0-6) ranging from unpolluted to highly polluted. The I_{geo} values for Cr show negligible contamination in all the sites, whereas in SS3 mild contamination of Pb is observed. SS5 and SS6 have fairly high I_{geo} values for Hg (Fig 4).

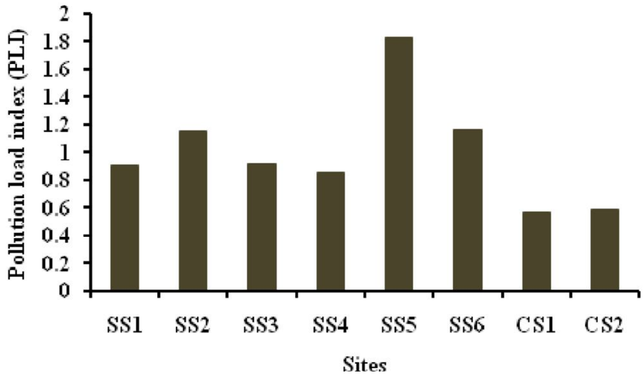

Fig 4 Pollution load index (PLI) in study sites (SS) and control stations (CS)

Pb and Hg in all the paddy grain samples including the control were found below detection limit (0.5 mg/kg for Pb, 0.05 mg/kg for Hg), whereas Cr in all the stations were found higher than the recommended limit (0.1 mg/kg) of FAO (1985). Paddy grain samples of SS1, SS2, SS3, SS4, SS5 and SS6 had Cr concentration of 0.91, 0.55, 0.43, 0.78, 0.51 and 0.93 mg/kg respectively. The control samples had Cr concentration below detection limit (0.1 mg/kg).

Conclusion

From the data obtained, we can conclude that amongst the three heavy metals analyzed the sewage effluent is primarily increasing the Hg concentrations in the agricultural soil, but the paddy grain is not yet infected by it. The electrical conductivity (EC) values in water samples are also beyond the permissible limit to such an extent which is not at all fit for agricultural purpose. Though Cr is found well within the threshold limit in both water and paddy soil, it is found in substantial amount in the paddy grains, which may in future act as detrimental to human and animal health. Out of all the stations studied irrigation waters and cultivable soil condition of SS5 is of severe concern.

Acknowledgement

Authors are grateful to Prof. Gautam Gupta and Dr. Vivekananda Mukherjee, Department of economics, Jadavpur University, for their valuable guidance.

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