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Redistribution of potentially toxic elements in the hydrosphere after the relocation of a group of tanneries

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HIGHLIGHTS

- Redistribution of toxic elements associated with tannery relocation (TR).
- About 97% reduced Cr(III) level in canal water containing wastewater after TR.
- Adversely, about 30-fold increased Cr (VI) level in canal water over time after TR.
- Median levels of Cr, Pb, Fe, and Mn exceeding the guideline values after TR.
- Removal of tannery-related toxic elements by hydrotalcite-like compounds.

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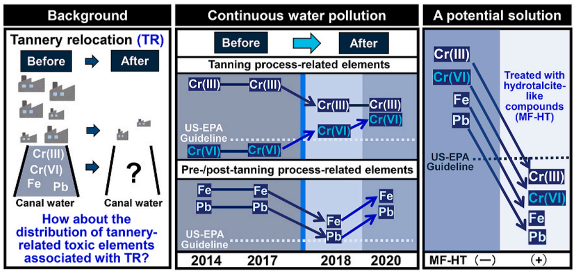
GRAPHICAL ABSTRACT



ABSTRACT

Simultaneous relocation of a group of pollutant sources in a heavily polluted area is a rare event. Such a relocation has been implemented in Hazaribagh, a tannery built-up area with heavy pollution, in Bangladesh. This provides a valuable opportunity to compare the changes in environmental conditions associated with the relocation of multiple putative sources. Our environmental monitoring for a period of 6 years at the stationary areas centered on Hazaribagh geographically revealed trivalent [Cr(III)], hexavalent [Cr(VI)] chromium, lead, iron, and manganese as tannery-related elements after the legal deadline for tannery relocation. The median Cr(III) level in canal water, into which wastewater from tanneries was directly discharged, after the relocation was 97% lower of that before the relocation, indicating a beneficial effect of the relocation. In contrast, the median Cr(VI) level in water samples just after the relocation and 2 years after the relocation were approximately 5-fold and 30-fold higher, respectively, than those before the relocation. These results indicate not only a harmful effect of the relocation but also the possibility of conversion from Cr(III) to Cr(VI) in nature. Although the health hazard indexes considering all of the tannery-related elements in all of the canal water samples before the relocation

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exceeded the safety thresholds, the percentages of samples in which the indexes exceeded their safety thresholds after the relocation decreased by 32.5%–45.0%. Treatment with our patented hydrotalcite-like compound consisting of magnesium and iron (MF-HT) resulted in decreases in the health hazard indexes in all of the water samples in which the indexes exceeded their safety thresholds to levels lower than their thresholds. Thus, this study shows the double-edged effects associated with the relocation and a potential solution.

Abbreviations

HPI	Heavy metal pollution index
HEI	Heavy metal evaluation index
MF-HT	Hydrotalcite-like compound consisting of magnesium and iron
HIC	Hazard index for children
HIA	Hazard index for adults

Credit author contribution statement

Fitri Kurniasari: Data curation, Validation, Writing-original draft; **Akira Tazaki**: Data curation, Methodology, Validation, Resources, Writing-original draft; **Kazunori Hashimoto**: Data curation, Validation, Writing-original draft; **Tian Yuan**: Investigation, Methodology; **M.M. Aeorangajeb Al Hossain**: Investigation, Resources; **Anwarul Azim Akhand**: Investigation, Resources; **Nazmul Ahsan**: Investigation, Resources; **Shoko Ohnuma**: Methodology, Formal analysis, **Masashi Kato**: Conceptualization, Funding acquisition, Project administration, Validation, Supervision, Writing-review & editing.

1. Introduction

The relocation of multiple pollutant sources within a short time frame is a rare event in the world. Such a relocation has been implemented in Hazaribagh, a tannery built-up area with severe pollution, in Bangladesh (Alam et al., 2019; The Daily Star, 2017). These relocations provide a valuable opportunity for practically assessing the associated changes in environmental conditions.

Generally, the operation of leather manufacture is classified into the 3 processes of pre-tanning, tanning, and post-tanning (Tsuchiyama et al., 2020). A large amount of trivalent chromium [Cr(III)] that is used in the tanning process is discharged into canals as tannery wastewater (Apte et al., 2005; Kibria et al., 2016; Yoshinaga et al., 2018). In fact, more than 99.99% of total Cr (t-Cr) in tannery wastewater has been reported to be Cr(III) (Tsuchiyama et al., 2020). Since omnifarious poisonous properties including carcinogenic, cutaneous, and renal toxicities of Cr (III) have been reported (Al Hossain et al., 2019; Tsuchiyama et al., 2020), monitoring of the Cr(III) level in the hydrosphere is important. As indicated by the large difference between the US Environmental Protection Agency (US-EPA) guideline values for surface water (Vaiopoulou and Gikas, 2020) for Cr(III) (570 μg/L) and Cr(VI) (16 μg/L), Cr(VI) toxicity is much higher than Cr(III) toxicity (Ohgami et al., 2015; Yoshinaga et al., 2018). In fact, most of the health issues with tannery pollution have been reported to be related to Cr(VI) rather than Cr(III) (Choppala et al., 2013). Furthermore, previous experimental studies showed the promoted conversion from Cr(III) to Cr(VI) in a small scale (2.5 g) of tannery sludge (Apte et al., 2005, 2006). Therefore, temporal monitoring of the Cr(VI) level, as well as the Cr(III) level on a large scale, is essential in a tannery built-up area. Although oxidation of geogenic Cr (III) has been reported as the main source of Cr(VI) pollution in groundwater in many countries (Liang et al., 2021), there has been no evidence of conversion of anthropogenic Cr(III) to Cr(VI) in the environment in any industrial sites including tannery built-up areas.

