



ECOTOXICOLOGICAL STUDIES ON THE BIOACCUMULATION OF THE HEAVY METALS IN THE VELLORE POPULATION, TAMILNADU, INDIA

R. Vidya*, N. Chandrasekaran

School of Biosciences and Technology, VIT University, Vellore-632014, Tamilnadu, India

Abstract

The study was totally aimed to know the extent of bioaccumulation through the plants from the sediments. Total heavy metals concentration (chromium, lead, zinc, nickel and cadmium) were undertaken in the food composites collected from Puliyanthangal village near Ranipet of Vellore district, Tamilnadu, India. There are around 240 tanneries in these areas, besides number of ceramic, refractory, boiler auxiliaries plant and chromium chemical factories. Since the ground water was heavily contaminated with heavy metals, studies were carried out to know if there was transfer of heavy metals in the food chain. Drinking water samples, sediment samples as well as food samples were collected and analysed for Chromium, Lead, Nickel, Zinc and Cadmium levels. The Environmental risk assessment was undertaken in the foodchain for all the above metals through water, sediment and through the grains and the crops grown in that area. Bioaccumulation factor was calculated with respect to the above parameters and it was concluded that the heavy metals were found to be concentrated through the various levels of food chain but not biomagnified through the food chain.

Key Words: Heavy metals; Bioaccumulation factor; Duplicate diet survey; Vellore District.

Introduction

Vellore district, Tamilnadu, India is highly polluted place due to tannery industries apart from chrome chemicals, refractories, ceramic, and other chemical industries which release heavy metals into the environment (Gowd and Govil, 2008). There are 230-240 tanneries in and around Vellore district. Vellore district lies between 12° and 13° 15' of Northern latitude and 78° 20' and 79° 50' of Eastern longitude. It slopes from East to West and the land in Eastern part is flat. Vaniyambadi, Ambur, Pernambattu, Melvisharum, Ranipettai, are municipal towns of Vellore district. As per 2001 census population of each of these towns is 103,841; 99,855; 41,323; 36,675 respectively, with 138 tanneries in Vaniyambadi, 83 tanneries in Ambur, 18 tanneries in Pernambattu, and 39 tanneries in Ranipettai (Data from French Institute Pondicherry). Number of unorganized tanneries is coming up day by day; therefore these numbers may not reflect the exact. Our study was confined to Ranipet and Ambur areas. Our study focused on the concentrations of heavy metals Zn, Cr, Ni, Cd, and Pb in sediment, water and duplicate food samples of the population of Ranipet and Ambur. Leather processing involves several chemical process. Therefore the resultant tannery effluent is found to be highly concentrated with heavy metals. When these tannery effluents percolate the ground water, it gets contaminated. Ground water is the major source of irrigation in these areas throughout the

year (Gowd and Govil, 2008). Heavy metals concentration in the ground water and surface water of Ranipet was in the higher limit compared to WHO permissible limit of heavy metals in drinking water. Human population in this area are seriously affected from occupational diseases such as asthma, Chromium ulcers and skin diseases (Gowd and Govil, 2008).

