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by Munawar Ali

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RESEARCH ARTICLE

Effect of leather tanning effluent on chromium contamination in paddy field

Kabul Fadilah[1*], Keukeu Kaniawati Rosada[2], Muhammad Aziz Affandy[2], Munawar Ali[1] & Sunardi Sunardi[2,3]

[1]Department of Environmental Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Jl. Rungkut Madya No.1, Surabaya 60294, Indonesia
[2]Department of Biology, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran. Jl. Raya Bandung-Sumedang Km. 21 Jatinangor, Sumedang 45363, Indonesia
[3]Graduate Program on Environmental Studies, Graduate School, Universitas Padjadjaran, Bandung 40132, Indonesia

*Email: kabul.fadilah.tl@upnjatim.ac.id

Abstract

Leather tanning industry effluent contains high chromium (Cr) concentrations and poses environmental threats. In this study, we investigated the impact of leather tanning effluent contamination in water, soil, paddy, its grain and its other morphometric parameters under the irrigated areas in the Ciwalen River, West Java. The result showed high Cr concentration in Ciwalen water stream, soil and paddy. The higher Cr concentrations of soil and paddy were found in the upstream area and closer plot to the main river stream. The bioaccumulation factor (BAF) values were <1, indicating that paddy has a low ability to accumulate Cr. However, paddy morphometric parameters, including total length, root length, and the number of leaves, decreased with higher Cr concentrations affected by leather tanning effluents.

Keywords

Contamination; chromium; leather tanning; paddy fields

Introduction

Leather tanning is one of the industries that produce large volumes of liquid waste. In one tonne of wet leather tanning, about ±40 m^3 of water is needed and disposed of as liquid waste. Chemical residues produced during this industrial process also get dissolved in the leather components (1). For example, the leather tanning industry in India emits large amounts of liquid waste, which amounts to about 52,500 m^3/per day (2). Conventional tanning using chromium (Cr) happens to have several impacts on the environment as it carries residual Cr into the wastewater (3,4). Although Cr used in leather tanning is trivalent chromium (Cr^{+3}), hexavalent chromium (Cr^{+6}) may be present in tannery wastewater (5). Thus, the liquid waste of the leather tanning industry potentially contaminates water bodies or rivers if the waste is directly discharged into the environment without special handling (6).

Cr is the most widely used tanning material and it is used by the leather tanning industry world over. About 85% of the leather produced in the world is tanned using Cr (7). The Cr usage is based on the fact that Cr is able to react and form bonds with the amino acids of the skin collagen protein (8). Leather tanned using Cr has advantages, including being suitable for producing various leather goods and the hard leather being better compatible for retaining the chemicals used for the fat-liquoring processing. Cr-leather also has high tensile strength, flexibility, more resistance to high temperatures gives good painting results (9) and has high hydrothermal stability (3).

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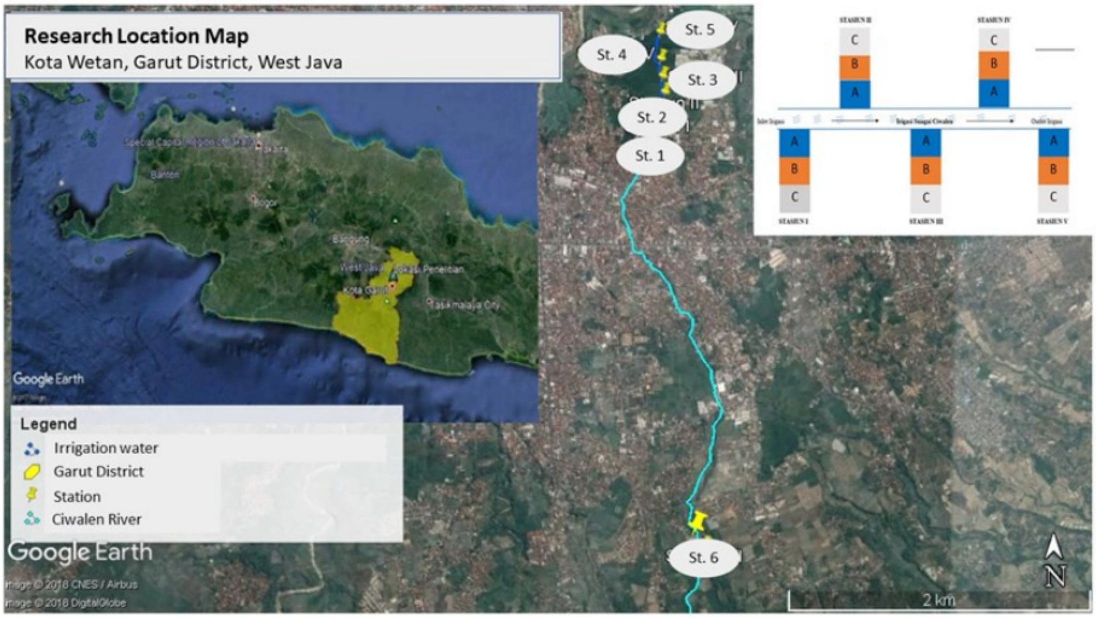

Fig. 1. Map of the study area and sampling location.

