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Eco-toxicological studies & impact of Pulp and Paper Mill effluent on crop and non-crop plants of the contaminated site at Chandilli (Odisha, India) - a case study.

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Highlights:

- The discharged untreated Paper mill effluent is deadly toxic and needs biological treatment.
- Significant amount of heavy metals like Hg, Cd & Pb were recorded in the nearby crop fields and crop field inhabiting plants. Other heavy metals like copper and chromium was not traceable in the effluent.
- Significant depletion of plant pigment content was recorded in all exposed plants tested.
- Exposed ragi plants showed higher accumulation of heavy metals and least impact on pigment content, hence considered more tolerant than rice, green gram and black gram.
- The BAF and TF values for heavy metal absorption and translocation indicated the adoption of ragi and black gram plant as alternate crop compared to rice and green gram plant.

Abstract

Pulp & Paper Mill effluent is deadly toxic and the effluent is directly discharged without biological treatment into River Nagavalli. The main objective of the study was to assess pollution status at Chandilli village caused by the effluent of the paper mill: its impact on the pigment content and production of crop plants. The effluent contaminated river water contained significant quantity of heavy metals. Significant amount of Cd, Hg and Pb was found in the crop field soil and water. Residual cadmium, mercury and lead were found in the crop field inhabiting important economic and non-economic plants. Significant depletion of plant pigment content was recorded in all exposed plants of the crop field tested. The observed effects were only due to the heavy metal accumulation in the leaves of the crop plants. Ragi plants showed highest accumulation of heavy metals and the impact was least on the pigment content when compared to other crop plants tested. Out of all crop plants tested, ragi crop plant was more tolerant when compared to rice, green gram & black gram crop plants.

Keywords: Pulp & Paper mill, Effluent, crop & non-crop plants, heavy metals, pigment.

Introduction

Heavy metal pollution caused by industries is a direct threat to the very existence of plant, animal and human life in nature. Pulp and Paper mills are the major players to contribute heavy metals like mercury, cadmium and lead in the environmental segment, polluting nearby water bodies and affecting aquatic flora and fauna. The paper mills use huge amount of fresh water drawn from water bodies in the manufacturing process and discharge significant amount of effluent as waste in to nearby water bodies. Chmielowska-Bak *et al.*, (2021) reported that "contamination of the environment with metals, their adverse impact on plant performance and transmission to the human food chain through crops and vegetables are important concerns worldwide". Jin *et al.*, (2018) reported that biosorption which was dependent on the special structure of the cell wall and was reported to be the primary mechanism of accumulation of heavy metals in plants. Dey *et al.* (2018) indicated that in India, more than 55% of the mills do not have adequate effluent treatment facilities and also do not adopt modern treatment technologies. The paper mill effluents are discharged from the industry into the nearby water body (Iqbal *et al*., 2013) after physical and chemical treatments (Tripathy *et al*., 2022) indicating the need of proper biological treatment.

The effluent can be treated primarily by physical and chemical treatment methods followed by biological treatment using potential & promising microphytes and macrophytes. Most of the industries do not follow these biological treatment methods. JK Paper Mills at Jaykaypur subjects the effluent to physical and chemical treatment and discharges its effluent without any biological treatment. Dixit *et al*., (2018) reported presence of mercury, cadmium and lead in the final discharged International Paper mill effluent even after biological treatment. Tripathy *et al*., (2022) reported that the effluent of the paper mill severely affected the flora and fauna in and around the effluent canal and impacted the water quality of the river affecting the flora and fauna. The same author also indicated that usage of this contaminated river water to irrigate the crop fields will have far reaching consequences. The Paper Mill effluent contains heavy metals like cadmium, mercury and lead. The protocol of biological treatment of the effluent by the industry was not complete and efficient as this protocol neither benefits the environment nor the dependent plants and animals. Waste generation by any industry and the quality of waste depends on the technology and adopted treatment protocol of any Pulp and Paper industry. It is not possible to eliminate waste generation by the system (Kaur *et al*., 2021) but cleaner & environment friendly technology can be used and periodically positive modifications in the technology or alterations in the treatment technology should be adopted. In the present study, it was planned to assess the physico-chemical status for a longer period and analyze the impact of effluent on nearby crop fields and crop field inhabiting plants where this contaminated river water is used for irrigation of the crop fields.

Material & Methods

JK Pulp & Paper Mills, Jaykaypur is located at latitude 19.247ºN and longitude 83.409 º E, the ET (effluent treatment) plant is located at latitude 19.248ºN and longitude 83.413º E. The effluent canal joins the River Nagavalli (Google map-1) at 19.252ºN and longitude 83.420º E. The industry collects Nagavalli river water from the upstream of the river for all its requirements and discharges its effluent in to the river at downstream. The effluent sample was collected and physico-chemical analysis was carried out at the site. Samples from the mid effluent canal [S] were collected (Google map-2) in plastic containers and brought to the laboratory for estimations and analyses.

(Photo map-1 & 2. Google photomaps showing JK Papers Ltd., Effluent canal (Site-SS), effluent soaking open site, effluent joining Nagavalli River and nearby crop fields contaminated by effluent and effluent mixed river water.

Analyses of effluent and soil samples of nearby crop fields were conducted following the procedure of APHA (1985), EC (1979) instruction manual of Systronics and standardized field analysis kit (Systronics, India) and portable instruments were used to measure pH, conductivity & temperature of effluent and crop field soil & water samples. Dissolved oxygen was measured by modified Winkler's method (APHA, 1985). Effluent and crop field soil samples were brought in plastic containers and stored in the refrigerator for analysis and for laboratory experimental work. Measurement of heavy metals of the collected soil, water, effluent and plant samples were carried out by following the protocols of Wanntorp and Dyfverman (1955) and Yoshida *et al*. (1976). Mercury, cadmium and lead in digested samples were estimated in with the help of Atomic Absorption Spectrophotometer.

Bioaccumulation factor (BAF): The *in situ* phytoremediation capability of the plants present in and around the effluent canal was estimated by calculating the bioaccumulation factor (BAF) as suggested by Yoon *et al*. (2006) by using the formula as described below.

BAF= Metal concentration in root / metal concentration in the waste

Translocation factor (TF): The *in situ* phytoremediation capability of the plants present in and around the effluent canal was also estimated by calculating the translocation factor (TF) as suggested by Gupta & Sinha (2008) by using the formula as described below.

TF=Metal concentration in root / metal concentration in shoot or leaf

The pigment content of crop plant leaves were measured and estimated by following the method of Vernon (1960). The observed data was statistically analyzed and presented as the mean of samples ± standard deviation.