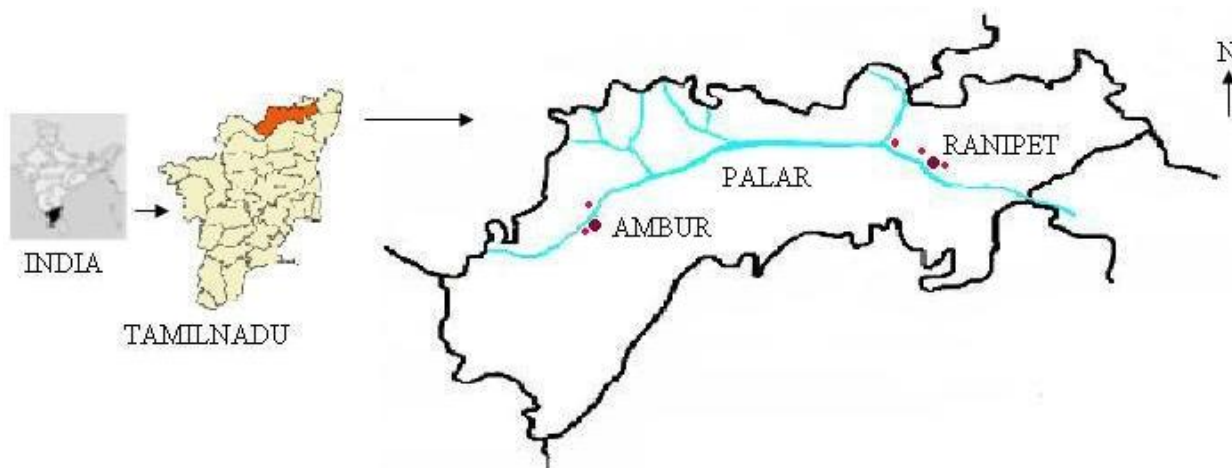
The aim of our study is to study the heavy metals concentrations in the sediment and also in the foodgrains and to determine the bioaccumulation as well as the biomagnification of the heavy metals through the environment. This study will throw light on the Environmental risk assessment on the population because of the tannery pollution.

Materials and Methods

Description of the sample site

The selected site namely Puliyanthangal lake near Ranipet of the Vellore district (earlier North Arcot district) India is a lake where the industrial effluents are let into the lake. Ranipet is not only known for leather tanneries but also for dyeing, electroplating industries and also for agricultural and the domestic wastes. (Raman and Sambandan 1998). One site of tannery effluent polluted soils were selected. The site namely Puliyanthangal village in the Ranipet Block was selected to know the Environmental risk exposure of the population.

* Corresponding Author, Email: rvidya@vit.ac.in



VELLORE DISTRICT WITH PALAR AND THE STUDY AREA

Sample Collection And Preparation

Food Samples were collected from farm families . The food samples were collected from the agricultural land and they were found to be cultivated in the same place.

The water samples were collected from deep tubewells and borewells The water samples were stored in polyethylene bottles prewashed with con. nitric acid, and after collection, Nitric acid was added as preservative.

The sediment samples were collected from the cultivated fields, using a plastic spatula, collected in a polyethylene cover, transported to the lab, dried in hot air oven at 50°C, until complete dryness is being achieved, powdered using pestle and mortar and sieved. Based on the water and sediment heavy metal level the food samples were collected from the farmlands. The paddy, pulses, oilseeds and the vegetables were irrigated with contaminated ground water. Some raw samples were collected from the farmland directly. Some raw samples were collected from the farm house where the stored food is available. After collection of samples the raw grain samples were packed and transported to the lab were dried in open air in shade followed by hot air oven drying at 50°C for complete dryness, Then they were manually transported. All the vegetables were cut into pieces were air dried, followed by hot air oven drying at 50°C allowed for complete dryness, powderd using homogenizer, sieved through a sieve. The uncooked rice, cereals, pulses were washed with deionised milli Q water, dried and powdered using homogenizer and sieved using a sieve.

Instrumentation and Sample Analysis

The microwave digestion system MARS from CEM Corporation with a rotor for digestion vessels was

used for sample digestion. Teflon vessels were used for digestion. The pressure was maintained upto 350 psi and the temperature upto 210°C. Seven samples were digested along with a control to know the recovery. The sediment samples along with the food samples were digested. The digester had 8 vessels.

Digestion Procedure

0.5g of (dry), finely powdered sample was weighed accurately into a dry, clean teflon digestion vessel. To the sample, 3ml of con. nitric acid, 2ml of hydrogen peroxide and 2ml of milli-Q water, were added. Then the Teflon vessels were closed and tightened. Eight vessels were placed together at each time in the microwave oven. After 45 min the vessels are opened slowly and allowed to release the pressure slowly.