Cr is one of the toxic heavy metals which is harmful to the environment and organisms. Several studies have shown that the detrimental effects of Cr contamination on crop quality and yield (10,11). The effects of chromium significantly exhibit plant growth and development (12). Phytotoxicity studies of heavy metals in Indonesia are still scarce, especially regarding the increase in the pollution of heavy metals in food crops. Paddy is a plant that needs much water resources to grow and has high yield demand. The accumulation of Cr in paddy ultimately destroys productivity and threatens human health (13).

The Ciwalen River area is surrounded by leather tanning industry and it is most likely impacted by Cr contamination. Ciwalen River is the main source of irrigation for the paddy fields of Kota Wetan, Garut District in West Java. The Cr-contaminated irrigation water inundates the paddy fields and leads to the deposition of Cr in the soil. Cr that has deposited in the soil will be absorbed by the paddy through the roots and it gets accumulated in the body. According to Ahmad P. et al., the impact of Cr accumulation on paddy in the long term will inhibit the growth and development of the plant (14). Soil contamination by Cr will also interfere with the fertility of the soil where paddy grows and disturbs the soil microbial activity (15).

The study aimed to investigate the Cr-contamination in water, soil and paddy alongside the Ciwalen River. The contamination of Cr potentially caused adverse effects on the quality of the water and soil. In addition, the impact of tannery effluent will also affect the morphometric parameters of paddy. The findings of this research may provide information on leather tanning effluent's impact on paddy and it can serve the function of a safety precaution as rice is the most widely consumed staple food for most people around the world.

Materials and Methods

Study Area

This study was carried out in Kota Wetan, Garut district, West Java Province. This area is occupied by leather tanning industries with 330 local production units and approximately produce 90,000 L tannery wastewater in a month (16). The leather tannery industry areas are crossed by the Ciwalen River and it is used as a source of irrigation for paddy fields in the surrounding areas. The paddy fields around the Ciwalen river are planted with the Ciherang rice variety which is commonly used for rice farming in Indonesia.

Six sampling stations were selected as sampling points, perpendicular to the river stream. Each sampling point consists of three grid bases of paddy fields based on the distance to river stream. Plot A was the first grid closest to the river stream, Plot B was the second grid with the mid -distance, and Plot C was the furthest from the river stream (Fig. 1). One plot has an area of ±6.25 m^2 that approximately consisted of 100 clumps of paddy. Station 6 was selected for comparison as there is no possibility for contamination from the possible leather tannery as it is far from the industrial area.

Sample Collection

Water, soil and paddy samples were collected from six stations related to the main stream of the Ciwalen River. Stations 1, 2, 3, 4, and 5 were located near the industrial areas which were highly exposed to leather tanning effluent. Meanwhile, Station 6 was located in upstream, far from industrial area and used as a comparison. The water sample was kept in 600 mL bottle samples and immediately transferred to the laboratory for analysis. Soil and paddy samples were collected in triplicates from three plots (Plot A, B, and C) of each sampling site. Soil samples (100 g) were collected at surface soil (0 - 20 cm) and were put into Ziplock plastic. Soil samples were preserved by

$$\mathrm{BAF} = \frac{\text{Chromium concentration in the plant}}{\text{Chromium concentration in the soil}}$$

cooling at 4℃ sample containers. Paddy samples consist of roots, stems, leaves, and rice grains.

Morphometrics of Paddy

Paddy morphometrics was measured during the harvest period (120 days). The length of the paddy and root were measured by using a centimeter scale. The total amount of leaves was counted in a clump of paddy.

Chromium Determination

Plant materials (leaf, root, grain) were washed in distilled water and oven-dried at 80°C for 24h and then ground to powder. Soil samples were oven air-dried at room temperature for 24h. Soil samples were air-dried and sieved through<2mm fraction (17). Samples (50 g) were ground and digested with concentrated HNO_3 and H_2O_2. Digested solutions were filtered, and the volume was raised to 50 ml by adding distilled water. Chromium was analyzed using AAS atomic absorption spectrophotometer (Hitachi Model 7JO-8024, Tokyo, Japan) and the data was calculated as mg/kg unit.