Canal water into which tannery wastewater is directly discharged is polluted with lead (Pb), iron (Fe), manganese (Mn), arsenic (As), and barium (Ba) because these elements are used in the pre- and post-tanning processes (Dixit et al., 2015; Hashem et al., 2017; Sarwar et al., 2018). Various poisonous properties including carcinogenic, allergic or neurologic toxicities have been reported for Pb (Boskabady et al., 2018; Kagawa et al., 2021; Xu et al., 2021a), Fe (Kumasaka et al., 2013; He et al., 2019), Mn (Ohgami et al., 2016; Kumasaka et al., 2017), As (Kato et al., 2020; Yajima et al., 2017, 2018) and Ba (Kato et al., 2013; Omata et al., 2018). Therefore, not only Cr but also other elements should be investigated as tannery-related pollutants. Previous studies showed that heavy metal pollution index (HPI) and heavy metal evaluation index (HEI) are useful for comprehensively assessing the combined effects of mixed metal contamination (Kumar et al., 2019). The hazard index for adults (HIA) and the hazard index for children (HIC) defined by the US-EPA are also useful for integrated health risk assessment in humans (Saha et al., 2017). However, there has been no study in which these indexes were used to evaluate the elemental pollution and health hazards in a tannery built-up area.

Our environmental monitoring for a period of 6 years to analyze the changes in levels of elements related to pre- and post-tanning processes (Pb, Fe, Mn, As and Ba), as well as tanning process-related elements [t-Cr, Cr(III), Cr(VI)], provided new insight into environmental pollution in the tannery built-up area before and after the relocation (Dixit et al., 2015; Hashem et al., 2017; Sarwar et al., 2018; Tsuchiyama et al., 2020). According to the actual pollution after the relocation, a potential solution was then considered. The sequence of our results provides novel information for understanding the double-edged effects associated with the relocation of a pollutant source.

2. Materials and methods

2.1. Study area and water sampling in the tannery built-up area

Our fieldwork study within a 7-km radius centered on a tannery built-up area was conducted in Hazaribagh, Bangladesh following the method previously described (Yoshinaga et al., 2018; Yuan et al., 2021). The wastewater from tanneries was directly discharged into the proximal canal (area b in Fig. 1) flowing to the distal canal through a sluice gate before entering into Buriganga River. The proximal canal is about 3–5 m in width and is filled with tannery sludge, while the distal canal also drains municipal wastewater into Buriganga River (Khan et al., 2020). Since there is no treatment plant for the discharged water from the tanneries, various pollutants including Cr(III) were widely spread in the hydrosphere centered on the tannery built-up area as shown in previous studies (Yoshinaga et al., 2018; Yuan et al., 2021). To reduce the heavy environmental pollution, the High Court of Bangladesh decided that the end of 2017 would be the legal deadline for the relocation of tannery operations from Hazaribagh to the new tannery estate equipped with a large wastewater treatment plant (Hoque et al., 2021; The Daily Star, 2017). However, about 30 percent of the tanneries were still conducting normal operations without treatment for wastewater in Hazaribagh after the end of 2017. The relocation processes were extended up to December 2020 (New Age, 2019).

Water samples (n = 203) collected in February 2014 (n = 42), February 2015 (n = 32) and February 2017 (n = 13) were classified as samples before the relocation of tanneries. Water samples collected in January 2018 (n = 98) and February 2020 (n = 18) were classified as samples after the relocation of tanneries. All of the water samples from

