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Risk Assessment of Heavy Metals Contamination in Soil and Two Rice (*Oryza sativa* L.) Varieties Irrigated with Paper Mill Effluent

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Abstract: Heavy metal pollution from industrial wastewaters has become an issue of global concern. These wastewaters are frequently used for inland irrigation which possess a serious risk of heavy metal contamination of both soil and cultivated crops. The problem is more common in developing countries like India where industrial wastewaters are often discharged without appropriate treatments. Therefore, this study aimed at assessing the impact of paper mill effluent for irrigation on the growth, productivity, and heavy metal accumulation potential of two rice (*Oryza sativa* L.) varieties (PB-1121 and PR-121). Water, soil, and rice crop samples were obtained from the vicinity of Saharanpur city, Uttar Pradesh, India, and subsequently analyzed for selected physicochemical and heavy metal parameters. Results showed that paper mill effluent and nearby Kali River water had significant ($p < 0.05$) loads of pollutants that impacted the soil properties. Moreover, the maximum plant height (123.48 ± 4.86 and 98.83 ± 2.02 cm); total chlorophyll (6.70 ± 0.25 and 6.64 ± 0.17 mg/g); leaf carotenoids (0.67 ± 0.08 and 0.63 ± 0.05 mg/g); starch content (71.08 ± 2.05 and 72.60 ± 1.63%); amylose content (25.10 ± 1.32 and 20.28 ± 1.24%); crop yield (4270.20 ± 75.12 and 5830.58 ± 63.10 kg/ha); and straw yield (5472.05 ± 93.90 and 6683.76 ± 61.26 kg/ha) of PB-1121 and PR-121, respectively, were observed using Kali River water irrigation source as compared to paper mill effluent and borewell water. The order of heavy metal accumulation in rice straw and grain followed: Fe > Mn > Zn > Cu > Cr > Cd. Similarly, the bioaccumulation factors for heavy metals in rice straw and grain were observed as >1 and <1, respectively. Moreover, the target hazard quotient (THQ) showed that there was no potential health risk of heavy metal in rice irrigated with contaminated water supply except for the PR-121 variety irrigated with Kali River water where the health risk index (HRI) value exceeded the limit (>1). As a result, the findings of this study provide useful information about the current state of heavy metal pollution and the health risks associated with rice crops irrigated with contaminated water sources.

Keywords: crop contamination; health risks; heavy metals; industrial pollution; wastewater irrigation

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1. Introduction

Water insecurity and pollution of limited available water resources are of the major challenges of the twenty-first century. According to the report of the United Nations [1], around 80% of wastewater is discharged into the environment without any pre-treatment. Among these wastewaters, industrial ones contain dangerous heavy metals, nitrates, nitrites, organic carbon, and organic and inorganic phosphorus of high concentration levels threatening humans and aquatic lives [2]. A direct result of such wastewaters' discharge into water sources is the eutrophication and the constitution of a toxin-producing waterborne pathogens' platform [3]. The impact study of such wastewaters' reuse in crop irrigation is usually investigated but lacks reliability in most cases [4]. It was reported that the type of wastewater and the sensitivity of plant species regulate the negative impact of industrial wastewater on cultivated crops [5]. Although these authors outlined that industrial wastewater did not affect seed germination of lettuce (*Lactuca sativa*) cucumber (*Cucumis sativus*), and muskmelon (*Cucumis melo*), it decreased the root and shoot length of *C. sativus*. However, the application of industrial wastewaters in common wheat (*Triticum aestivum*) resulted in reductions in seed germination, seedling fresh and dry weights, vigor and tolerance indices, plant height, number of leaves, root fresh and dry weights, shoot fresh and dry weights [6]. The pesticide residues, oils as well as heavy metals found in industrial wastewater are considered threatening contaminants that impart disorders in soil microbiota functioning and deleterious effects on crop productivity, crop composition, and thus pose as potential human health risks [7].

On the other hand, soil chemical composition may contribute to heavy metals' leaching and their increased mobility when soil pH decreases [8]. In this context, positive correlations were found between soil pH and amounts of manganese (Mn), cadmium (Cd), and lead (Pb) with Cd and Pb being the most highly mobile heavy metals in soil [9]. Besides their increased mobility and leaching potential in low pH soil, heavy metals are high competitors to adsorption and subsequent uptake by plants [10], which inhibits other essential metals' absorption by the latter. Regarding soil microbiota, it was reported that chromium (Cr) significantly limits soil bacteria and *Actinomycetes* populations [11]. These microbiotas have shown a decrease in their biological activity in acidic soils, translated by the inhibition of free nitrogen fixation and therefore a decrease in arable land fertility [12]. The strong correlation between soil organic matter and available nitrogen on one hand and richness and diversity in soil microbiota on the other hand further explains how heavy metals directly affect the latter [13]. Furthermore, two Gram-positive isolates found naturally in soil (*Paenibacillus* sp. and *Bacillus thuringeinsis*) have shown some tolerance for increased Cd and zinc (Zn) concentrations for the former and copper (Cu) concentration for the latter [14]. Although these findings are promising, most soil microbiotas including the two isolates still suffer from increased heavy metal concentrations as being highly sensitive, pushing them to adopt defensive mechanisms to survive [15]. Moreover, a human intervention consisting of the raise of soil pH can contribute to the suppression of Cd and Cu accumulation in wheat grains [16]. However, once soil microbiotas are affected, crop yield, composition, and quality are consequently altered. Lead-contaminated wheat fields showed reduced chlorophyll *a* and *b* and carotenoid contents besides increased human health risk. Potassium, phosphorus, and protein contents were also decreased by 55, 60, and 81%, respectively. The number of seeds per plant, seed weight per plant, and harvest index were reduced by 90, 88, and 61%, respectively [6]. Another study mentioned that high Cd concentrations in *L. sativa*, *Pichia* spp. and *Azotobacter chroococcum* soils hindered roots' growth and development, reduced yield, and inhibited seeds germination [17].