Results

Effluent samples were collected from effluent canal at two years interval from the same spot to compare and assess the quality of the effluent released from the industry and discharged into River Nagavalli located at a distance of 1.0km. The effluent color ranged from deep yellowish brown to yellowish brown and odour was pungent with filthy smell. The locality area suffers from this pungent H_2S smell. The effluent was slightly alkaline and no significant variation in pH was noted and the values ranged between 7.5 ± 0.6 – 7.9 ± 0.4. The temperature of the effluent ranged within 31.2 ± 1.2°C to 32.5 ± 0.7°C. The effluent is discharged initially into a soaking cum drying open field located nearby and from there the effluent gets discharged into the river continuously. Significantly higher conductivity value to the tune of 1824.4 ± 18.4mho/cm was noted in 2015 and conductivity values decreased in 2017 and 2019. In 2019, 1731.5 ± 26.2mho/cm conductivity of the effluent sample was recorded (Table-1). The dissolved oxygen of the effluent was significantly low and ranged between 1.5 ± 0.4 mg l^{-1} to 1.8 ± 0.3 mg l^{-1}. When we compared the BOD status, the BOD value of the effluent sample decreased from 139.7 ± 22.8mg.l^{-1} (in 2015) to 126.8 ± 17.2mg.l^{-1}(in 2019). Significant variation in COD value was noted at all study periods but no increase or decrease trend was observed. The total suspended solids (TSS) content of the effluent was significantly high and the TSS value increased from 806.2±17.6 to 826.8 ± 11.5mg/liter with time period. The total dissolved solids (TDS) depleted with time period but no trend of interest was noted. The hardness of the effluent samples collected in different time periods indicated increase in hardness from 498.8 ± 45.6mg/liter in 2015 to 586.4 ± 18.4mg/liter in 2019. The increase in hardness might be due to chemical treatment of the effluent by chemical methods. No notable variation was noted in total phosphate content of the effluent samples tested. The amount of phosphate available in the effluent samples was low (2.65±0.9mg/L, 2.45±0.7mg/L and 1.12 ± 0.4mg/L in 2015, 2017 and 2019 respectively but sufficient enough to support algal growth. Significant amount of total sulphate was recorded in the effluent samples collected from the effluent canal in different time periods. Interestingly, the sodium and potassium content recorded in the effluent was very high and almost similar quantity was recorded in the past three select years (Table-1)

Table-1: Comparison of physico-chemical parameters of the samples collected from the effluent canal in different years (Tripathy *et al*., 2021 & 2022).

Parameters of study	Present study by the authors in different years.		
	2015	2017	2019
Colour & Odour	Deep Yellowish brown, Pungent, Filthy H_2S smell	Yellowish brown, Pungent, Strong H_2S smell	Yellowish brown, Pungent. Filthy smell
pH	7.8±0.5	7.5±0.6	7.9±0.4
Temperature, °C	32.5±0.7	32.2±0.4	31.2±1.2
Conductivity, mho / cm	1824.4±18.4	1792.2±11.5	1731.5±26.2
Dissolved oxygen (mg /L)	1.6±0.5	1.8±0.3	1.5±0.4
BOD (mg /L)	139.7±22.8	131.5±9.6	126.8 ± 17.2
COD (mg /L)	242.2±38.6	235.2±19.5	318.5 ± 11.8
TSS (mg /L)	806.2±17.6	811.4±22.4	826.8 ± 11.5
TDS (mg /L)	1485.1±31.4	1376.3±41.8	1392.3±11.4
Hardness (mg /L)	498.8±45.6	525.1±26.6	586.4±18.4
Total Phosphates (mg /L)	2.65±0.9	2.45±0.7	1.12 ± 0.4
Total Sulphate (mg /L)	154.2±24.3	141.8±5.6	146.5±11.2
Sodium (mg /L)	54.2±4.4	61.1±11.5	61.8 ± 5.2
Potassium (mg /L)	51.6 ± 3.8	50.09±4.05	49.5±3.8
Cadmium (mg /L)	0.39±0.11	0.31±0.05	0.32±0.05
Mercury (mg/L)	0.38±0.12	0.49±0.06	0.46±0.07
Lead (mg /L)	0.12±0.06	0.09±0.03	0.21±0.09

Toxic metals like cadmium, mercury and lead were found in the effluent collected from site-S. Significant amount cadmium was recorded in the collected effluent sample in 2015, 2017 and 2019 to the tune of 0.39 ± 0.11, 0.31 ± 0.05 and 0.32 ± 0.05mg/liter respectively. The amount of cadmium in the effluent sample looks by number very small but significant and toxic and much more than stipulated guidelines prescribed by Pollution Control Board (PCB). Significant amount mercury was recorded in the collected effluent sample in 2015, 2017 and 2019 to the tune of 0.38±0.12, 0.49±0.06 and 0.46±0.07mg/liter respectively. The amount of mercury in the effluent sample was significant and highly toxic. All the values were much more than stipulated guidelines prescribed by Pollution Control Board (PCB, India). Minimal amount of lead 0.12±0.06mg/L, and 0.09±0.03mg/L was recorded in 2015 and 2017 but we could detect higher lead level in 2019 to the tune of 0.21±0.09mg/L in the collected effluent samples (Table-1). In few collections at different time period particularly in rainy season lead was not detectable in the effluent, might be due to heavy dilution. It was observed that the effluent samples collected from the effluent canal in different years indicated almost the same status except few significant variations in different time periods.

Table-2: Heavy metal analysis of water & soil samples of crop fields; rice plant leaves and algal mixture collected from the two crop fields nearby opposite to the Pulp & Paper mill industry and River Nagavalli at Chandilli, Rayagada district, Odisha, India. Crop filed-A (on the bank of the Nagavalli river) & Crop filed-B (50meters away from the river bed). Dwt= Dry weight Data presented are the mean of samples ± standard deviation.

Parameters studied.	Collection and analysis of samples from the crop field-1 (Google Map) from the contaminated site during rice cultivation period, opposite to the industry and Nagavalli River at Chandilli.							
	Crop filed-A				**Crop filed-B**			
	Soil	Water	Rice plant leaves	Algal mixture	Soil	Water	Rice plant leaves	Algal mixture
pH	7.93	7.88	-	-	7.91	7.87	-	-
Temperature, °C	23.5 ± 0.5	24.6 ± 0.3	-	-	23.4 ± 0.3	24.5 ± 0.4	-	-
Heavy metals.	µg/g dwt	µg/Liter	µg/g dwt	µg/g dwt	µg/g dwt	µg/Liter	µg/g dwt	µg/g dwt
Cadmium	81.5 ± 9.8	53.8 ± 11.4	6.1 ± 0.6	0.28 ± 0.06	78.2 ±11.6	52.9 ±13.8	6.4 ± 0.9	0.25 ± 0.05
Lead	12.5 ± 1.5	8.8 ± 2.6	1.8 ± 0.7	0.17 ± 0.05	12.2 ± 1.6	7.8 ± 1.7	1.4 ± 0.9	0.18 ± 0.07
Mercury	83.2 ±14.6	48.6 ± 8.8	5.2 ± 0.32	0.76 ± 0.11	79.4 ±18.8	46.4 ± 11.4	5.3 ± 0.54	0.74 ± 0.09

The pH of both the crop fields ranged between 7.87 to 7.95 and the soil pH was little higher than the water pH in both the fields selected. The soil and water temperature ranged between 23.4 to 24.6°C. The data presented in table-3, indicated presence of all the three tested heavy metals in the crop field soil & water, residual heavy metals in rice crop plant leaves absorbed from the crop fields and in the algal scum collected from the crop fields. The farmers use Paper mill effluent contaminated Nagavalli river water for irrigation of crop fields at regular intervals. The source of heavy metals in the crop fields being the water used for irrigation from the Nagavalli River. In crop field-A, significant amount of cadmium, lead and mercury was available in the crop field soil to the extent of 81.5 ± 9.8, 12.5± 1.5 and 83.2 ±14.6µg /g dry weight respectively. In crop field-B significant amount of cadmium, lead and mercury was available and the amounts were significantly different from crop field-A, when we consider standard deviation of each data. In crop field-A, significant amount of cadmium, lead and mercury was available in the crop field water to the extent of 53.8 ± 11.4, 8.8 ± 2.6 and 48.6 ± 8.8µg /g dry weight respectively. In crop field-B water, significant amount of cadmium, lead and mercury was available and the amounts were not significantly different from crop field-A (Table-2). Cultivated rice plants absorbed mercury, lead and cadmium from the water and soil of the crop fields and accumulated in the plant leaves. Rice plant leaves accumulated cadmium, lead and mercury to the tune of 6.1± 0.6, 1.8± 0.7 and 5.2 ± 0.32µg/g dry wt respectively in crop field-A and 6.4± 0.95µg of cadmium/g dry wt, 1.4± 0.95µg of lead/g dry wt and 5.3± 0.5µg of mercury /g dry wt in crop field-B (Table-2 & Fig.A-1).