Data Analysis

Average values and standard deviations for all data were calculated using Microsoft Excel. The two-way analysis of

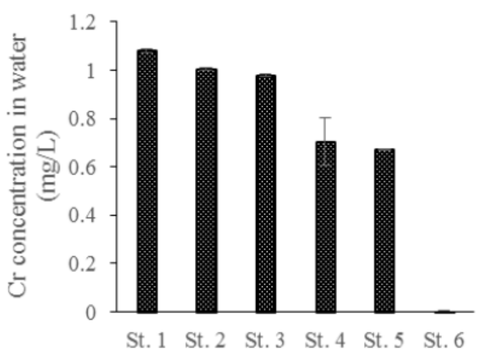

Fig. 2. Chromium concentration in the water of the Ciwalen river.

variances (ANOVA) test was performed using SPSS 17 to test significant differences between Cr concentration in soil, paddy and morphometric parameters among different plots. Pearson Correlation Analysis was applied to evaluate the relationship between Cr in soil and Paddy. Bioaccumulation factor (BAF) indicates the ratio of Cr concentration in plant and Cr concentration in the soil. It was calculated using the method described by Miao and Yan (18).

Results and Discussion

Chromium Contamination in Ciwalen Water Stream

The concentrations of Cr in the Ciwalen River are shown in

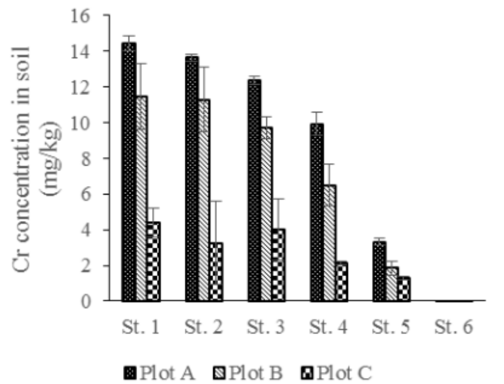

Fig. 3. Chromium concentration in the soil of paddy field along the Ciwalen river.

Fig. 2. The Cr level from upstream (St.1) to downstream (St.5) showed a decrease in the Cr concentration with the highest Cr content in water at St. 1 (1.082 mg/L), whereas the lowest Cr content in water was at St. 5 (0.670 mg/L). The concentrations of Cr in all stations were much higher than comparison station, St. 6 (0.002 mg/L). According to *Regulation No. 82 2001 on Water Quality And Water Pollution Management* 2001, Government of Republic of Indonesia. *Government*(19), the Cr concentrations in the Ciwalen River have exceeded the maximum threshold (1 mg/L) for agriculture purposes at St.1 and St.2. The consequences of that contamination may threaten the surrounding environment, including paddy fields and water resources. Cr contamination in Ciwalen waterstream may be due to the usage of various chemicals in leather tannery manufacturing such as tanning agents, textile pigments and preservatives (20). Besides, many local leather tanning industries dispose the waste to the Ciwalen waterstream without appropriate pre-treatment.

Chromium Concentration in Soil

The Cr concentrations in paddy soil ranged from 0.006 to 14.43mg/kg across the study sites (Fig. 3). In general, the closer distance to the river, the more Cr concentration level in paddy soil. The decreasing order of Cr content in paddy soil was found to be Plot A> Plot B> Plot C. The

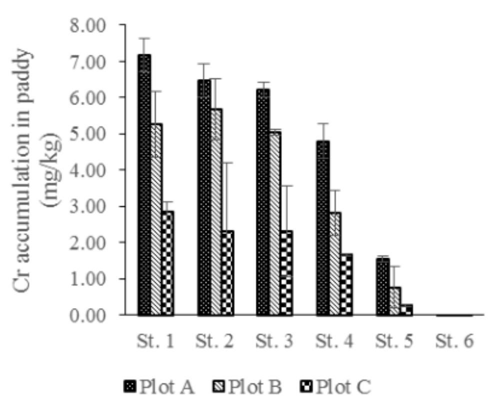

Fig. 4. Chromium accumulation in paddy around the Ciwalen river.