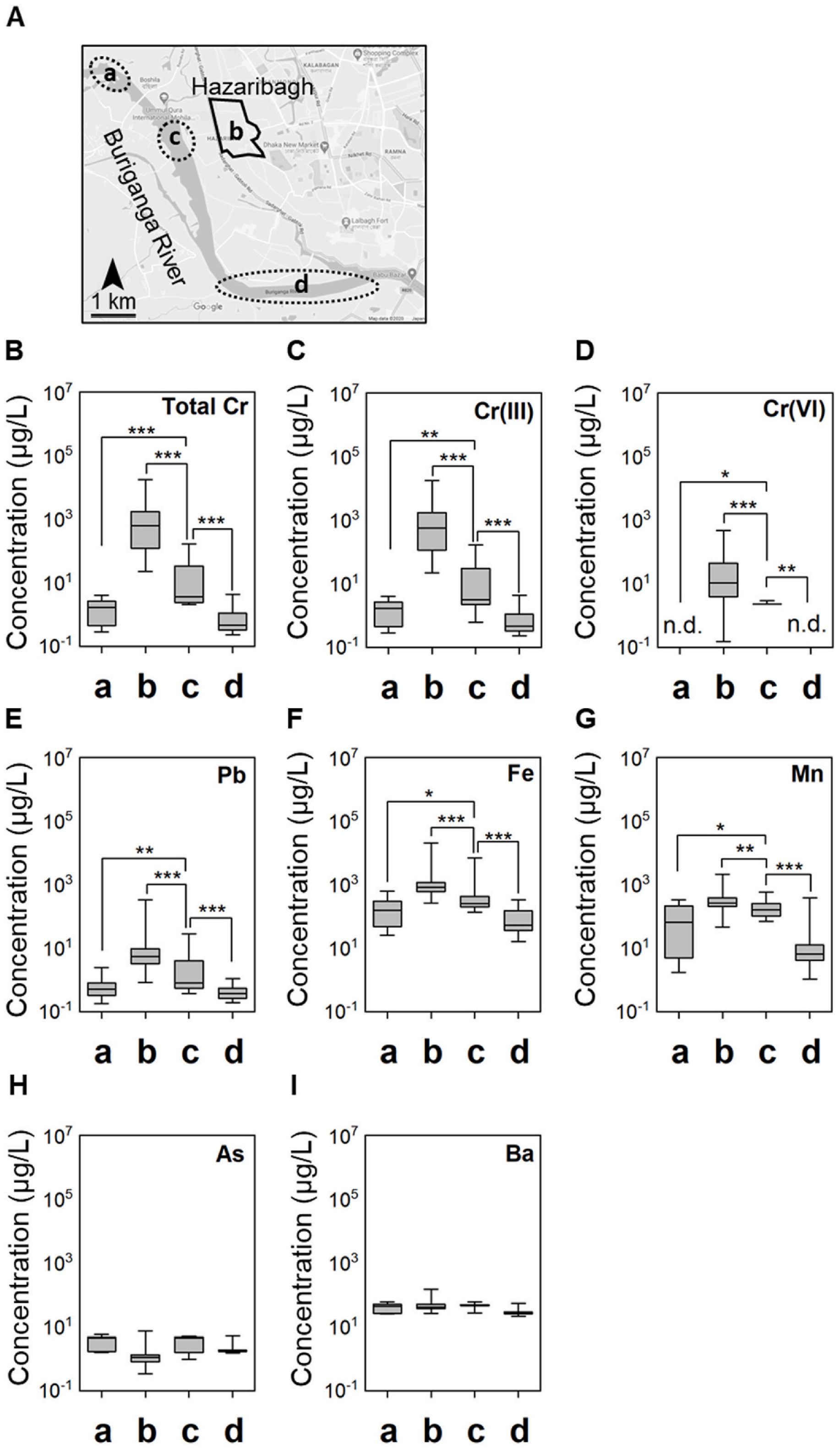

Fig. 1. Elemental pollution in water samples around Hazaribagh after the relocation of tanneries. (A) A schematic map of water sampling areas in the canals of the tannery built-up area (b), at the confluence between Buriganga River and the canals (c), and upstream (a) and downstream (d) of the confluence in Buriganga River is presented. (B–I) Levels of total Cr, trivalent Cr [Cr(III)], hexavalent Cr [Cr(VI)], Pb, Fe, Mn, As and Ba in water samples collected from the upstream area of Buriganga River (a, $n = 15$), the canals (b, $n = 40$), the confluence (c, $n = 22$) and the downstream area of Buriganga River (d, $n = 33$) after the relocation are presented. Significant differences (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$) by the Kruskal-Wallis test are indicated.

canals (area b in Fig. 1A), the confluence (area c in Fig. 1A) between canals and Buriganga River, and upstream (area a in Fig. 1A) and downstream (area d in Fig. 1A) of the confluence before and after the relocation of tanneries were collected in the stationary areas confirmed by using a global positioning system (GPS). Water samples were collected in polyethylene bottles and kept at room temperature for a few weeks before sending to Nagoya University, Japan. The water samples were then kept at 4 °C in a refrigerator until analysis was conducted by our previous method (Sudo et al., 2020). This study was approved by the ethical committee of Nagoya University (approval no. 2013–0070) in Japan and the University of Dhaka in Bangladesh.