Rice (*Oryza sativa* L.) crop is considered the staple food for over half of the global population. According to a recent report, around 510 million metric tons of rice are produced annually in the world [18]. China and India are the leading producers and consumers (around 50% of the world's production) and their traditional cuisine relies on this nutritious crop. By the end of 2022, around 515 million metric tons of rice are expected to be produced with 25.04% in India alone (https://worldpopulationreview.com/

country-rankings/rice-production-by-country (accessed on 20 September 2022)). Rice is a rich source of antioxidants, carbohydrates, minerals, proteins, and vitamins essential for the human diet and health [19]. However, these outstanding properties risk being seriously affected if rice fields are subjected to heavy metal contamination. Rice grains tend to actively bioaccumulate heavy metals originating from contaminated soils; therefore, soil properties are considered the most influencing factor [16]. Rice grown in the vicinity of Turag Riverbank (Bangladesh), in which large disposal of industrial effluents occur, was reported to be highly infested leading to low fertility and yield. High Cd, Pb, and nickel (Ni) concentrations were observed in both water and soil being above the safe limits. In brief, these industrial effluents resulted in dangerous soil degradation (decrease in soil quality by 100%), making these fields inappropriate for subsequent cultivation [20]. Moreover, dermal diseases were detected among nearby locals which poses a serious human health risk.

Star Paper Mill is a paper manufacturing mill located in Saharanpur District, Uttar Pradesh. Its production is estimated at 2500 tons per day [21]. The factory disposes of its effluent through a long canal into the Kali River. These effluents are subsequently and directly used by farmers to irrigate PB-1121 and PR-121 hybrid rice varieties. These varieties are the major and most prestigious species cultivated in India owing to their high productivity and superior quality attributes. Thus, the current study aims to investigate the risk associated with potentially toxic heavy metals accumulation in soil and two rice varieties (PB-1121 and PR-121) irrigated with paper mill effluent.

2. Materials and Methods

2.1. Description of Study Area

The present study was carried out in the suburban vicinity of Saharanpur city, Uttar Pradesh, India. The study site was in north-west of the Saharanpur city with several residential and agricultural establishments (29°56′20.20″ N and 77°34′17.10″ E). Herein, rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.), and sugarcane (*Saccharum officinarum* L.) are the most grown crops. In this region, Star Paper Mill Ltd. is the biggest industrial unit of the district with estimated paper production of more than 2500 tons per day [21]. This paper mill generates a huge load of effluent, which is released into the nearby river, namely Kali. This mill discharges its water in a 2 m wide and 3 km long drain, which passes through agricultural fields and connects to the Kali River. Several farmers of nearby fields directly utilize the effluent from the drain to irrigate their lands. Moreover, several farmers also exploit the water from the Kali River to irrigate their crops. Figures 1 and 2a,b show the location of Star Paper Mill Ltd. and selected sampling sites. In this study, a total of nine sampling sites were taken, including three borewell irrigated sites as control, three sites irrigated with absolute paper mill effluent, and three sites irrigated with Kali River water (after the disposal of paper mill effluent).

2.2. Description of Studied Rice Varieties

The two selected rice varieties viz., Pusa Basmati (PB) 1121 and PR-121 are commonly grown in North India due to their specific marketable and profitable features. PB-1121 is a popular rice variety developed with help of Basmati 370 and Type 3 varieties. With exceptional elongation, expansion, and aromatic features, this variety best suits the soils of the Saharanpur district thereby making it highly marketable and preferred by farmers. PB-1121 achieves a plant height of 120–130 cm, matures in 130–150 days, and gives an average yield of 5500 kg/ha [22]. Additionally, this variety is highly preferred for creating more resistant and beneficial crop seeds. On the other hand, PR-121 is a semi-dwarf and high-yielding rice variety developed by Punjab Agricultural University, Ludhiana, India. PR-121 achieves an average plant height of 98 cm, has long slender translucent grains, and gives a yield of 7601 kg/ha in 140 days [23]. PR-121 is resistant to nearly 10 pathogenic diseases including bacterial blight. These distinct features make this variety popular in the Saharanpur district. Therefore, the current study was carried out to assess the impact of paper mill effluent for irrigation on soil and selected rice varieties (PB-1121 and PR-121) grown in the semi-urban vicinity of Saharanpur city.