Table 1. Bioaccumulation Factor (BAF) of chromium in paddy

	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6
Plot A	0.50 ± 0.02	0.47 ± 0.03	0.50 ± 0.03	0.48 ± 0.02	0.46 ± 0.04	0.29 ± 0.32
Plot B	0.46 ± 0.04	0.50 ± 0.02	0.52 ± 0.03	0.43 ± 0.07	0.41 ± 0.22	0.25 ± 0.83
Plot C	0.65 ± 0.09	0.71 ± 0.32	0.58 ± 0.11	0.78 ± 0.04	0.20 ± 0.02	0.56 ± 0.28

highest Cr concentration was found in Plot A of St.1. In contrast, the lowest Cr concentration was found in Plot C of St. 6. Accumulation of Cr in soil may be attributed to the contamination of the Ciwalen waterstream from leather tanning waste. This contamination may affect soil fertility and nutrient content of the soil which in turn can affect growth of paddy (21).

Chromium Accumulation in Paddy

A similar trend was also observed in Cr accumulation in paddy (Fig. 4). The accumulation of Cr in paddy increased with closer proximity to the river. Plot A was the nearest with the highest Cr concentration, followed by Plot B and Plot C. The highest Cr accumulation was found in Plot A of St. 1(7.17mg/kg), while the lowest Cr accumulation was found in Plot C of St. 6(0.003mg/kg).

In the case of Cr accumulation in paddy, correlation analysis showed a strong relationship (r=0.98, p<0.01). The distance to the pollutant source exposed to Cr contamination may cause a gradient of bioaccumulation levels in paddy (18). The result revealed that the highest Cr accumulation in soil and paddy occurred in the upstream station and gradually decreased in the downstream station. Contaminated irrigation water with Cr for a particular time may lead to continuous Cr deposition. Moreover, this deposition resulted increased Cr concentration in the soil, which eventually accumulated in paddy (22).

BAF was used to estimate the ability of Paddy to accumulate chromium from soil. In this study, the highest BAF value was 0.78 at St. 4 plot C and the lowest value was 0.25 at St. 6 plot B (Table 1). According to Aladesanmi et al. (23), BAF values less than 1 indicate plant's ability to accumulate chromium was low. The accumulation factor may be influenced by Cr uptake and transport from the soil to plant.

Chromium Accumulation in Grain

Rice grain is one of the most important indicators for plant yields. In a polluted environment such as tannery waste, rice grain would be impacted by the adverse effect of chromium contamination. The Cr accumulation in rice grains from St. 1 to St. 5 showed a gradual decrease in concentration (Fig. 5). The highest Cr content was found in Plot A St. 1(1.81mg/kg) and the lowest Cr accumulation was at St 5 (0.07mg/kg). The Cr accumulation at St. 6 (for comparison) was 0.05-0.08mg/kg. Based on Global Agricultural Information Network (GAIN) Report on China's Maximum Levels for Contaminants in Foods (24), the maximum limit of heavy metal contamination in grain products stated as the safety limit is 1 mg/kg. This finding showed that the Cr content in the rice grains in Kota Wetan exceeded the maximum threshold.

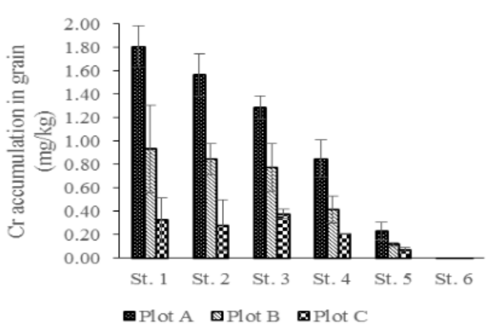

Fig. 5. Chromiumaccumulation in grains of paddy around the Ciwalen river.

Cr concentration in grain indicated the possible influence of pollution from tannery waste. Rice grains are the product of plant metabolic processes which are strongly influenced by physiological and environmental factors. Singh HP *et al.,* reported that the effect of Cr pollution resulted in a decrease in rice yields (25). The consequence of the impact of this waste pollution is the decrease in productivity and quality of the yield. Cr accumulation in rice grain might lead to a serious threat to human health (26), especially because rice is the primary food consumed by most people in Indonesia.

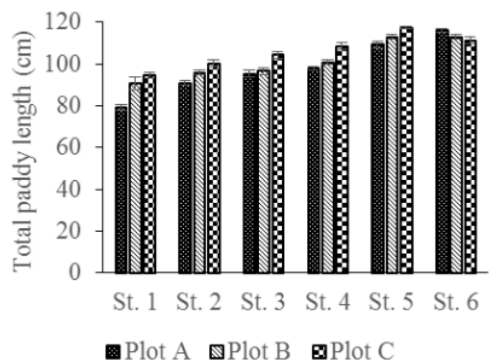

Fig. 6. Total paddy length_affected by leather tanning industry around the Ciwalen river.