Each digested solution was transferred quantitatively to a 25-ml volumetric flask and made up with Millipore water. Finally it was filtered with a whatman No.1 filter paper and preserved for analysis. The standard reference materials, blank and the spiked samples were digested under the same conditions. Digestion procedure for the digester was similar as it was followed by Roychowdhury et.al (2002).

Instrumentation with ICP-OES

The digested samples were analysed with Perkin Elmer precisely Optical Emission Spectrometer (ICP-OES) Optima 5300 DV. The instrument sensitivity was checked by spiking known levels of standards of 0.2ppm, 1ppm and 2ppm levels to the milli-Q water sample. The recovery was of high percentage of 90%. The Detection Limits for the Instrument ICPOES is as below:

Element	Detection Limits
Chromium	0.1-1ppb
Lead	1-10ppb
Zinc	0.1-1 ppb
Nickel	0.1-1ppb
Copper	0.1-1ppb
Cadmium	<0.1ppb

Chemicals and Reagents

All the reagents and chemicals used were of Analytical grade. Nitric acid, Hydrogen Peroxide were of high purity standard. The stock solutions and standards used for standardization are of Merks standards ICP multi element standard. Initially the stock solutions were of 1000mg/lit. Later on an intermediate stock solution of 100mg/lit was prepared. From this aliquots of 1ppm, 2ppm, 5ppm, 10ppm etc. were prepared and analysis was carried out.

Tomato leaves (SRM 1573a), was got from National Institute of Standards and Technology (NIST), (Gaithersburg, MD, USA), Riceflour (SRM 1568a), wheat flour (SRM 1567a) from National Bureau of Standards, (Gaithersburg, MD, USA) were used as SRMs (Joaquin soil (SRM2709), non fat milk powder (SRM 1549).

Bio-accumulation factor (BAF)

Bioaccumulation

Terrestrial rates of uptake of contaminants from the environment (Melwani, 2009)

Bioaccumulation, the net increase of a chemical by an organism because of uptake from all environmental sources, is frequently modelled using bioaccumulation factors (BAFs) and biota-sediment accumulation factors (BSAFs). Bioaccumulation factors are the ratio of biota to sediment contamination concentration - $BAF = C_t/C_s$ where C_t is the tissue concentration, C_s is the sediment concentration.

BAF = soil-to-plant bioaccumulation factor for prey (kg soil/kg tissue). Bioaccumulation refers to the uptake via all the exposure routes including food, sediment as well as water (Richard et.al 2008). Similarly BSAF refers to the concentration in the biota to the concentration in the sediment. The extent of chemical bioaccumulation from the sediment is typically expressed using either a BAF or a biota-sediment accumulation factor.(BSAF).The sediment BAF is the

ratio of chemical concentration in the fish to the chemical concentration in the sediment. Values greater than 1 are often interpreted as evidence for biomagnifications of chemical residues coupled with little or no biotransformation. Values less than 1 have been attributed to biotransformation. $BAF_{plant} = \text{soil to plant bioaccumulation factor (mg/kg dry plant per mg/kg dry soil)}$ as per SADA (Spatial Analysis and Decision Assistance) calculations. In our study the BAF as well as BSAF in respect to bioaccumulation of heavy metals from ground water to plant parts as well as sediment to plant parts is determined by the above formulae.

Biomagnification

As tissue concentrations of accumulated chemical compounds are passed up trophic levels, the tissue residue concentrations increase systematically as trophic level increases.(critical review of soil criteria methods,1999).

Biomagnification factor (Richard et.al 2008) is a unitless factor by which the concentration of a substance in an organism at one trophic level exceeds the concentration in organisms that occupy the next trophic level. The extent of biomagnification is defined using a BMF which is the lipid normalized chemical concentration in a predator divided by that of its prey. For a given trophic transfer step, a compound is said to biomagnify when the BMF is greater than 1. Within a simple food chain BMFs for each trophic transfer step it can be multiplied. Based on the above discussions we calculate the BAF plant or BCF= soil to plant bioaccumulation factor = C_t/C_s where C_t is the plant tissue concentration, C_s is the sediment concentration, BCF- bioconcentration factor.