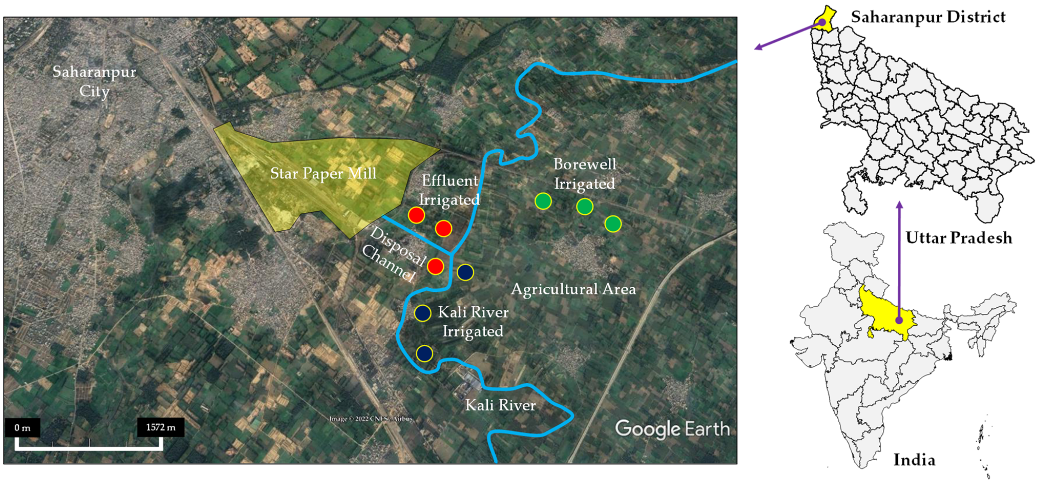

Figure 1. Map view of the Star Paper Mill situated in Saharanpur district of Uttar Pradesh, India, and its adjoining agricultural areas (Source: Google Earth Pro).

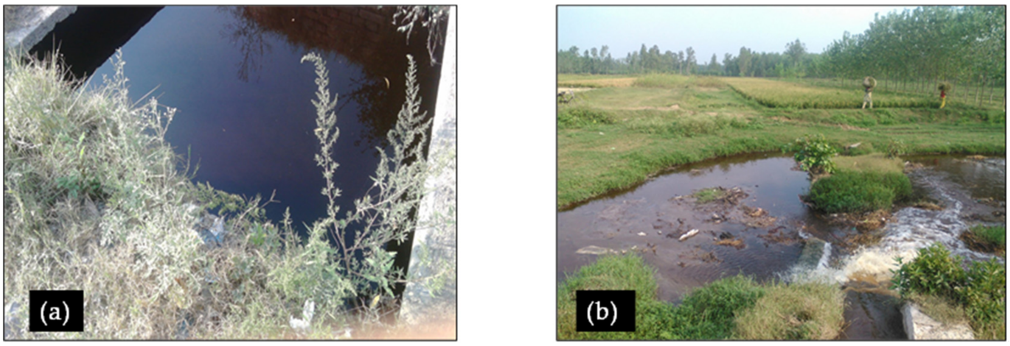

Figure 2. (**a**) Disposal channel carrying effluent of Star Paper Mill and (**b**) disposal point connecting to Kali River with a view of rice fields (Photos: Jogendra Singh).

2.3. Sample Collection and Chemical Analysis

For the current study, water, soil, and rice plant samples were collected from July to November 2021. The water samples (borewell, paper mill effluent, and Kali River water) were collected in 5 L capacity plastic cans while soil and rice samples were collected in 2 kg capacity zip-locked polyethylene bags. The soil and water samples were collected in three phases, i.e., vegetative growth stage (0–10 days after transplanting), reproductive stage (60–70 days), and grain filling (100–140 days). However, the straw and grain samples were collected after the final harvesting and drying stage. Purposely, the water and soil samples were analyzed for selected physicochemical and heavy metal parameters following the standard protocols described by APHA [24] and AOAC [25]. In this, pH, electrical conductivity, and total dissolved solids were determined by using a microprocessor-based multi-meter (1611, ESICO, Parwanoo, India). Biochemical and chemical oxygen demands (BOD_5 and COD) were estimated by using a digital dissolved oxygen meter (1801, ESICO, Parwanoo, India) and an open-reflux digester, respectively. Nitrogen contents were determined following Kjeldahl's method [26]. Organic matter of soil was analyzed following Walkley and Black method [27]. Similarly, the contents of potassium (K) were determined by using a flame-photometer (1382, ESICO, Parwanoo, India) while phosphorus was determined by using a UV-Vis spectroscopy (Cary 60, Agilent Technologies, Santa Clara, CA, USA) as previously described by Kumar et al. [28]. Finally, the contents of six heavy metals (Cd, Cr, Cu, Fe, Mn, and Zn) were determined by using atomic absorption spectroscopy (Analyst 800, PerkinElmer, Waltham, Massachusetts, USA) [29]. The detection limit of AAS for selected heavy metals was (Cd: 3 μg/L; Cr: 4 μg/L; Cu: 4 μg/L; Fe: 5 μg/L; Mn: 3 μg/L; and Zn: 3 μg/L). The certified reagent materials and analytical conditions are described earlier in our previous study [28]. Selective hollow cathode lamps were cast-off at optimum current and operated in accordance with the manufacturer's standard operating procedures (SOPs). The slit width was set to 0.5 nm, and the AAS was run with an air/acetylene gas mixture. Calibration curves were created using standard heavy metal solutions (0 as the control, 0.5, 1, 5, 10, 50, and 100 mg/L). The maximum recovery percentage (>98%) was used to perform quality assurance of the heavy metal analysis results. All analyses were carried out in triplicate.