(Photos showing growth of algae in the contaminated crop fields at Chandilli village area.)

Algae in the algal mat (Algal mat consists of Oscillatoria sp., Calothrix sp., Scenedesmus sp., Spirogyra sp., Chlamydomonas sp., Phormidium sp. and diatom) showed heavy metal accumulation to the tune of 0.28± 0.06, 0.17 ± 0.05 and 0.76 ± 0.11µg/g dry wt in crop field-A and 0.25± 0.05, 0.18 ± 0.07 and 0.74 ± 0.09µg/g dry wt in crop field-B (Table-2). The obtained values in table-2 indicated the pollution status of the nearby crop fields contaminated with Paper mill effluent mixed with river water.

The crop fields situated near the bank of River Nagavalli are generally irrigated by pumping water from the contaminated river. The economically important plant leaf samples collected from the crop fields before flowering, contained significant amount of heavy metals like mercury, cadmium and lead. Rice plant leaves contained 5.2±0.4µg of Hg /g dry weight, 6.1±0.2µg of Cd /g dry weight & 1.8±0.2µg of Pb /g dry weight; ragi plant leaves contained 5.5±0.7µg of Hg /g dry weight, 5.3±0.9µg of Cd /g dry weight & 2.6±0.6µg of Pb /g dry weight; green gram plant leaves contained 3.2±1.1µg of Hg /g dry weight, 3.7±0.6µg of Cd / g dry weight & 2.85±0.9µg of Pb /g dry weight; black gram plant leaves contained 3.6±0.4µg of Hg /g dry weight, 3.9±0.5 µg of Cd /g dry weight & 1.95±0.21µg of Pb /g dry weight and the algal scum contained 0.7±0.11µg of Hg /g dry weight, 0.69±0.04µg of Cd /g dry weight & 0.19±0.06µg of Pb /g dry weight (Table-3). The weed plants collected from the contaminated crop field growing along with crop plants are generally weeded out periodically in normal crop fields. But in our site of study such an activity was not carried out regularly by the farmers due to cost constraints. Periodically these grasses were weeded out and fed to cows. The collected weeds belonging to the family Poaceae grazed by grazers were tested for residual accumulation of heavy metals. *Cynodon dactylon* contained 1.38±0.32µg of Hg /g dry weight, 1.42±0.18µg of Cd /g dry weight & 0.71±0.22µg of Pb /g dry weight and *Cyperus rotundus* contained 1.29±0.26µg of Hg /g dry weight, 1.31±0.16µg of Cd /g dry weight & 0.68±0.14µg of Pb /g dry weight (Table-3). The plants growing at the inner ridges of the crop fields coming in contact with contaminated river water were collected and analyzed for heavy metal accumulation. *Boerhavia repens* accumulated 3.14±0.29µg of Hg /g dry weight, 2.26±0.17µg of Cd /g dry weight & 0.96±0.21µg of Pb /g dry weight; *Chloris barbata* accumulated 0.82±0.14µg of Hg /g dry weight, 0.46±0.22µg of Cd /g dry weight & 0.26±0.18µg of Pb /g dry weight; *Cleome viscosa* accumulated 1.96±0.61µg of Hg /g dry weight, 0.89±0.34µg of Cd /g dry weight & 0.41±0.18µg of Pb /g dry weight; *Commelina benghalensis* accumulated 0.69±0.19µg of Hg /g dry weight, 0.81±0.17µg of Cd /g dry weight & 0.34±0.21µg of Pb /g dry weight; *Desmodium triflorum* accumulated 1.14±0.06µg of Hg /g dry weight, 0.92±0.14µg of Cd /g dry weight & 0.51±0.09µg of Pb /g dry weight; *Digitaria ciliaris* accumulated 1.14±0.26µg of Hg /g dry weight, 1.22±0.17µg of Cd /g dry weight & 0.65±0.09µg of Pb /g dry weight; *Phyla nodiflora* accumulated 1.58±0.54µg of Hg /g dry weight, 1.48±0.36µg of Cd /g dry weight & 0.88±0.21µg of Pb /g dry weight and *Phyllanthus reticulatus* accumulated 1.36±0.91µg of Hg /g dry weight, 1.18±0.54µg of Cd /g dry weight & 1.13±0.36µg of Pb /g dry weight (Table-3).

Table-3: Showing changes heavy metal (Hg, Cd, Pb) residue content of crop plants, algal mixture and weed plants collected from the contaminated crop fields located on the opposite side of the Nagavalli river bank, 200meters & 300meters (irrigation points) from effluent meeting point. NT=Not traceable.

Sl. No.	Collected Plant Names	Status	Residual heavy metal content, µg/g leaf dry weight.		
			Hg	**Cd**	**Pb**
Plant samples collected from the crop fields					
A. Economically important plants with high food value					
1	Rice- *Oryza sativa*,L.	Cont	NT	NT	NT
		Exp	5.2 ± 0.4	6.1 ± 0.2	1.8 ± 0.2
2	Ragi-*Eleusine coracana*, Gaertn	Cont	NT	NT	NT
		Exp	5.5 ± 0.7	5.3 ± 0.9	2.6 ± 0.6
3	Green gram- *Vigna radiata*, (L) Wilczek	Cont	NT	NT	NT
		Exp	3.2 ± 1.1	3.7 ± 0.6	2.85 ± 0.9
4	Black gram-*Vigna mungo*, (L.) Hepper	Cont	NT	NT	NT
		Exp	3.2 ± 0.4	3.1 ± 0.5	1.95 ± 0.21
5	Algal mixture collected from crop field	Cont	NT	NT	NT
		Exp	0.7 ± 0.11	0.69 ± 0.04	0.19 ± 0.06
B. Weed plants growing along with crop plants (economically important plants for grazers as food)					
6	*Cynodon dactylon*, (L.) Pers; F-Poaceae	Cont	NT	NT	NT
		Exp	1.38 ± 0.32	1.42 ± 0.18	0.71 ± 0.22
7	*Cyperus rotundus*, L. ; F-Poaceae	Cont	NT	NT	NT
		Exp	1.29 ± 0.26	1.31 ± 0.16	0.68 ± 0.14
C. Plants samples (Non-economically important but grazed by grazers) collected from the ridges of the crop fields coming in contact with crop field contaminated water, received from the polluted river by irrigation.					
8	*Boerhavia repens*, L. ; F-Nyctaginaceae	Cont	NT	NT	NT
		Exp	3.14 ± 0.29	2.26 ± 0.17	0.96 ± 0.21
9	*Chloris barbata*, Sw ; F- Poaceae	Cont	NT	NT	NT
		Exp	0.82 ± 0.14	0.46 ± 0.22	0.26 ± 0.18
10	*Cleome viscosa*, L. ; F- Capparaceae	Cont	NT	NT	NT
		Exp	1.96 ± 0.61	0.89 ± 0.34	0.41 ± 0.18
11	*Commelina benghalensis*, L.; F-Commelinaceae	Cont	NT	NT	NT
		Exp	0.69 ± 0.19	0.81 ± 0.17	0.34 ± 0.21
12	*Desmodium triflorum*, (L.) DC ; F- Fabaceae	Cont	NT	NT	NT
		Exp	1.14 ± 0.06	0.92 ± 0.14	0.51 ± 0.09
13	*Digitaria ciliaris*,(Retz.)Koeler*;* F- Poaceae	Cont	NT	NT	NT
		Exp	1.14 ± 0.26	1.22 ± 0.17	0.65 ± 0.09
14	*Phyla nodiflora*, (L.) Greene; F-Verbenaceae	Cont	NT	NT	NT
		Exp	1.58 ± 0.54	1.48 ± 0.36	0.88 ± 0.21
15	*Phyllanthus reticulatus*, Poir ; F-Euphorbiaceae	Cont	NT	NT	NT
		Exp	1.36 ± 0.91	1.18 ± 0.54	1.13 ± 0.36

Table-4: Showing changes in total heavy metal (Hg, Cd, Pb) residue content and pigment content of crop plants, algal mixture and weed plants collected from the crop fields near the opposite side of the Nagavalli river bank. Crop fields located at 93.77meters from the river bank. Values in parentheses indicate percent change (-indicate decrease and + indicate increase) in exposed systems compared to their respective control values. ND= Not detected.