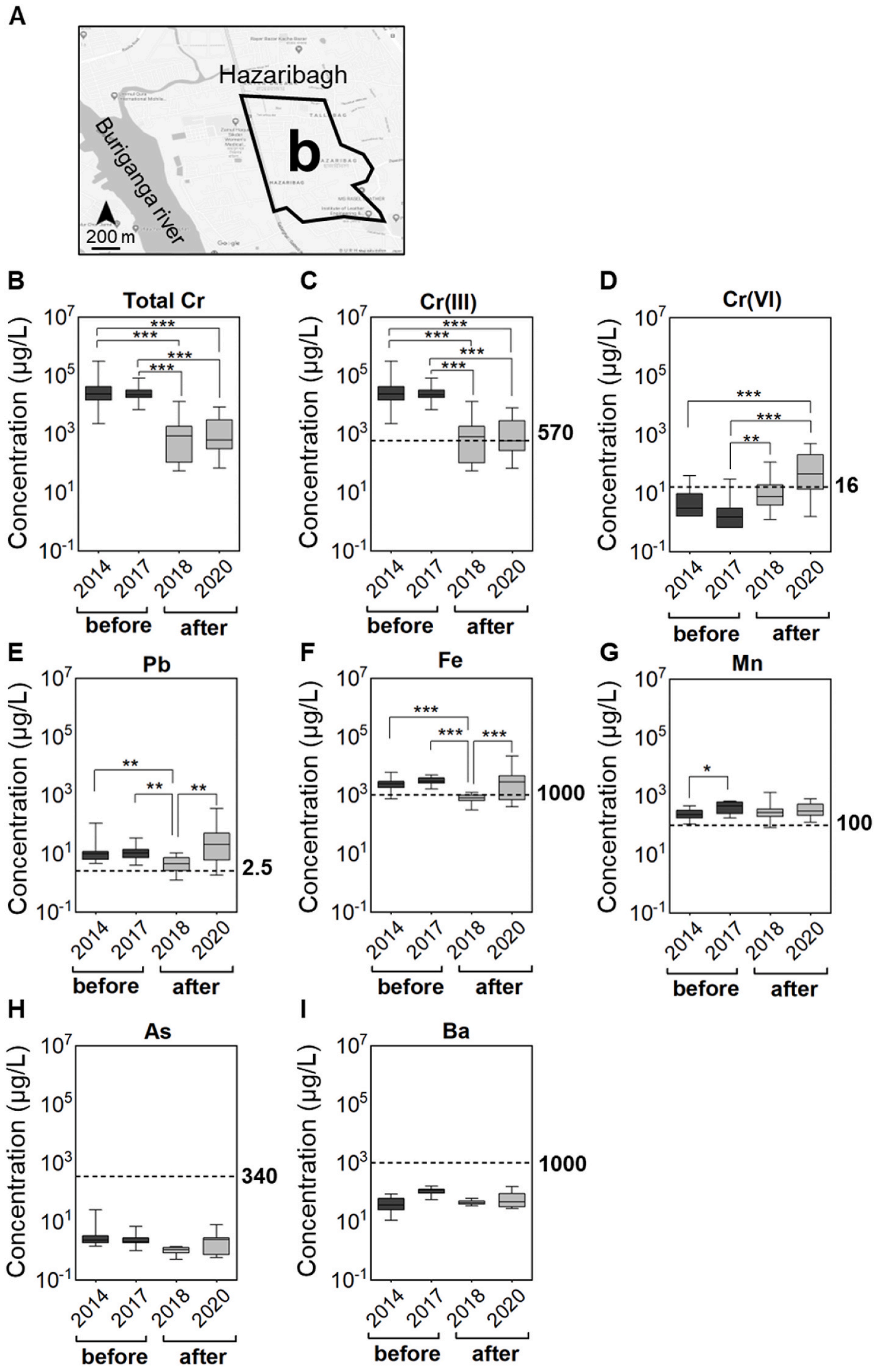

Fig. 2. Temporal changes in levels of elements in the canal water of the tannery built-up area (A) A schematic map of water sampling sites in the canal of the tannery built-up area (b) is presented. (B–I) Levels of total Cr (B), trivalent Cr [Cr(III)] (C), hexavalent Cr [Cr(VI)] (D), Pb (E), Fe (F), Mn (G), As (H) and Ba (I) in the canal water in 2014 ($n = 19$) and 2017 ($n = 13$) (before the relocation) and in 2018 ($n = 28$) and 2020 ($n = 12$) (after the relocation) are presented by boxplots. The guideline value of US-EPA for each element in surface water is indicated by a dotted line. Significant differences (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$) by the Kruskal-Wallis test adjusted by Bonferroni correction are indicated.