2.4. Data Analysis

Heavy metals are known to accumulate in plant tissue, but the amount accumulated by each plant varies. The bioaccumulation factor (BF) is a measure of how much a plant can absorb in comparison to the surrounding soil. This indicator is very important because it can help researchers understand how plants react to contamination and subsequent amelioration of the contaminated sites [6]. In this study, BF was used to assess the heavy metal accumulation potential efficiency of two rice varieties irrigated with different water sources. The form of the index is given in Equation (1):

$$\text{Bioaccumulation factor (BF)} = \text{HMR}/\text{HMS} \quad (1)$$

where, HMR and HMS represent the heavy metal concentration in rice (grain) and soil, respectively. Also, the health risk of heavy metal accumulation in two rice varieties was investigated using the target hazard quotient (THQ) tool [30]. The form of the index is given in Equation (2):

$$\text{THQ} = 10^{-3} \times \frac{Ef \times Ed \times Ir \times HMc}{Bw \times Cp \times Rd} \quad (2)$$

where, *Ef* is exposure frequency, *Ed* is exposure duration (365 days), *Ir* is the rice ingestion rate, *HMc* is the heavy metal concentration in rice sample (mg/kg), *Bw* is the average body weight (70 Kg for adult and 16 Kg for child group), *Cp* is the consumption period (25,550 days for adult and 5840 days for child groups), *Rd* is the reference doses (Cd: 5.0×10^{-4}; Cr: 3.0×10^{-3}; Cu: 4.2×10^{-2}; Fe: 7.0×10^{-1}; Mn: 1.4×10^{-2}, and Zn: 3.0×10^{-1}), and 10^{-3} is the conversion factor, respectively. The combined toxicity of heavy metal intake from rice varieties was calculated by using the following Equation (3):

$$\text{HRI} = \sum \text{THQ}_{\text{Cd} + \text{Cr} + \text{Cu} + \text{Fe} + \text{Mn} + \text{Zn}} \quad (3)$$

Moreover, the data obtained in this study were tested using a one-way analysis of variance (ANOVA) to derive the significant difference between water source, irrigated soils, and rice plant growth/yield parameters. The level of statistical significance was adjusted as the probability (p) < 0.05.

2.5. Software and Tools

In this study, Microsoft Excel 2019 (Microsoft, Redmond, WA, USA) and OriginPro 2022b (OriginLab, Northampton, MA, USA) software packages were used for the data analysis and visualization.

3. Results and Discussion

3.1. Characteristics of Effluent and Agricultural Soils

The chemical analysis results of the studied irrigation water sources are shown in Table 1. Results revealed that all water sources had a pH value within the safe limits for surface disposal and inland irrigation set by the Central Pollution Control Board of India (CPCB) and Bureau of Indian Standards (BIS), respectively, with the following decreasing order: paper mill effluent > borewell > Kali River water. Paper mill effluent and Kali River water both had significantly higher EC values compared to borewell water. All water sources' TDS were below the safe limit for surface disposal, and their values in paper mill effluent > Kali River water surpassed the borewell's TDS value. A TDS level lower than 700 mg/L is considered adequate for crop irrigation; whereas, a range of 700–2000 mg/L may be slight to moderately restricted for use [31]. A similar trend was observed regarding BOD where paper mill effluent and Kali River water had 200.0-fold and 69.2-fold higher contents, respectively, compared to borewell. The former surpassed the safe limit for both surface disposal and inland irrigation. However, COD levels were in the following decreasing order: paper mill effluent > Kali River water > borewell with the first two sources having higher values than the latter. High BOD and COD levels in irrigation water led to lower oxygen availability for crops as a result of decreased soil permeability and therefore a direct effect on plant growth [32]. Similarly, paper mill effluent and Kali River water had significantly higher TKN values compared to borewells. The higher TKN level in Kali River water compared to paper mill effluent simulates possible discharge of sewage or leached manure already applied to nearby crop fields. Total K and total P contents were higher in paper mill effluent and Kali River water compared to the borewell. It was reported that high K levels can decrease water infiltration in irrigated soils [33], whereas the high P levels in water sources (probably originating from extensive use of fertilizers) can accelerate eutrophication and lead to ravaging algal blooms [34]; thus, causing devastating impacts on rice fields.

Table 1. Average characteristics of irrigation water sources (borewell, paper mill effluent, and Kali River water) of the study area.

Parameters	Irrigation Water Sources			Limit for Surface Disposal [a]	Limit for Inland Irrigation [b]
	Borewell	Paper Mill Effluent	Kali River Water		
pH	7.56 ± 0.11 b	8.14 ± 0.24 c	6.09 ± 0.37 a	5.50–9.00	5.50–9.00
Electricidal Conductivity (EC: dS/m)	0.61 ± 0.35 a	5.30 ± 0.09 c	4.07 ± 0.18 b	*Na*	*Na*
Total Dissolved Solids (TDS: mg/L)	110.36 ± 9.12 a	1409.62 ± 15.02 c	850.04 ± 29.05 b	1900.00	*Na*
Biochemical Oxygen Demand (BOD: mg/L)	4.05 ± 0.35 a	810.09 ± 20.38 c	280.26 ± 11.47 b	100.00	30.00
Chemical Oxygen Demand (COD: mg/L)	8.20 ± 0.26 a	1610.50 ± 18.01 c	709.45 ± 17.60 b	250.00	250.00
Total Kjeldahl's Nitrogen (TKN: mg/L)	8.12 ± 0.54 a	110.43 ± 3.70 c	140.06 ± 10.31 b	100.00	100.00
Total Potassium (K: mg/L)	6.41 ± 2.29 a	106.93 ± 4.58 c	82.24 ± 7.40 b	*Na*	*Na*
Total Phosphorus (*p*: mg/L)	4.46 ± 0.18 a	98.20 ± 5.07 c	31.03 ± 3.17 b	*Na*	5.00
Cadmium (Cd: mg/L)	*Bdl*	0.69 ± 0.08 a	3.70 ± 0.46 b	2.00	2.00
Chromium (Cr: mg/L)	*Bdl*	5.43 ± 0.12 b	2.50 ± 0.23 a	2.00	*Na*
Copper (Cu: mg/L	0.03 ± 0.01 a	1.90 ± 0.06 b	4.85 ± 0.39 c	3.00	3.00
Iron (Fe: mg/L)	0.62 ± 0.03 a	5.62 ± 0.17 b	11.07 ± 0.74 c	1.00	3.00
Manganese (Mn: mg/L)	0.38 ± 0.04 a	3.88 ± 0.21 b	6.28 ± 0.29 c	1.00	2.00
Zinc (Zn: mg/L)	0.26 ± 0.02 a	2.54 ± 0.19 b	9.64 ± 0.41 c	15.00	5.00