Results and Discussions

Heavy metals in water and sediments (Tables 1 and 2).

The average concentration, permissible limits (BIS 1991 and USEPA 2003) for the water samples are presented in the Table 1. From the results, all the five heavy metals are present in the water samples. In the water samples Cr, Ni, Zn and Pb are above the USEPA permissible limits. The other heavy metals are below the permissible limits mentioned. The Cadmium level was negligible. The sediments had a higher level of Cr, Ni, Zn and Pb when compared to EC (2000) limit. The Cd level in the sediments was lower than the permissible levels. Due to the discharge of tannery wastes into the fresh water sources, the accumulation

of heavy metals in the ground water occurs. Dumping of tannery wastes also leads to leaching of heavy metals in the ground water and also to the surface soils. Cultivation of crops in the polluted soils and the irrigation using polluted ground water with a high concentration of heavy metals naturally causes the entry of heavy metals into the food chain. Gowd and Govil (2008) have reported a high concentration of heavy metals in the ground water in Ranipet and has also confirmed that due to the anthropogenic activity the heavy metals are released into the ground water.

Table 1. Heavy metal concentration in sediments mg/kg Puliyanthangal Site - Ranipet n=5					
	Cr	Ni	Zn	Pb	Cd
EC (2000) Maximum Permissible Limit	60	50	150	70	1
Range	197-523	63-220	200-372	47-117	0.02-0.32
Minimum	197.2	63.58	200.5	47.52	0.02
Maximum	523.2	220.76	372.3	117.3	0.32
Mean	351.5	129.1	277.7	83.1	0.108
SD	136.1	62.6	68.6	31.59	0.12

Table 2: Puliyanthangal lake n=11 Heavy metal concentration in water samples					
	Cr	Ni	Zn	Pb	Cd
Mean	0.225	0.072	2.84	0.772	0.0035
Max value	0.315	0.175	8.53	2.3125	0.0105
Min value	0.01	0.0016	0.013	0.0022	nd
BIS(1991)-Bureau of Indian Standards	0.05	-	0.3	0.05	0.01
Threshold value: Maximum permissible concentration as defined by USEPA (2003).	0.05	0.02	0.3	0.01	0.01

Table 3	Calculation of BSAF from sediments to food crops				
sediments to food crops	Site: Puliyanthangal-Ranipet				
	Cr	Ni	Zn	Pb	Cd
BAF in Rice	0.001	0.004	0.027	0.0004	0.185
BAF in pulses Redgram	0.0008	0.0001	0.05	-	-
BAF in leafy vegetables	0.004	0.013	0.045	0.022	1.85
BAF in non- leafy vegetables	0.002	0.004	0.049	0.009	0.25

It was observed that the people in the area are seriously affected and suffering from occupational diseases such as asthma, chromium ulcers and skin diseases. Incidence of respiratory diseases among workers exposed to occupational and environmental risks of tannery industry at Ranipet industrial area is reported (Mahimairaja et al. 2000). The concentration levels of these metals are much above the permissible limits in surface water and are health hazards especially for the people working in the tannery industries. In these areas of Tamilnadu, groundwater is not suitable for domestic use, forcing villagers to travel 4-5 km for water. Much of the groundwater is unsuitable for irrigation, and hundreds of wells in the region can no longer be used (Thangarajan 1999;

Selvakumar and Manoharan 2002; Mondal et al. 2005). Higher levels of Cr, Ni, Zn, Pb are present in the soil due to the chemicals use during tanning and accumulation of discharged wastes into the ground water and in the soil. Sharma et.al (2009) has also reported higher concentration of Zn (109 mg/kg), Cd (1.27 mg /kg) and lead (6.39mg/kg) in the agricultural soils. Lokeshwari and Chandrappa (2006) showed the presence of Fe, Zn, Cu, Ni, Cr, Pb and Cd in the irrigated land used for growing crops and vegetables which is confirmed by our study.