2.2. Measurement of elements

Levels of t-Cr, Pb, Fe, Mn, As, and Ba were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (7500cx, Agilent Technologies Inc, CA) as described previously (Kato et al., 2013). Levels of Cr (VI) were measured by ICP-MS-combined with high-pressure liquid chromatography (HPLC) (SCL-10AVP, Shimadzu Corporation, Japan) following a previously reported method with slight modification (Nizam et al., 2013). Briefly, a Cr speciation column (G3268-80001, 30 mm × 4.6 mm, Agilent Technologies Inc) was used under the following conditions: mobile phase, 4 mM EDTA (2Na)- 4 mM NaH_2PO_4/12 mM Na_2SO_4 at pH 7.0 (adjusted with NaOH solution); flow rate, 1.2 mL/min; column temperature, room temperature; and injection volume, 100 µL. Quantitative analysis of Cr(VI) was performed by using Mass Hunter Software (Agilent Technologies, Inc.). Levels of Cr(III) were determined by subtracting the level of Cr(VI) from the level of t-Cr as shown in a previous study (Yoshinaga et al., 2018).

2.3. Assessment of water pollution and human health risk

HPI and HEI were used to evaluate the water pollution in canal water according to previous studies (Edet and Offiong, 2002; Mohan et al., 1996). HPI was calculated by the following equations (Eqs. (1) and (2)):

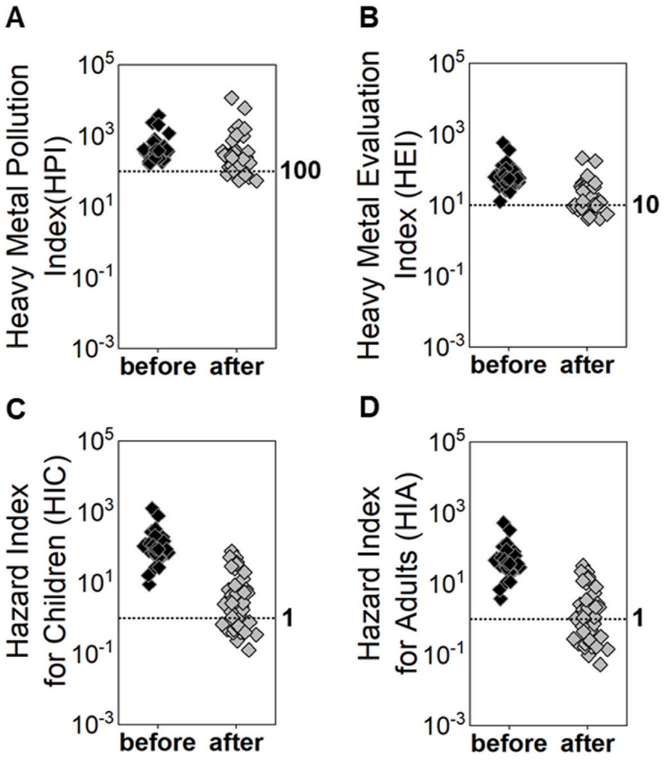

Fig. 3. Indexes for environmental pollution and human health risk in canal water samples before and after the relocation of tanneries. (A–D) HPI (A), HEI (B), HIC (C) and HIA (D) of canal water samples before (black dots; n = 32) and after (gray dots; n = 40) the relocation of tanneries are presented. Safety thresholds of HPI and HEI have been set at 100 and 10, respectively, following previous studies (Prasad and Bose, 2001; Prasanna et al., 2012). Safety thresholds of both HIA and HIC have been set at 1 based on a previous study (Ojemaye et al., 2020). The percentages of samples above the thresholds after the relocation for HPI, HEI, HIA, and HIC were 82.5%, 52.5%, 67.5%, and 55.0%.

$$HPI = \frac{\sum_{i=1}^{n} Wi.Qi}{\sum_{i=1}^{n} Wi} \tag{1}$$

$$Qi = \sum_{i=1}^{n} \frac{Mi}{Si} x\, 100. \tag{2}$$

HEI was calculated by the following equation (Eq. (3)):

$$HEI = \sum_{i=1}^{n} \frac{Mi}{Si}. \tag{3}$$

i refers to the ith element, n is the number of elements considered, W is the unit weightage as a value inversely proportional to the recommended standard (W = 1/S), Si is the standard value of the ith element defined by the US-EPA guideline for surface water (U.S. Environmental Protection Agency, 2004a), Qi is the sub-index of the ith element and Mi is the concentration of the ith element.

HIA and HIC, which were defined by the US-EPA Human Health Risk Assessment (U.S. Environmental Protection Agency, 2004b), were calculated by previously described methods (Nguyen et al., 2019; Wang et al., 2017; Wu et al., 2009) (Eqs. (4) and (5)):

$$ADD = \frac{EC\ x\ SA\ x\ ET\ x\ EF\ x\ ED\ x\ Kp\ x\ CF}{(BW\ x\ AT)}. \tag{4}$$

$$HIA \Big/ HIC = \Sigma \frac{ADD}{RfD} \tag{5}$$

ADD is the average daily dose, EC is the concentration of elements, SA is the exposed skin area, ET is the exposure time, EF is the exposure frequency, ED is the exposure duration, Kp is the skin permeability coefficient, CF is the conversion factor, BW is body weight and AT is the mean time of exposure, RfD is the reference dose of each element. Further information on parameters for calculation of HIA and HIC is shown in Supplemental Table 1.