Different letters (a–c) indicate a significant difference ($p < 0.05$) between irrigation water sources; *Bdl*: below detectable limits; *Na*: not available; [a]: Central Pollution Control Board of India (CPCB); [b]: Bureau of Indian Standards (BIS).

In the case of heavy metals, Cd and Cr levels were very low in the borewell; therefore, they were undetectable. Kali River water had both Cd and Cr levels higher than the safe limit for surface disposal and inland irrigation. High Cd levels in irrigation water can lead to the disruption of plant mechanisms, nutrient uptake, and translocation in water and plants besides soil contamination [35], whilst high Cr levels in irrigation water can lead to oxidative stress, thus inhibiting some crop growth parameters [36] and subsequent bioaccumulation affecting human health [37]. Similarly, Cu, Fe, Mn, and Zn levels were higher in paper mill effluent and Kali River water than in borewell water. Specifically, Cu and Zn levels in paper mill effluent were below the safe limits for both surface disposal and inland irrigation, whereas Fe and Mn levels within the same irrigation water source surpassed these limits. Although the Zn level in Kali River water was below the safe limit for surface disposal, it was higher than that for inland irrigation. High Cu levels in irrigation water were associated with severe phytotoxicity symptoms [38]. Moreover, the Fe-enrichment of irrigation water was previously reported to adversely affect rice productivity [39], whereas high Mn levels in irrigation water were associated with potential toxicity stress imposed on cultivated crops [40]. Furthermore, reduced crop growth was earlier reported due to high zinc levels in water irrigation; this impact is accentuated if salt stress occurs [41].

Results presented in Table 2 depicted that although there were significant differences between irrigated soils in terms of pH, all of them were neutral. The rice crop is to some extent tolerant to acidity. It was reported that a pH of 6 is suitable for this crop's cultivation and pH values ranging between 5 and 8 are acceptable [42]. In this study, paper mill effluent- and Kali River water-irrigated soils had a higher EC compared to borewell-irrigated soils. Moreover, soils irrigated with paper mill effluent and Kali River water had a higher organic matter content compared to borewell-irrigated soils. This may improve soil aeration and reduce soil compaction around roots [43]. Also, TKN increased in soils irrigated with paper mill effluent and Kali River water. Such increases simulate increased ammonia in soils which were reported to halt the growth of crops, i.e., alfalfa [44]. Similarly, paper mill effluent and Kali River water-irrigated soils were richer in K than those irrigated using borewells. Although K is an essential component for crop yield improvement and soil enrichment, extremely high amounts can inhibit Mg uptake by crops [45]. For the heavy metals (Cd, Cr, Cu, Fe, Mn, and Zn), their contents increased maximally in paper mill effluent irrigated soils followed by Kali River water. Increased heavy metals in soils were associated with reduced microbial populations, their diversity, and activity; cytotoxic effect on soils, and phytotoxicity in plants leading to reduced plant growth and chlorosis [46].

Table 2. Average characteristics of soils irrigated with borewell, paper mill effluent, and Kali River water in the study area.

Parameters ^	**Irrigated Soils**		
	Borewell	**Paper Mill Effluent**	**Kali River Water**
pH	7.24 ± 0.05 b	7.69 ± 0.07 c	6.80 ± 0.20 a
Electricidal Conductivity (EC: dS/m)	2.27 ± 0.16 a	4.80 ± 0.22 c	3.10 ± 0.19 b
Organic Matter (OM: %)	2.86 ± 0.12 a	5.10 ± 0.42 bc	4.74 ± 0.34 b
Total Kjeldahl's Nitrogen (TKN: mg/kg)	124.16 ± 3.09 a	261.20 ± 10.08 c	210.42 ± 7.25 b
Potassium (K: mg/kg)	56.72 ± 8.26 a	220.89 ± 6.07 c	190.65 ± 10.81 b
Total Phosphorus (TP: mg/kg)	34.61 ± 5.32 a	128.48 ± 3.31 c	110.29 ± 8.03 b
Cadmium (Cd: mg/kg)	0.21 ± 0.05 a	5.10 ± 0.12 b	6.16 ± 1.15 bc
Chromium (Cr: mg/kg)	1.07 ± 0.09 a	9.89 ± 0.21 c	4.32 ± 0.38 b
Copper (Cu: mg/kg)	2.90 ± 0.14 a	16.43 ± 0.10 b	29.60 ± 2.42 c
Iron (Fe: mg/kg)	16.07 ± 0.26 a	47.21 ± 1.03 b	59.07 ± 3.95 c
Manganese (Mn: mg/kg)	1.50 ± 0.09 a	8.43 ± 1.04 b	11.51 ± 0.46 c
Zinc (Zn: mg/kg)	2.43 ± 0.12 a	12.08 ± 0.67 b	18.02 ± 1.28 c

^: The unit of all parameters is mg/kg except for pH, EC, and OM; Different letters (a–c) indicate a significant difference ($p < 0.05$) between irrigated soil parameter values.