BSAF

The food samples collected from the 10 families from the Puliyanthangal village of Ranipet. The

sediments levels of Ranipet soils a maximum range of 523mg/kg Cr, 117mg/kg Pb, 220mg/kg Ni and 372 mg/kg Zn which was found to be very high but the Cadmium level was very negligible upto a level of 0.32 mg/kg in the location. The Zinc BCF of 0.05 is observed in redgram samples which tends to magnify to a greater extent in the Vellore environment. The leafy vegetables show a BCF of 1.85 which infers that Cadmium also tend to magnify in the environment. In the Ranipet the ground water samples analysed, the heavy metals namely Cr, Zn, Ni and Pb was high above the permissible limit as given by WHO. The levels of Cd was below permissible limit given by WHO in both the locations. The same report has been given in the surface waters of Ranipet (Gowd and Govil 2008). In the case of sediment samples, the concentration in the sediment samples were very higher compared to water samples. Since the site is being dumped with tannery wastes for decades together, when the food crops are cultivated in such a type of farmland there will be a transfer of heavy metals through the food chain. Based on the above preliminary investigation the food samples were collected and the Environmental risk factor was calculated. The trophic magnification is more from the ground water to the crops compared from the sediments to the food crops. According to Zhuang et al (2009), the BCF for heavy metals indifferent vegetables showed a decreasing trend in the following order. $Cd > Zn > Cu > Pb$. The BCF of heavy metals were significantly higher for the leafy vegetables compared to the non leafy vegetable. Our study also showed that the food grains had the maximum BAF for Cadmium followed by Zinc. The BCF criterion of 5000 as identified in the persistence and Bioaccumulation regulations denotes chemicals which are high bio accumulative at the organism level and may also suggest the potential for biomagnifications (CEPA registry 2009). Our study shows that leafy vegetables accumulate more heavy metals than grains similar report was given by Mapanda et. al 2005. According to the study the heavy metals are easily accumulated in the edible parts of leafy vegetables as compared to the grains or the food crops. Highest chromium accumulation occurs in vegetable of Brassicaceae family (Zayed et al. 1998). Several authors have reported the heavy metal accumulation in vegetables. Cd and Pb in potato (Davis & Crews 1983). The accumulation of Cd, Zn and Pb in vegetables were reported by Zhuang et al (2009). The accumulation of concentration factor of Ni was highest when compared to Cr, Co, Cu, Zn, Pb and Cd in the vegetables grown on sludge amended soils. (Chandrasekhar et al 2001). In our studies the BCF was the highest in Cd, for the leafy vegetables accumulated from the soils (1.85) which is said to be biomagnified followed by the heavy metal Zn (0.05). This is confirmed by the report given by Smical et al (2008) who has reported that the heavy metal transfer

factor from the polluted soil into the lettuce crop is high in case of Cu followed by Zn.

BCF in the food grains and the vegetables found to be high in the food crop from water compared to soil. This is also confirmed by the report given by Mishra and Tripathi (2008) which reports that accumulation of Fe, Zn, Cu, Cr, and Cd by the aquatic macrophytes from the waste water.

According to report given by Gowd and Govil (2008) the Ranipet ground water sample contained heavy metals above the permissible level given by WHO. Our study reveals the same. Similarly the values in the sediment samples was also very high since the site is being dumped with tannery waste for decades together. When the food crops are cultivated in such a type of farm land there will be a transfer of heavy metals through the food chain. The bioaccumulation and biomagnification is observed in the ratio calculated between the concentration of heavy metals from ground water to food crops. The Biomagnification is observed in the case where the BAF exceed one.

Conclusion

Based on the above studies we conclude that the bioaccumulation or the bioconcentration for Cadmium is highest from the sediments to the plant tissues followed by Zinc. Moreover the leafy vegetables are concentrated with the highest level of heavy metal than other food grains. The heavy metals are transferred from one trophic level to another i.e. from irrigation water to sediments then again translocated to the plant tissues. This means when the population consumes the heavy metal concentrated tissues then they would be subjected to health risks. Suitable remedial measures should be suggested for the tanneries contaminated sites of Vellore district.

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