Sl .No.	Name of the plant specimens	Status	Residual total heavy metal (Hg, Cd, Pb) load in plant leaves, µg/g dry weight.	Pigment content, mg/g dry weight	
				Chlorophyll	**Phaeophytin**
A.	**Economically important plants with high food value**				
1	Rice- *Oryza sativa*, L.; F: Poaceae	Control	ND	2.776±0.044	1.932±0.041
		Exposed	13.14±0.33	1.845±0.056 (-33.5)	1.082±0.032 (-43.9)
2	Ragi- *Eleusine coracana*, Gaertn ; F: Poaceae	Control	ND	1.244±0.195	1.116±0.074
		Exposed	13.47±0.72	1.014±0.042 (-18.5)	0.792±0.035 (-29)
3	Green gram- *Vigna radiata*, (L) Wilczek, F: Fabaceae	Control	ND	2.345±0.211	2.188±0.144
		Exposed	9.78±0.84	1.062±0.096 (-54.7)	1.112±0.094 (-49.2)
4	Black gram- *Vigna mungo*, (L.) Hepper, F; Fabaceae	Control	ND	2.214±0.112	1.924±0.036
		Exposed	8.25±0.39	1.349±0.227 (-39.1)	1.086±0.024 (-43.6)
5	Algal mixture collected from crop field	Control	ND	2.371±0.185	1.991±0.078
		Exposed	1.58±0.09	2.384±0.232 (+0.6)	2.014±0.094 (+1.2)
B.	**Weed plants growing along with crop plants (economically important plants for grazers)**				
6	*Cynodon dactylon*, (L.) Pers; F- Poaceae	Control	ND	1.231±0.094	1.186±0.018
		Exposed	3.51±0.26	0.964±0.072 (-21.7)	0.884±0.032 (-25.5)
7	*Cyperus rotundus*, L.; F- Cyperaceae	Control	ND	1.119±0.096	0.846±0.047
		Exposed	3.28±0.19	0.882±0.024 (-21.2)	0.721±0.025 (-14.8)
C.	**Plants samples (Non-economically important but grazed by grazers) collected from the ridges of the crop fields coming in contact with crop field contaminated water, received from the polluted river by irrigation.**				
8	*Boerhavia repens*, L. ; *F-* Nyctaginaceae	Control	ND	1.178±0.035	1.212±0.044
		Exposed	6.36±0.22	1.011±0.061 (-14.2)	0.981±0.047 (-19.1)
9	*Chloris barbata*, Sw ; F- Poaceae	Control	ND	0.841±0.037	0.884±0.051
		Exposed	1.54±0.18	0.796±0.026 (-5.4)	0.791±0.032 (-10.5)
10	*Cleome viscosa*, L. ; F- Capparaceae	Control	ND	1.104±0.102	1.114±0.056
		Exposed	3.26±0.37	0.886±0.074 (-19.8)	0.811±0.039 (-27.2)
11	*Commelina benghalensis*, L.; F- Commelinaceae	Control	ND	1.351±0.036	0.994±0.088
		Exposed	1.84±0.19	1.114±0.019 (-17.5)	0.796±0.036 (-19.9)
12	*Desmodium triflorum*, (L.) DC ; F- Fabaceae	Control	ND	1.519±0.028	1.261±0.031
		Exposed	2.57±0.09	1.124±0.036 (-26)	0.997±0.081 (-20.9)
13	*Digitaria ciliaris*,(Retz.)Koeler; F- Poaceae	Control	ND	1.424±0.095	1.312±0.075
		Exposed	3.01±0.16	1.165±0.049 (-18.2)	1.118±0.042 (-14.8)
14	*Phyla nodiflora*, (L.) Greene; F- Verbenaceae	Control	ND	0.819±0.036	0.887±0.028
		Exposed	3.94±0.37	0.692±0.031 (-15.5)	0.685±0.051 (-22.8)
15	*Phyllanthus*	Control	ND	1.168±0.065	0.9840.052

	reticulatus, Poir ; F-Euphorbiaceae	Exposed	3.67±0.63	0.886±0.035 (-24.1)	0.714±0.038 (-27.4)

The changes in pigment content of the collected plant leaves indicated the impact of the stress caused due to the use of contaminated river water. In case of *Oryza sativa* the chlorophyll content decreased from 2.776±0.044 to 1.845±0.056 mg/g dry weight showing 33.5% decrease and the phaeophytin content decreased from 1.932±0.041 to 1.082±0.032 mg/g dry weight showing 43.9% decrease compared to the control values, in *Eleusine coracana* the chlorophyll content decreased from 1.244±0.195 to 1.014±0.042mg/g dry weight showing 18.5% decrease and the phaeophytin content depleted from 1.116±0.074 to 0.792±0.035mg/g dry weight showing 29% decrease compared to the control values; in *Vigna radiata* the chlorophyll content decreased from 2.345±0.211 to 1.062±0.09mg/g dry weight showing 54.7% decrease and the phaeophytin content decreased from 2.188±0.144 to 1.112±0.094 mg/g dry weight showing 49.2% decrease compared to the control values; in *Vigna mungo* the chlorophyll content decreased from 2.214±0.112 to 1.349±0.227mg/g dry weight showing 39.1% decrease and the phaeophytin content decreased from 1.924±0.036 to 1.086±0.024 mg/g dry weight showing 43.6% decrease compared to the control values and in case of algal mixture, the total chlorophyll content increased from 2.371±0.185 to 2.384±0.232mg/g dry weight showing an insignificant increase by 0.6% and the phaeophytin content increased from 1.991±0.078 to 2.014±0.094mg/g dry weight showing an insignificant increase by 1.2% compared to the control values (Table-4).In case of *Cynodon dactylon* the chlorophyll content decreased from 1.231±0.094 to 0.964±0.072mg/g dry weight showing 21.7% decrease and the phaeophytin content decreased from 1.186±0.018 to 0.884±0.032mg/g dry weight showing 25.5% decrease compared to the control values and in *Cyperus rotundus*, the chlorophyll content depleted from 1.119±0.096 to 0.882±0.024mg/g dry weight showing 21.2% decrease and the phaeophytin content decreased from 0.846±0.047 to 0.721±0.025mg/g dry weight showing 14.8% decrease compared to the control values (Table-4). In case of *Boerhavia repens*, the chlorophyll content depleted by 14.2% and the phaeophytin content depleted by 19.1% compared to the control values; in *Chloris barbata*, the chlorophyll content depleted by 5.4% and the phaeophytin content depleted by 10.5% compared to the control values; in *Cleome viscosa*, the chlorophyll content depleted by 19.8% and the phaeophytin content depleted by 27.2% compared to the control values in *Commelina benghalensisa*, the chlorophyll content decreased by 17.5% and the phaeophytin content depleted by 19.9% compared to the control values; in *Chloris barbata*, the chlorophyll content depleted by 5.4% and the phaeophytin content decreased by 10.5% compared to the control values; in, *Desmodium triflorum* the chlorophyll content decreased by 26% and the phaeophytin content decreased by 20.9% compared to the control values; in *Digitaria ciliaris*, the chlorophyll content depleted by 18.2% and the phaeophytin content depleted by 14.8% compared to the control values; in *Phyla nodiflora*, the chlorophyll content decreased by 15.5% and the phaeophytin content depleted by 22.8% compared to the control values and in case of *Phyllanthus reticulatus*, the chlorophyll content decreased by 24.1% and the phaeophytin content decreased by 27.4% compared to the control values (Table-4). Residual accumulation in economically important plant leaves were significant and warrant attention to avoid a future environmental catastrophe.