3.2. Growth and Productivity of Selected Rice Varieties

Rice yield can be significantly influenced by water quality. Low germination rates, reduced plant growth, and increased susceptibility to disease can all be caused by poor water quality. In extreme cases, it can even cause crop death. However, when water contains sufficient levels of bioavailable nutrients, rice yield is impacted positively. In general, however, effluent irrigation can have a positive impact on rice yields, especially in areas where water is scarce. Additionally, using effluent to irrigate crops can help to reduce water pollution and the spread of disease. At the same time, if effluent contains noxious chemicals, it may be dangerous for both soil health and crop plants [47]. Table 3 shows the impact of irrigation water sources on the growth and productivity of selected rice varieties. Results showed that the average height of PB-1121 did not vary significantly ($p < 0.05$) among all irrigated soils. However, PR-121 outlined a significant increase in plant height in Kali River-irrigated soils compared to borewell-irrigated as control. This increase may assume an overexpression of *OsMPH1* which regulates rice crop height and subsequently grain yield [48]. In addition, total chlorophyll and carotenoid contents increased significantly in PB-1121 and PR-121 varieties when irrigated with paper mill effluent and Kali River water as compared to borewell water. This result simulates an interaction between *NRL3* and *NAL9/VYL* regulating the leaf morphology of rice and inducing the accumulation of chlorophyll [49]. Such an increase was previously reported to be the consequence of *OsDXS2* and *OsGLK1* overexpression [50]. In another study, increased total chlorophyll and carotenoid contents per leaf area were outlined as responses to increased salinity in wheat [51]. Our findings also confirm this simulation as high salinity levels were found in irrigation water sources used and in soils of grown fields. In the case of harvested rice grain properties, the starch and amylose content increased significantly ($p < 0.05$) in PB-1121 and PR-121 varieties when irrigated with paper mill effluent and Kali River water. Increased starch content in rice was associated with better consumer health pronounced by improved digestibility [52]. Increased rice quality was mainly attributed to an increased amylose percentage within rice grains. Moreover, the yield of both rice varieties increased when irrigated with paper mill effluent and the Kali River. As aforementioned, increased grain yields can be attributed to the overexpression of *OsMPH1* [48]. Besides that, the increased leaf area surface may have promoted the photosynthesis mechanism and subsequently total chlorophyll and grain yield. Similarly, the straw yield of both varieties also improved significantly.

Table 3. Impact of different irrigation water sources on growth and productivity performance of two rice varieties.

Parameters	Irrigated Soils and Rice Varieties					
	Borewell		Paper Mill Effluent		Kali River	
	PB-1121	PR-121	PB-1121	PR-121	PB-1121	PR-121
Plant Height (cm)	113.47 ± 5.02 c	93.82 ± 3.68 a	118.38 ± 7.15 c	97.64 ± 2.40 ab	123.48 ± 4.86 cd	98.83 ± 2.02 b
Total Chlorophyll (mg/g)	5.09 ± 0.13 a	5.12 ± 0.10 a	5.86 ± 0.22 bc	5.45 ± 0.17 b	6.70 ± 0.25 d	6.64 ± 0.17 d
Leaf Carotenoids (mg/g)	0.51 ± 0.05 a	0.53 ± 0.09 a	0.60 ± 0.07 ab	0.57 ± 0.04 a	0.67 ± 0.08 b	0.63 ± 0.05 b
Starch Content (%)	60.70 ± 3.70 a	62.76 ± 2.10 a	67.39 ± 1.82 b	69.98 ± 2.28 b	71.08 ± 2.05 bc	72.60 ± 1.63 c
Amylose Content (%)	21.01 ± 1.20 a	19.49 ± 0.97 a	23.35 ± 1.70 ab	20.09 ± 0.69 b	25.10 ± 1.32 bc	20.28 ± 1.24 bc
Crop Yield (kg/ha)	3710.50 ± 150.40 a	5244.02 ± 69.10 d	4050.92 ± 81.53 b	5566.12 ± 131.09 e	4270.20 ± 75.12 c	5830.58 ± 63.10 f
Straw Yield (kg/ha)	5110.17 ± 86.53 a	6035.20 ± 80.18 c	5318.17 ± 30.85 b	6481.30 ± 45.73 d	5472.05 ± 93.90 b	6683.76 ± 61.26 e

Different letters (a–f) indicate a significant difference ($p < 0.05$) between irrigated rice parameter values.