Morphometrics of Paddy Plant

The impact of Cr contamination not only causes accumulation in soil and paddy but also has an impact on rice morphometric parameters. In Fig. 6, Cr accumulation also affects the total length of paddy and was significantly different at each station. The lowest total length of paddy was found in Plot A of St. 1(79.33 cm), while Plot C of St. 5 has the highest total length (117.33 cm). Meanwhile, at St. 6 (comparison), the total length ranged from 111–116 cm. The result showed that the average total lengths of paddy at St.1, 2, 3, and 4 were below the standard stipulated by Ministry of Agriculture of Indonesia (27), namely 107–115 cm. Environmental factors play a vital role in promoting

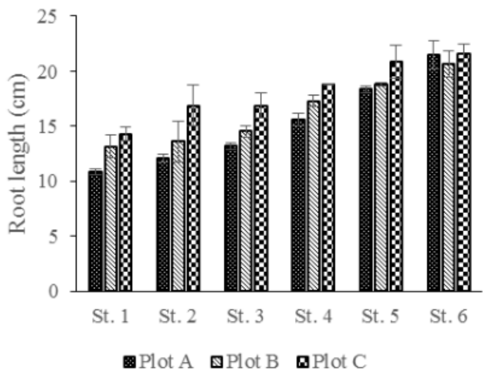

Fig. 7. Root length affected by leather tanning industry around the Ciwalen river.

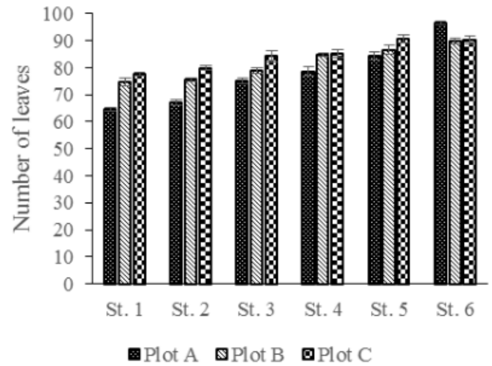

Fig. 8. The number of paddy leaves affected by leather tanning industry around the Ciwalen river.

plant growth which may produce high yield. Pollutant contamination will inhibit plant growth caused by some adverse effects of pollutants such as nutrient transport disturbance and plant parts deterioration (28).

The exposure of chromium may affect root growth in plants. The paddy in the downstream has significantly higher root length compared to the upstream (Fig. 7). The lowest root length of paddy was found in Plot A of St. 1 (10.90 cm), where as the highest was found in Plot C of St. 5 (20.86 cm). At St. 6 (for comparison), the length of rice roots ranged from 21.50–21.63 cm. Cr may inhibit cellular activity for elongation as a result of toxic effects. The impact of Cr contamination on the root growth of paddy was also reported by Xu B, *et al.*(29). The role of roots becomes unfavorable in absorbing essential nutrients such as N, P, K, Ca and Fe. In addition, a decrease in root length may reduce the capacity of roots to absorb water in the soil (30).

The number of paddy leaves at each site is presented in Fig. 8. The number of leaves of paddy from downstream (St.5) to upstream (St.1) was found to be significantly decreased, along with an increase in the level of Cr accumulation in paddy. The lowest number of leaves was found in Plot A of St.1(64.66), while the highest number of leaves was found in Plot C of St.5, with a total amount of 90.66. In contrast, St. 6 (comparison) has the greatest number of leaves ranging from 90–96.66.

The number of leaves has an important role in determining crop yields. This factor is related to photosynthetic activity. The accumulation of Cr can reduce the efficiency of carbon dioxide fixation and the activity of enzymes involved in photosynthesis in plants. Furthermore, Shanker et al. stated that the effect of Cr may reduce leaf size and caused burning at the leaf margins (31).

Conclusion

The result of this study indicated that the Ciwalen River was subjected to high chromium (Cr) contamination from leather tanning effluents. Accumulation of chromium was also found in soil and paddy alongside the waterstream. Consequently, paddy fields were exposed to chromium contamination, showing detrimental effects in morphometric parameters, including the total length, root length, and the number of leaves.

We suggested that evaluation and assessment are needed for monitoring the potential transfer of Chromium from soil to grains which can threaten human health. Further research may focus on the effect of Chromium on physiological processes coming from the leather tanning industry.

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Authors contributions

KF: carried out the experiment and performed analysis. MAF: carried out the experiment and writing the manuscript. SS, KKR and MA: help designed the study and supervise during the research. All authors provided critical feedback and helped shape the research, analysis and manuscript.

Compliance with ethical standards

Conflict of interest: Authors do not have any conflict of interests to declare.

Ethical issues: None.

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