Basing on the results of table-3 & 4, it was planned to study the absorption and distribution of metals like Hg, Cd and Pb in root, stem / petiole and leaf of different crop plants after 75days of exposure to effluent mixed river water. Fig.1-3 showed a clear picture of differential absorption and distribution of heavy metals during most active vegetative growth phase before flowering. In root of rice plants mercury accumulated by 8.2±0.7µg/g dry weight, cadmium accumulated by 9.1±0.8µg/g dry weight and lead accumulated by 4.5±0.4µg/g dry weight; in petiole of rice plant leaves mercury accumulated by 7.9±0.3µg/g dry weight, cadmium accumulated by 8.4±0.3µg/g dry weight and lead accumulated by 3.9±0.2µg/g dry weight and rice plant leaf accumulated mercury accumulated by 5.2±0.4µg/g dry weight, cadmium accumulated by 6.1±0.2µg/g dry weight and lead accumulated by 1.8±0.2µg/g dry weight. No heavy metal accumulation was noted in the respective control rice plant parts collected from a distance area, where bore well water was used for irrigation. In root of ragi plants mercury accumulated by 8.9±0.5µg/g dry weight, cadmium accumulated by 9.3±0.4µg/g dry weight and lead accumulated by 5.6±0.4µg/g dry weight; in petiole of ragi plant leaves mercury accumulated by 8.3±0.2µg/g dry weight, cadmium accumulated by 8.6±0.5µg/g dry weight and lead accumulated by 4.8±0.7µg/g dry weight and ragi plant leaf accumulated mercury accumulated by 5.5±0.4µg/g dry weight, cadmium accumulated by 5.3±0.9µg/g dry weight and lead accumulated by 2.6±0.6µg/g dry weight. No heavy metal accumulation was noted in the respective control ragi plant parts. In root of green gram plants mercury accumulated by 6.1±0.4µg/g dry weight, cadmium accumulated by 6.9±0.4µg/g dry weight and lead accumulated by 4.1±0.3µg/g dry weight; in the stem of green gram plant mercury accumulated by 6.4±0.7µg/g dry weight, cadmium accumulated by 6.2±0.2µg/g dry weight and lead accumulated by 3.3±0.5µg/g dry weight and green gram plant leaves accumulated mercury accumulated by 3.2±1.1µg/g dry weight, cadmium accumulated by 3.7±0.6µg/g dry weight and lead accumulated by

2.85±0.9µg/g dry weight. No heavy metal accumulation was noted in the respective control green gram plant parts. In root of black gram plants mercury accumulated by 6.6±0.6µg/g dry weight, cadmium accumulated by 6.7±0.2µg/g dry weight and lead accumulated by 4.2±0.4µg/g dry weight; in the stem of black gram plant mercury accumulated by 5.8±0.4µg/g dry weight, cadmium accumulated by 6.6±0.4µg/g dry weight and lead accumulated by 3.2±0.7µg/g dry weight and black gram plant leaves accumulated mercury accumulated by 3.2±0.4µg/g dry weight, cadmium accumulated by 3.1±0.5µg/g dry weight and lead accumulated by 1.95±0.21µg/g dry weight. No heavy metal accumulation was noted in the respective control green gram plant parts (Fig. 1-3).

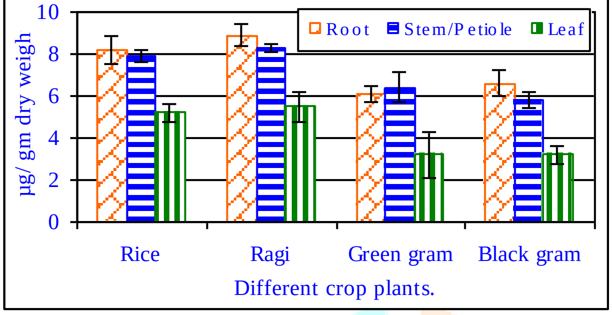


Fig. 1. Showing residual mercury concentration in different parts of the plant body of 4 cultivated crops after 75d of sowing.

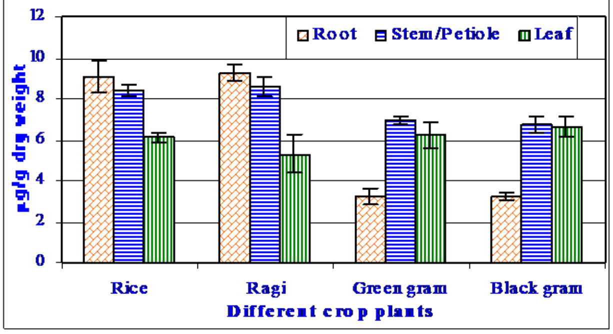


Fig.2: Showing residual cadmium concentration in different parts of the plant body of 4 cultivated crops after 75d of sowing..

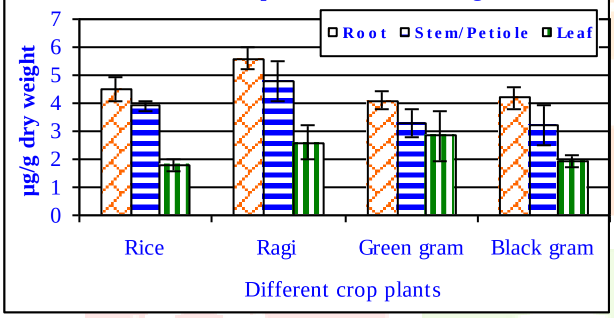


Fig.3: Showing residual lead concentration in different parts of the plant body of 4 cultivated crops after 75d of sowing..

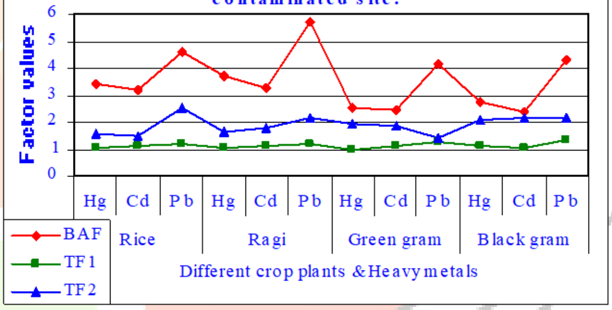


Fig. 4. Showing the BAF, TF1 and TF2 values of heavy metals (Hg, Cd, Pb) in four different 75d old crop plants collected from the contaminated site.