3.3. Heavy Metal Accumulation in Selected Rice Varieties

The results of heavy metal concentrations in straw and grain of grown rice varieties in different irrigated soils are reported in Table 4. Specifically, Cd, Cr, Cu, Fe, Mn, and Zn accumulated in the straw of PB-1121 and PR-121 rice varieties were in the following ranges: 0.19–0.27 mg/kg and 0.20–0.31 mg/kg; 0.82–1.40 mg/kg and 0.92–1.51 mg/kg; 13.52–21.67 mg/kg and 14.10–23.04 mg/kg; 178.76–290.53 mg/kg and 212.65–310.98 mg/kg; 78.54–112.67 mg/kg and 62.40–105.43 mg/kg; 19.26–28.66 and 21.58–30.32 mg/kg. In this study, both varieties' grains enclosed acceptable ranges of Cd (0.03–010 mg/kg), Cr (0.15–0.41 mg/kg), Cu (1.30–2.10 mg/kg), Fe (14.09–24.29 mg/kg), Mn (1.48–2.81 mg/kg) and Zn (1.87–3.21 mg/kg) being lower than the safe limits (0.1–0.2 mg/kg, 1.0 mg/kg, 20.0 mg/kg, 425.5 mg/kg, 500.0 mg/kg, and 100.0 mg/kg, respectively) set for cereals and legumes [53–55]. Moreover, the bioaccumulation factor (BF) of heavy metals in the straw of both rice varieties followed a decreasing order of Fe > Mn > Zn > Cu > Cr > Cd. However, higher bioaccumulation of heavy metals was encountered in paper mill effluent irrigated rice followed by Kali River and borewell. The bioaccumulation factors in rice straw of PB-1121 and PR-121 are depicted in Figure 3. In fact, all bioaccumulation factors in rice grains were acceptable (<1.0) [56], except for Mn in PB-1121 and PR-121 varieties irrigated with borewell. Although high heavy metal accumulation was observed in both soil and water, they did not have serious impacts on the final product. This was also observed in the case of other crops grown on industrial media with high heavy metal accumulation [28]. This may be attributed to a high Mn adsorption and/or high Mn transport across the plasma membrane into root cell walls [57]. Moreover, increased Mn concentrations in food can lead to neurotoxicity expressed by neuroinflammation, oxidative stress, and cognitive dysfunction possibly impairing Parkinson's disease [58]. Rice straw is generally burned in fields resulting in increased greenhouse gas emissions and further pollutant enrichment of rice soils and crops in subsequent cycles [59].

Table 4. Impact of different irrigation water sources on heavy metal accumulation (mg/kg) in grains of two rice varieties.

Rice Parts	Heavy Metals	Irrigated Soils and Rice Varieties					
		Borewell		Paper Mill Effluent		Kali River	
		PB-1121	PR-121	PB-1121	PR-121	PB-1121	PR-121
Straw	Cd	0.19 ± 0.02 a	0.20 ± 0.03 a	0.23 ± 0.02 a	0.25 ± 0.03 ab	0.27 ± 0.04 b	0.31 ± 0.02 b
	Cr	0.82 ± 0.05 a	0.92 ± 0.08 ab	1.40 ± 0.13 c	1.51 ± 0.09 c	1.10 ± 0.15 b	1.22 ± 0.07 b
	Cu	13.52 ± 0.28 a	14.10 ± 0.51 a	18.16 ± 1.02 b	20.45 ± 0.92 b	21.67 ± 1.36 bc	23.04 ± 0.65 c
	Fe	178.76 ± 6.91 a	212.65 ± 10.75 b	254.02 ± 12.08 c	272.18 ± 20.78 c	290.53 ± 12.45 d	310.98 ± 21.04 d
	Mn	78.54 ± 3.35 b	62.40 ± 6.02 a	110.78 ± 11.21 cd	90.65 ± 9.42 c	112.67 ± 8.22 d	105.43 ± 7.60 cd
	Zn	19.26 ± 0.70 a	21.58 ± 0.56 a	25.02 ± 1.40 b	27.02 ± 1.01 b	28.66 ± 0.95 bc	30.32 ± 1.24 c
Grain	Cd	0.03 ± 0.01 a	0.04 ± 0.02 a	0.06 ± 0.02 ab	0.07 ± 0.01 b	0.09 ± 0.02 bc	0.10 ± 0.02 c
	Cr	0.15 ± 0.02 a	0.16 ± 0.03 a	0.39 ± 0.06 b	0.41 ± 0.04 b	0.31 ± 0.02 b	0.36 ± 0.05 c
	Cu	1.60 ± 0.05 a	1.68 ± 0.04 a	1.73 ± 0.04 ab	1.82 ± 0.12 b	2.02 ± 0.09 c	2.10 ± 0.11 c
	Fe	14.09 ± 0.36 a	15.04 ± 0.82 a	20.11 ± 1.27 b	21.18 ± 0.96 b	22.30 ± 1.55 bc	24.29 ± 0.83 c
	Mn	1.72 ± 0.20 ab	1.48 ± 0.13 a	2.34 ± 0.32 c	2.05 ± 0.07 c	2.81 ± 0.16 d	2.57 ± 0.29 c
	Zn	1.87 ± 0.03 a	1.92 ± 0.09 a	2.52 ± 0.14 b	2.69 ± 0.08 b	3.10 ± 0.25 c	3.21 ± 0.08 c

Same letters (a–d) indicate no significant difference ($p < 0.05$) between irrigated rice parameter values.

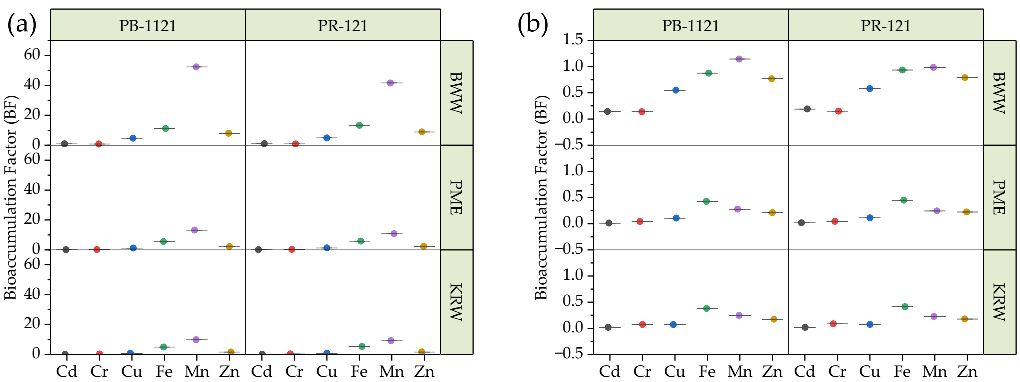

Figure 3. Bioaccumulation factor (BF) of heavy metals in (**a**) straw and (**b**) grain of PB-1121 and PR-121 rice varieties irrigated with different water sources in Saharanpur district of Uttar Pradesh, India (BWW: borewell, PME: paper mill effluent, and KRW: Kali River water; the same color dots correspond to values of same heavy metal).