2.4. *Adsorption of toxic elements*

The hydrotalcite-like compounds consisting of magnesium and iron (MF-HT) were synthesized as previously described (Kumasaka et al., 2013). Adsorption capacities of MF-HT for Pb and Mn were then investigated by a previously reported method (Kato et al., 2016). Briefly, 1% (w/v) of MF-HT and a solution containing $Pb(NO_3)_2$ and $Mn(SO_4)$ at concentrations ranging from 50 to 2000 mg/L were mixed and shaken at 300 rpm for 1 h at 25 °C until reaching an equilibrium. The equilibrium data were evaluated by a non-linear adsorption model of the Langmuir isotherm (Eq. (6)) and Freundlich isotherm (Eq. (7)) to determine the adsorption capacity of MF-HT.

$$Qe = Qm\ x\ k_1\ x\ Ce\ /\ (1 + k_1\ x\ Ce) \tag{6}$$

$$Qe = k_2\ x\ Ce^{(1/n)} \tag{7}$$

Qe (mg/g) is the amount adsorbed on MF-HT at equilibrium, Qm (mg/g) is the estimated maximum adsorption capacity, Ce (mg/L) is the concentration after adsorption, k_1 (L/mg) is the Langmuir isotherm constant, k_2 $((mg/g)/(L/mg)^{1/n})$ is the Freundlich isotherm constant, and 1/n is a parameter reflecting the intensity of sorption.

Then the ability of MF-HT for removal of tannery-related toxic elements was evaluated in canal water samples with high levels of the elements in Hazaribagh. After raw samples with a pH range of 5.6–7.6 had been directly treated with 1% (w/v) of MF-HT, the samples were shaken at 300 rpm for 1 h at 25 °C as reported previously (Kato et al., 2016). The concentrations of residual elements in the supernatant were measured by ICP-MS after centrifugation at 15,000 rpm for 10 min and filtration through a 0.45-μm filter membrane.

2.5. *Statistical analysis*

Statistical analyses were performed by using the software SPSS version 27.0 (IBM Corp) according to a previously reported method (Ohgami et al., 2010).

3. Results

3.1. *Extensive environmental monitoring to identify the tannery-related water pollution*

Levels of total Cr [t-Cr], Cr(III) and Cr(VI), Pb, Fe, Mn, As and Ba were investigated in canal water into which wastewater from the tanneries in Hazaribagh was discharged (area b in Fig. 1A), water from the confluence between canals and Buriganga River (area c in Fig. 1A), and water from upstream of the confluence (area a in Fig. 1A) and downstream of the confluence (area d in Fig. 1A) after (2018 and 2020) the legal deadline for tannery relocation.

Wastewater from tanneries, which contains high levels of different Cr species (Yoshinaga et al., 2018; Tsuchiyama et al., 2020), was identified as a pollutant source in the hydrosphere by the distributions of t-Cr (Fig. 1B), Cr(III) (Fig. 1C) and Cr(VI) (Fig. 1D) after the relocation of tanneries. Pb (Fig. 1E), Fe (Fig. 1F) and Mn (Fig. 1G), but not As (Fig. 1H) or Ba (Fig. 1I), were also identified as tannery-related elements after the relocation by their distributions. Our results indicated continuous water pollution by toxic elements (Cr, Pb, Fe and Mn) caused by the tanneries after the relocation.