Fig.1-3 showed the absorption and accumulation of mercury, cadmium and lead after 75days of exposure to effluent mixed river water in rice, ragi, green gram and black gram crop plants collected from the effluent affected crop fields. Mercury and cadmium accumulated almost at the same rate and lead accumulation was least might be due to less availability of lead in the contaminated water. The total heavy metal accumulation was maximum in ragi plants than rice plants, green gram and black gram crop plants. Minimum heavy metal accumulation was observed in black gram than green gram crop plants. Basing on the results of total heavy metal accumulation, it appears that ragi crop plants accumulated more heavy metals showing least impact on the pigment content than black gram, green gram and rice crop plants. From the observed data ragi and black gram crops can be recommended to replace rice and green gram cultivation in the contaminated sites at Chandilli village contaminated area. Fig. 3 shows accumulation of total Hg, Cd & Pb in whole plant and different parts available plants in the contaminated crop fields. Highest accumulation of 64.9µg / g dry weight of total Hg, Cd & Pb was recorded in rice plants. In case of ragi plants the total heavy metal accumulation was 62.2µg / g dry weight. Black gram and green gram plants accumulated 37.67µg / g dry weight and 35.68µg / g dry weight. From the whole plant, roots accumulated more than other plant parts. In case of rice plants, roots accumulated 24.9µg / g dry weight, leaf accumulated 16.0µg / g dry weight, petiole accumulated 22.3 µg/g dry weight and the grains accumulated 1.7µg / g dry weight (Fig.3). Fig.4 showed the BAF (bioaccumulation factor), TF! (Translocation factor from root to stem) and TF2 (translocation factor from root to leaf) of Hg, Cd and Pb in different crop plants collected from the contaminated crop fields near the Nagavalli river on the opposite site of effluent mixing point. The BAF for total heavy metals Green gram, Black gram and rice plants showed the highest value compared to ragi plants. In case of TF1 and TF2, black gram showed the highest value indicating strong translocation of heavy metals in the plant body compared to green gram, rice and ragi plant. Ragi plant has the highest BA Factor compared to translocation factor. Hence, ragi cultivation can be recommended for cultivation in the contaminated fields instead of rice and other crops.

Fig. 5: Accumulation of Hg, Cd, and Pb residue in different parts of the 75d old plants collected from the crop field

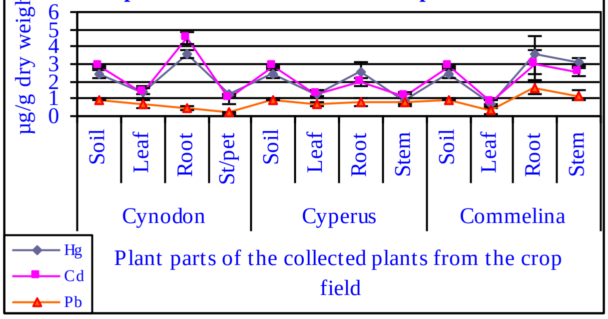
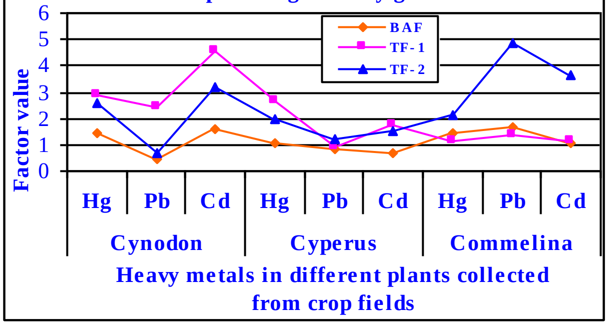


Fig.-6: Changes in BAF,TF-1 and TF-2 of Hg, Pb and Cd in 75d old plants collected from the crop fields grazed by grazers.



In the crop fields even after weeding out the unwanted plants periodically, we found three types of plants present along with crop plants. These weed pants were collected and tested for heavy metal residue. It was observed that all the three weed plants collected accumulated heavy metals significantly. The roots contained highest amount of all the three heavy metals compared to leaf and petiole. *Cyperus rotundus* accumulated less heavy metal than *Cynodon dactylon* and *Commelina benghalensis* (Fig.5). The probable reason was periodic removal of these weeds from the crop fields. The retention time/ exposure time of these non crop plants/ weeds was less than 120days. *Cyperus rotundus* and *Cynodon dactylon* after harvesting, was fed to the cows and bullocks as regular feed. Higher depostion of Hg, Cd & Pb in these plants may be less in quantity but significant from bioaccumulation of heavy metals and its biomagnification in food chain. *Commelina benghalensis* was not used as feed for any animal but when these grazers graze in the field, they consume this plant also along with other grasses. In case of weed plants collected from the contaminated crop fields (Fig.6) the bioaccumulation factor for the three heavy metals, it was observed that the BAF value in case of Hg was high in *Commelina* compared to *Cynodon* and *Cyperus*. Whereas in case of cadmium, the BAF value was higher in *Cynodon* and was lower in case of *Cyperus*. In case of lead the BAF value was highest in *Commelina* and was lowest in case of *Cynodon*. The translocation factor 1 and translocation factor-2 (TF1 & TF2) for the same three heavy metals has been shown in Fig.6. It was marked that the TF1 value in case of Hg was high in *Cynodon* compared to *Cyperus* and *Commelina*. Whereas in case of cadmium the TF1 value was higher in *Cynodon* and was lower in case of *Commelina*. In case of lead the TF1 value was highest in *Cynodon* and was lowest in case of *Cyperus* compared to *Commelina*. It was marked that the TF2 value in case of Hg was high in *Commelina* compared to *Cynodon* and *Cyperus*. Whereas, in case of cadmium the TF2 value was higher in *Commelina* and was lower in case of *Cyperus* (Fig. 6). In case of lead the TF2 value was highest in *Commelina* and was lowest in case of *Cynodon* compared to *Cyperus*. From the calculated data no indication was available pertaining to a particular species behavior towards heavy metals, their accumulation and translocation. It is a fact that the BAF depends strongly on the availability of heavy metals (Hg, Cd, Pb) in the surrounding soil around the root from where the heavy metal is absorbed. The translocation factor1 depends on the amount of heavy metals absorbed from the soil, which gets translocated to the stem/ petiole of the plant. The translocation factor-2 depends on the amount of heavy metals reached the stem / petiole from root and then it gets translocated to the leaf, a site of photosynthesis from where the produced food gets translocated to all parts of the plant body including the flower and then in to the fruiting structure and finally seeds (Fig. 6). We could not collect seeds during this particular study hence the TF3 was not calculated. From BAF and TF values it was clear that these three non crop plants (weeds) which are important for grazers accumulated and translocated heavy metals to different parts of the plant body significantly. Hence these weed plants are supposed to be removed periodically and disposed safely.

Fig.7: Residual heavy metal content in different parts of the effluent exposed plants after 120days of sowing.

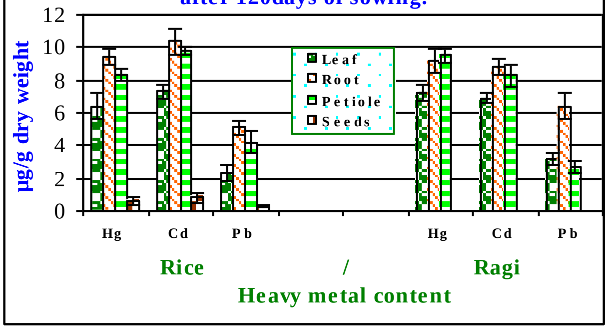


Fig.8: Residual heavy metal content in different parts of the effluent exposed plants after 120days of sowing.