3.4. Health Risk Assessment of Heavy Metals Accumulation

Heavy metals are abundant in the environment and can be absorbed by crops. Rice is an important food source for Indians, so it is critical to assess the health risk of heavy metals in rice. The study of THQ and HRI gives a broader spectrum of possible health risks of food consumption by humans [30]. An HRI value of 1.0 or less indicates that the heavy metal is unlikely to be harmful to human health. However, HRI values greater than 1.0 indicates that the heavy metal may be hazardous to one's health. Table 5 summarizes the obtained THQs and HRIs found in both rice varieties grown in different irrigated soils. Surprisingly, child THQs were always higher than adult ones despite the rice variety and irrigated soil. Heavy metal levels in Indian varieties reported in that study were much higher than found in the current one simulating different soil physicochemical characteristics and water quality used in rice growing and production besides the variability in used crop varieties. Child and adult HRIs followed the following decreasing order: PR-121 Kali River > PB-1121 Kali River > PR-121 Paper Mill Effluent > PB-1121 Paper Mill Effluent > PR-121 Borewell > PB-1121 Borewell. It is noteworthy that the PR-121 variety had higher HRIs compared to PB-1121 in all irrigated soils which simulates a possible effect of consumed varieties on human health. All HRIs except child HRI of PR-121 variety in Kali River-irrigated soil were below 1; therefore, they are considered safe. The alarming increase in child HRI may be attributed to Cd content which can lead to heart, kidney, and lung diseases as well as nervous tissue disorders [60]. Thus, special attention should be given to the PR-121 rice variety originating from soils irrigated with Kali River water to children. Previously, Lien et al. [60] found in the Yilan area (Taiwan) an endangering health risk of rice on children pronounced by high HRIs and attributed that to Cd levels being concomitant with our findings. A similar observation was acknowledged by Guo et al. [61] regarding the direct influence of Cd levels on rice HRI in Chinese polluted paddy soils simulating possible carcinogenic impacts. Therefore, the THQ and HRI approaches successfully detected minor and possible risk(s) associated with grown rice varieties in different irrigated soils of Saharanpur District.

Table 5. Target hazard quotient (THQ)-based health risk assessment of heavy metals accumulation in two rice varieties irrigated with different water sources.

Heavy Metals	Health Risk Variables	Irrigated Soils					
		Borewell		Paper Mill Effluent		Kali River	
		PB-1121	PR-121	PB-1121	PR-121	PB-1121	PR-121
Cadmium (Cd)	THQ (Child)	0.156	0.175	0.212	0.231	0.298	0.387
	THQ (Adult)	0.124	0.132	0.148	0.156	0.172	0.280
Chromium (Cr)	THQ (Child)	0.147	0.150	0.221	0.228	0.197	0.292
	THQ (Adult)	0.120	0.121	0.152	0.155	0.141	0.148
Copper (Cu)	THQ (Child)	0.136	0.137	0.138	0.140	0.145	0.147
	THQ (Adult)	0.115	0.116	0.116	0.117	0.119	0.120
Iron (Fe)	THQ (Child)	0.019	0.120	0.027	0.028	0.019	0.032
	THQ (Adult)	0.018	0.019	0.011	0.012	0.013	0.024
Manganese (Mn)	THQ (Child)	0.115	0.099	0.156	0.137	0.187	0.171
	THQ (Adult)	0.049	0.042	0.067	0.059	0.080	0.073
Zinc (Zn)	THQ (Child)	0.116	0.016	0.018	0.018	0.019	0.012
	THQ (Adult)	0.012	0.013	0.013	0.014	0.014	0.014
HRI	Child	0.689	0.697	0.772	0.782	0.865	1.041
	Adult	0.438	0.443	0.507	0.513	0.539	0.659

4. Conclusions

The findings of this study concluded that effluent release from Star Paper Mill Ltd., Saharanpur, India had significant untreated pollutants that exceeded the permissible limits of both inland irrigation and surface discharge. Effluent disposal showed a significant ($p < 0.05$) increase in the water quality of Kali River thereby exceeding its pollution level. In addition, the soils irrigated with paper mill effluent and Kali River water showed a comparatively high level of physicochemical and heavy metal parameters suggesting potential contamination. The two rice varieties (PB-1121 and PR-121) irrigated with paper mill effluent and Kali River water showed a significant ($p < 0.05$) increase in growth, yield, and productivity. However, the PR-121 variety showed relatively higher growth, yield, and heavy metal accumulation in straw and grains as compared to PB-1121. The health risk investigation showed potential health risks of heavy metal exposure through consumption of rice irrigated with paper mill effluent and Kali River water. Further studies on biomonitoring of other toxic heavy metals in paper mill effluent and Kali River is highly recommended while local farmers are advised not to use the noxious paper mill effluent or contaminated Kali River water for their field irrigation.

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