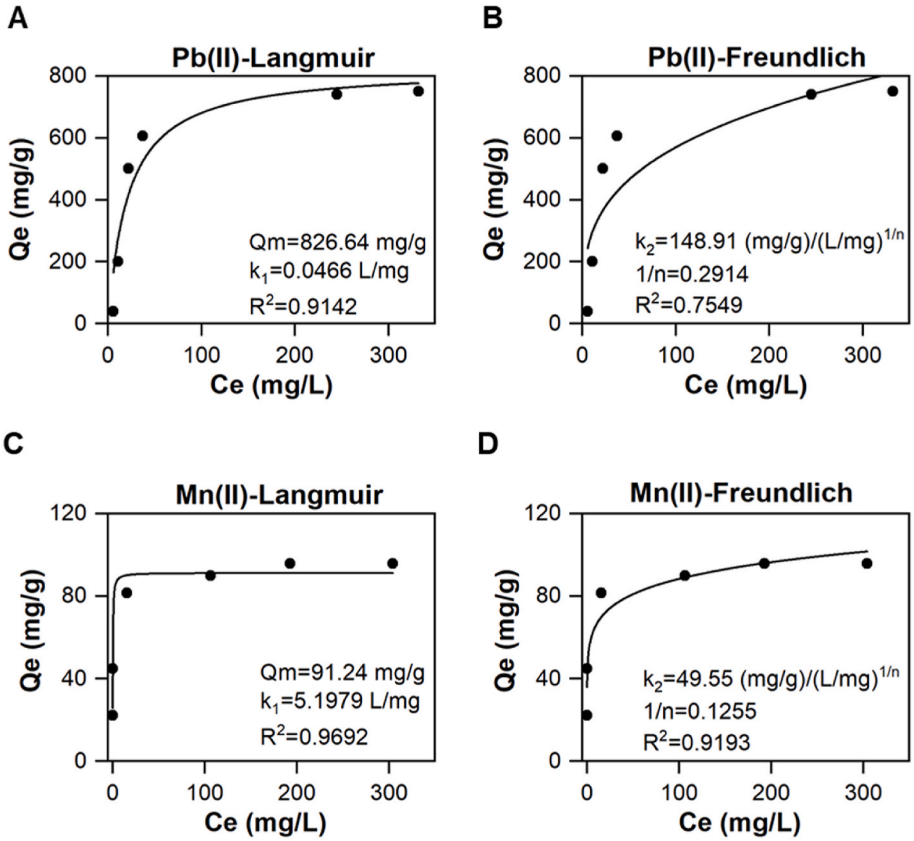

Fig. 4. Adsorption capacities of MF-HT for Pb and Mn. (A–D) The non-linear Langmuir isotherm model (A, C) and non-linear Freundlich isotherm model (B, D) for adsorption of Pb (A, B) and Mn (C, D) are presented. The values of C_e (mg/L) are the equilibrium concentrations of Pb and Mn by adsorption to MF-HT. The values of Q_e (mg/g) are the amounts of Pb and Mn adsorbed by MF-HT (per unit mass) at equilibrium.

3.2. Temporal changes of elemental pollution in canal water associated with the relocation of tanneries

After identifying the pollutants (Cr, Pb, Fe and Mn) in the hydrosphere, temporal changes of the pollutant levels in the canals (area b in Fig. 2A) before and after the relocation were further investigated (Fig. 2). The median levels of t-Cr and Cr(III) after the relocation of tanneries were approximately 97% lower than those before the relocation (Fig. 2B and C).

The median levels of Cr(VI) before the relocation of tanneries were lower than the guideline value of US-EPA. Since Cr(VI) accounted for less than 0.1% of t-Cr in our analysis of wastewater inside the tanneries (Tsuchiyama et al., 2020), the low level of Cr(VI) in samples of canal water, into which the wastewater from tanneries was directly discharged, before the relocation was reasonable. However, the median level of Cr(VI) just after the relocation (in 2018) was >2-fold and 5-fold higher than that before the relocation in 2014 and 2017, respectively (Fig. 2D). Moreover, the median level of Cr(VI) 2 years after the relocation (in 2020) was about 15-fold and 30-fold higher than the median levels before the relocation in 2014 and 2017, and 6-fold higher than those of just after the relocation (in 2018), respectively.

The median levels of Pb, Fe and Mn (Fig. 2E–G) just after the relocation were 57%, 73% and 39% lower, respectively, compared to those before the relocation. However, the median levels of Pb and Fe 2 years after the relocation were 4.5-fold and 3.5-fold higher, respectively, than those just after the relocation. On the other hand, the median levels of both As and Ba were comparably lower than the guideline values of US-EPA throughout our analyses for 6 years.

We further analyzed the temporal changes in the percentages of sampling points where the pollutant concentrations exceeded the guideline values of US-EPA. The percentage of sampling points where the Cr(III) concentration exceeded the guideline value of US-EPA decreased from 100% to 50% after the relocation (Fig. 2C). The percentages of sampling points where the concentrations of Pb and Fe exceeded the guideline values decreased just after the relocation in 2018 but the levels were increased again 2 years after the relocation (Fig. 2E–G). The levels of Cr(VI) increased year by year from 8% −11% before the relocation to 29% and 75% after the relocation.

3.3. Pollution and hazard indexes before and after the relocation of tanneries

HPI (Fig. 3A) and HEI (Fig. 3B) (Kumar et al., 2019) were used to comprehensively assess the pollution levels of canal water samples before ($n = 32$) and after ($n = 40$) the relocation of tanneries. While both HPI (Fig. 3A) and HEI (Fig. 3B) in all of the water samples before the relocation exceeded their safety thresholds, the percentages of water samples in which HPI and HEI exceeded their safety threshold after the relocation were decreased to 82.5% and 50.0%, respectively. To comprehensively assess the health hazards for children and adults in the canal water samples before and after the relocation, HIC (Fig. 3C) and HIA (Fig. 3D) defined by the US-EPA were also examined (Saha et al., 2017). Both HIA and HIC values in all of the water samples before the relocation exceeded the safety thresholds. However, the percentages of water samples in which HIA and HIC exceeded their safety thresholds after the relocation were decreased to 67.5% and 55.0%, respectively. These results indicate that environmental pollution and health hazards remained after the relocation of tanneries, though they were partially improved compared to those before the relocation.