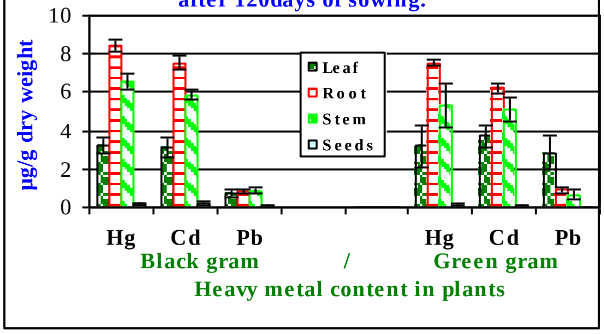


Fig.7-8 showed accumulation of Hg, Cd and Pb in plant parts within a period of 120days after sowing. All the crop plants tested showed notable amount of mercury and cadmium accumulation in roots, leaves and seeds/grains. In root of rice plants highest deposition of mercury and cadmium was noted compared to leaf, petiole and grains. Cadmium accumulation was more than mercury and lead. In case of ragi plants, root accumulated more than other parts of the plant. In case of ragi plants, interestingly no heavy metal accumulation was recorded in the seeds. This point is vital, hence this plant was recommended for cultivation. In case of ragi plants, roots accumulated 24.4µg / g dry weight, leaf accumulated 17.3µg / g dry weight, petiole accumulated 20.5µg / g dry weight and in the grains no accumulation of heavy metals was noted. In case of black gram plants, roots accumulated 16.86µg / g dry weight, leaf accumulated 7.07µg / g dry weight, stem accumulated 13.3µg/g dry weight and the grains accumulated 0.41µg / g dry weight. In case of green gram plants, roots accumulated 14.65µg / g dry weight, leaf accumulated 9.75µg / g dry weight, stem accumulated 11.02µg/g dry weight and the grains accumulated 0.26µg / g dry weight (Fig.7). Ragi plant and plant part showed less accumulation of heavy metals, when compared to rice plants and plant parts. Fig.7-8 showed heavy metal accumulation in green gram and black gram plants and plant parts. In all plant parts accumulation of mercury, cadmium and lead was noted. In case of these two crop plants highest accumulation was recorded in roots than stems than seeds. Green gram plants showed less accumulation than black gram plants. In these two plants mercury accumulated more than cadmium and lead was least accumulated within a period of 120days after sowing. Residual availability in all the four plants is significant. It was noted that the root portion of all the 4 cultivated crop plants accumulated the heavy metals maximum than the stem or petiole part and least amount is accumulated in the leaves of the crop plants. Mercury and cadmium accumulation was highest when compared to lead accumulation in all the 4 cultivated plants. It was also observed that the amount of Hg and Cd availability in the crop field soil was maximum compared to lead concentration. It can be inferred that the residual accumulation of heavy metals in different parts of the plant body is directly related heavy metal availability and concentration in the base which receives the contaminated water from the river.

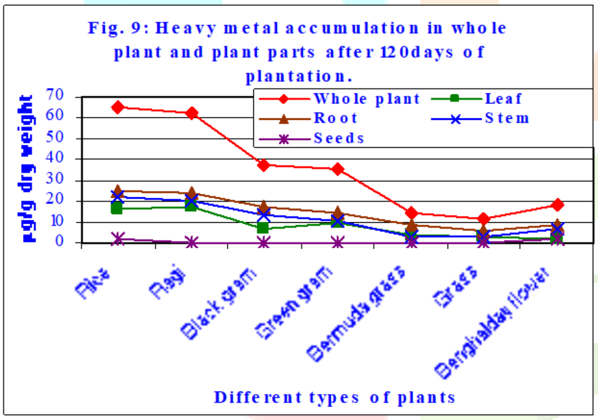


Fig. 9: Heavy metal accumulation in whole plant and plant parts after 120days of plantation.

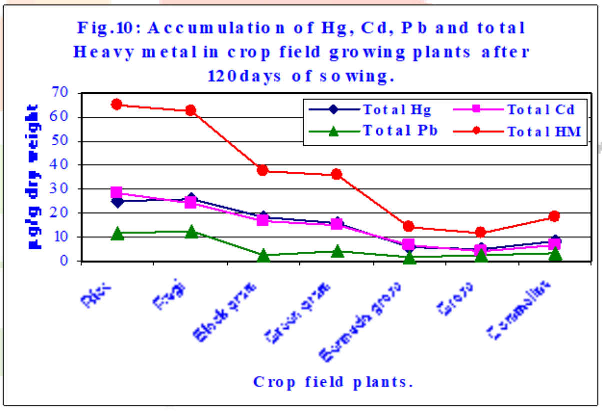


Fig.10: Accumulation of Hg, Cd, Pb and total Heavy metal in crop field growing plants after 120days of sowing.

Fig.9-10 indicated residual accumulation of mercury, cadmium, lead and total heavy metal in whole plant of 7 different plants collected in different seasons of the year. Rice plants accumulated 24.7µg of mercury /g dry weight, 28.3µg of cadmium /g dry weight, 11.9µg of lead /g dry weight and total heavy metal burden was 64.9µg / g dry weight. Ragi plants accumulated 25.9µg of mercury /g dry weight, 24µg of cadmium / g dry weight, 12.3µg of lead /g dry weight and total heavy metal burden was 62.2µg / g dry weight. Black gram plants accumulated 18.5µg of mercury /g dry weight, 16.7µg of cadmium /g dry weight, 2.5µg of lead /g dry weight and total heavy metal burden was 35.7µg / g dry weight. Green gram plants accumulated 16.2µg of mercury /g dry weight, 15.1µg of cadmium /g dry weight, 4.4µg of lead /g dry weight and total heavy metal burden was 35.7µg / g dry weight (fig.9-10). Bermuda grass plants accumulated 6.2µg of mercury /g dry weight, 6.9µg of cadmium /g dry weight, 1.4µg of lead /g dry weight and total heavy metal burden was 14.5µg / g dry weight. Grass plants accumulated 4.8µg of mercury /g dry weight, 4.4µg of cadmium /g dry weight, 2.4µg of lead /g dry weight and total heavy metal burden was 11.5µg / g dry weight. *Commelina* plants accumulated 8µg of mercury /g dry weight, 6.9µg of cadmium /g dry weight, 3.5µg of lead /g dry weight and total heavy metal burden was 18.4µg / g dry weight (fig.9-10).

Discussion

Pulp and Paper mill wastes (effluent) are generally treated to remove the contaminants which can cause serious pollution problem and a threat to the aquatic ecosystem and organisms living therein. The idea of treatment is to remove all toxicants from the waste and convert into an eco-friendly effluent which can be discharged in to natural environment and can be returned to water cycle. All the industries adopt either physical methods or chemical methods or both, for the treatment of waste effluent. It was observed that the Pulp and Paper mill located at Jaykaypur is discharging their treated waste effluent in to River Nagavalli, which is deadly toxic as evinced from the reports of Tripathy *et al*., (2021, 2022a,b) and Mishra *et al*., (2013). This study revealed the status of the effluent by periodic monitoring of the effluent at different time periods and clearly indicated that the effluent waste is highly toxic to aquatic flora & fauna. Report of Mishra *et al*., (2013) and the data presented in this study (2015- 2019) indicated that from 2013 to 2019, the nature and status of the paper mill effluent has not changed notably. No significant variation was noted in the discharged effluent from 2015 to 2019, except few parameters either increased or decreased. This insignificant increase or decrease in effluent parameters can be linked to the use of fresh water in the process of physico-chemical treatment. Higher levels of TSS, TDS, Hardness and lower level of DO in the effluent, indicate toxic nature of the effluent and needs biological treatment. Higher BOD values of the effluent depletes the dissolved oxygen of the effluent and also the flowing water when effluent was added (Nwaehiri *et al*., 2019). The same authors also indicated that high TSS & TDS will increase turbidity and higher turbidity levels may not support diversity of aquatic organisms. High turbidity will reduce penetration of sunlight and restrict the photosynthetic zone only to surface layer. Monitoring, analyzing and characterizing all types of toxicants including heavy metals in aquatic environments indicates the water resource condition, status, usability of water for drinking purposes and agricultural purposes and above all protection of plants, animals, environmental health and human health (Stahl *et al*., 2021). The same author also indicated that aquatic organisms may accumulate contaminants to significant levels much more than the stipulated USEPA (2000) guidelines. This type of bioaccumulation of non-degradable heavy metals in different economically & non-economically important plants, in trophic levels might lead to biomagnification in the ecosystem. Human health ultimately suffers is a major concern for all environmentalists and biologists of the world. Pulp and Paper mill wastes (effluent) are generally treated to remove the contaminants which can cause serious pollution problem and a threat to the aquatic ecosystem and organisms living therein. International Paper Mill at Rajmundry discharges its effluent in to a tank containing *Eichhornia*, *Pistia* and *Azolla* but the retention time of the effluent in treatment pond was very low (Dixit *et al*., 2018) and the so called biologically treated effluent was actually toxic for fish. The idea of treatment is to remove all toxicants from the waste and convert into an eco-friendly effluent which can be discharged in to natural environment and can be returned to water cycle. All the industries adopt either physical methods or chemical methods or both, for the treatment of waste effluent. One most important point to note was the presence of cadmium, mercury and lead in the effluent. Three years obtained data indicated that the industry has paid no interest to improve the physico-chemical status of the effluent even after the report of Mishra *et al*., (2013). Significant decrease in dissolved oxygen followed by significant increase in COD and BOD levels of the discharged effluent of the paper mill warrants attention. Higher values of COD and BOD were due to higher amount of organic matter in the effluent. Heavy metals like cadmium, mercury and lead was found in the effluent of the paper mills collected from site-S. Significant amount cadmium was recorded in the collected effluent sample in 2015, 2017 and 2019.The amount of cadmium in the effluent sample looks very small but significant and toxic and much more than stipulated guidelines prescribed by Pollution Control Board (PCB). Significant amount mercury was recorded in the collected effluent sample in 2015, 2017 and 2019. The amount of mercury in the effluent sample was significant and highly toxic. All the values were much more than stipulated guidelines prescribed by Pollution Control Board (PCB). Minimal amount of lead was recorded in 2015 and 2017 but we could not detect lead in 2019 in the collected effluent samples. Non availability of lead in the effluent sample (2019) is a good sign from environmental stand point. The report submitted by the industry to authorities indicated a different managed story contradicting our reports, which is almost natural and expected. Screening of the literature clearly divulges that the effluent analyzed by different authors from different paper industries indicated the availability of significant amount of heavy metals in the discharged effluent. All the industries in India including JK Paper mills physicochemically treat the effluent before discharge into natural aquatic ecosystems. Most of the treatment processes are either physical or chemical as suggested by recovery technology adopted by industries. None of the industries made any significant attempt to treat the treated effluent biologically before discharge to ensure heavy metal free effluent for discharge in to the aquatic ecosystems. Waste generation and the quality of wastes depend on the technology and used treatment technology by Pulp and Paper industries. It is not possible to eliminate waste generation by the industrial system (Kaur *et al.,* 2021) but cleaner & environment friendly technology can be used and periodically positive modifications in the technology or alterations in the treatment technology should be adopted.

The total heavy metal load in different crop plants was highly significant. Ragi crop plants accumulated 61.65±0.35µg of total heavy metals like Hg, Cd & Pb /g dry weight followed by rice crop plants. Rice crop plants accumulated 55.18±0.47µg of total heavy metals like Hg, Cd & Pb /g dry weight followed by green gram crop plants where the total heavy metal load was 42.75±0.47µg of total heavy metals like Hg, Cd & Pb /g dry weight. Least but significant amount of total heavy metal was absorbed and accumulated in black gram crop plant, where 41.35±0.87µg of total heavy metals like Hg, Cd & Pb /g dry weight. When we compare the heavy metal pollution and its impact on the pigment content of the crop plants, it was clear that heavy metals caused severe injury and affected the metabolic systems of the crop plants. Depletion in pigment content in effluent exposed crop plants when compared to control plant pigments indicated the acute toxic nature of the heavy metals. Residual accumulation in economically important plant leaves were significant and warrant attention to avoid a future environmental catastrophe. Mercury, cadmium and lead are the major abiotic heavy metal stresses. These metals significantly affect the growth, development and gross production of the crop plants. Accumulation of cadmium leads to disturbance of chloroplast function and inhibits the enzymes required for chlorophyll biosynthesis and for CO_2 fixation (Noor *et al*., 2018). Li *et al* (2021a) indicated that "high levels of heavy metal stress may cause irreversible damage to microalgal chloroplasts and prevent photosynthesis, thereby leading to cell death" (Yu *et al*, 2019 and Alho *et al*., 2019). The review article of Hussain *et al* (2021) working on cadmium stress in paddy fields is supportive of our observation and conclusion. Decease in chlorophyll and phaeophytin pigment content in crop plants reduces photosynthesis and ultimately gross production gets affected. Hussain *et al*., (2021) indicated that cadmium stress influences rice growth and suggested that immobilization, adsorption and precipitation of cadmium can reduce plant cadmium uptake. We agree with the findings and suggestions of above authors. The same authors also suggested developing rice genotype with restricted cadmium uptake and for the use of novel microbial strains which can help to reduce plant cadmium uptake. We also agree to the above suggestions. But we are of the opinion that instead of using genetically modified bacteria for cadmium resistance, it will be always wiser to treat the effluent biologically by novel aquatic plants and microalgae and ensure 100% heavy metal removal to save the crop plants from heavy metal stress. Nagarajan *et al.*, (2020) clearly indicated that the discharge of huge amounts of heavy metals in to the different environmental segments and their bioavailability is a potential threat to human, animal and plant life. Borah *et al* (2018) indicated "high mobility factor values represented relatively higher biological activity of cadmium and copper in paper mill effluent exposed soil samples and hinted that the industry could pose serious environmental threats in the surrounding areas of the Paper mill". Li *et al.*, (2021b) reported cadmium contamination in crop fields as a serious human health concern because of its extreme toxicity and wide spread pollution. We do agree with their concern basing on our findings. The same authors indicated that much progress has been made in elucidating the mechanisms involved in Cd uptake, transport and transformation from paddy soils to rice grains. All the three heavy metals like Hg, Cd, and Pb present in the paper mill effluent is deadly toxic and seriously affects all types of plants and animals once exposed. All the plants and animals readily absorb and accumulate these heavy metals in their body tissues from the surrounding environment. Accumulation of heavy metals in the crop field weeds were also equally significant as these two weeds of the crop field is grazed by the grazers and the possibility of biomagnification of heavy metals in the food chain can not be rules out. The significant accumulation of other weeds tested at higher concentrations of the heavy metals may cause death but from ecological stand point it is a process of removal of heavy metals from the contaminated crop fields. We feel to suggest that periodically these crop fields should be abandoned and non-economical plants should grown, so that accumulated heavy metals can be absorbed and removed from the crop fields a process of detoxification of the contaminated crop fields.

Conclusion

Pulp & Paper Mill effluent collected from Jaykaypur in different years was found to be highly toxic. The effluent waste is discharged into River Nagavalli after physicochemical treatment inside the premises of the industry. No proper biological treatment of the effluent is made prior to discharge into the natural environment. Effluent contained highly toxic organic debris and inorganic chemicals including toxic metals like Hg, Cd and Pb. The effluent is loaded with organic debris with high BOD & COD value with significant amount of TDA & TSS. Higher bioaccumulation of heavy metals like Hg, Cd and Pb in crop plant tissues reduced the photosynthetic efficiency by depleting the pigment content, ultimately reducing vegetative and reproductive production. Heavy metal accumulation in crop plants is a serious concern for all. Accumulation of heavy metals on non crop plants grazed by grazers is also a serious matter needs attention. Bioaccumulation leading to biomagnification is another area of concern where human beings will ultimately suffer. Hence, 100% removal of heavy metals from the effluent by proper biological treatments is necessary and the contaminated river water should not be used to irrigate the crop fields. Government should provide alternate water supply like tube or bore wells for irrigation.

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Declarations

Author contribution statement

Prof. A.K. Panigrahi: Conceptualization, planning and execution of the project, Original draft preparation, supervision, reviewing and editing; Research work conducted by scholar - A. P. Tripathy paper mill effluent collection of samples, analysis and related experimental work. Tripathy contributed reagents, glassware and field related work.

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