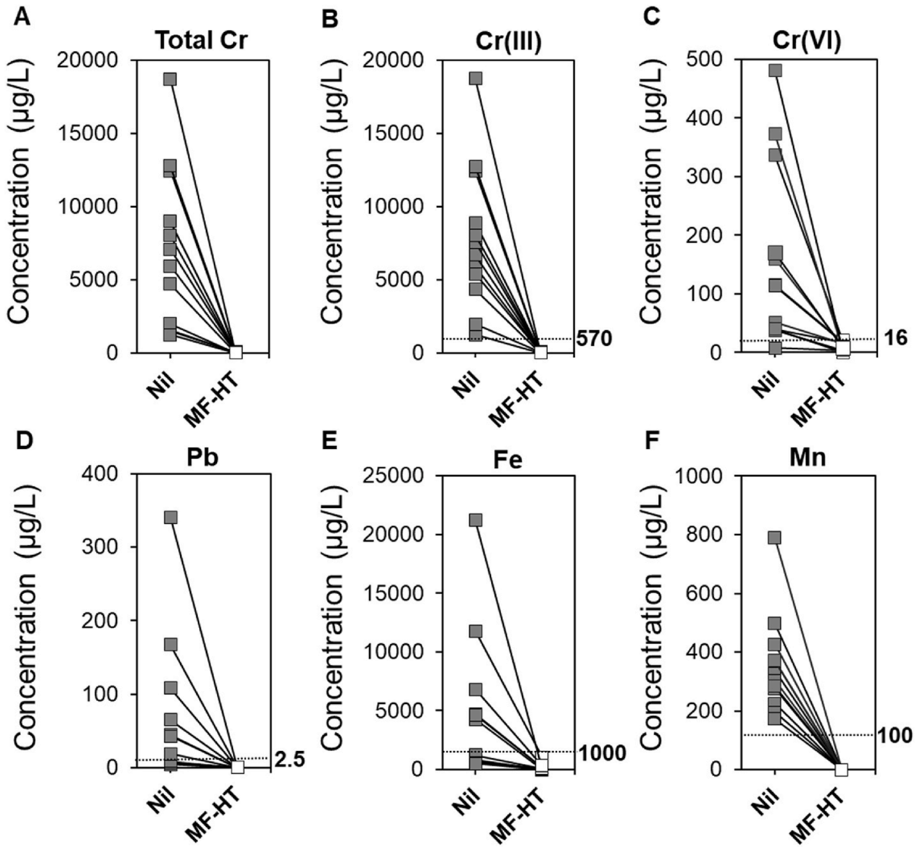

Fig. 5. Remediation of tannery-related pollutants in canal water samples by MF-HT.
(A–F) Individual values (n = 10) of total Cr (A), trivalent chromium [Cr(III)] (B), hexavalent chromium [Cr(VI)] (C), Pb (D), Fe (E) and Mn (F) in canal water samples after the relocation of tanneries without (Nil) or with (MF-HT) treatment with 1% (w/v) MF-HT for 1 h are presented. The guideline value of each element by US-EPA is indicated by a dotted line.

3.4. Adsorption abilities of Pb and Mn by treatment with MF-HT

Since adsorption of Cr(III) and Cr(VI) (Yoshinaga et al., 2018) and Fe (Kumasaka et al., 2013) by MF-HT has been reported, the capacity of MF-HT to adsorb other tannery-related elements (Pb and Mn) was newly investigated in this study (Fig. 4). The ability of MF-HT to adsorb bivalent Pb [Pb(II)] and bivalent Mn [Mn(II)] was examined by the non-linear adsorption models of Langmuir and Freundlich isotherms (Kato et al., 2016; Yoshinaga et al., 2018; Yuan et al., 2021). The results of equilibrium data for Pb and Mn are shown in Fig. 4A–D. Since the equilibrium results of the Langmuir isotherm [$R^2 = 0.9142$ (Pb) and 0.9692 (Mn)] (Fig. 4A, C) were more suitable than those of the Freundlich isotherm [$R^2 = 0.7549$ (Pb) and 0.9193 (Mn)], the Langmuir model was chosen to examine the equilibrium adsorption of Pb and Mn. Theoretically, the maximum abilities of MF-HT to remove Pb and Mn were 826.6 mg/g and 91.2 mg/g, respectively, as estimated from the Langmuir isotherm model.

3.5. Application of MF-HT to canal water samples in Hazaribagh

After confirming the adsorption abilities of MF-HT that were theoretically estimated, it was investigated whether MF-HT could actually remediate the elemental pollution of canal water (Fig. 5A–F). Canal water samples (n = 10) after the relocation of tanneries with ranges of minimum to maximum concentrations of 1259–18,721 μg/L for t-Cr, 1221–18,713 μg/L for Cr(III), 7–480 μg/L for Cr(VI), 4–340 μg/L for Pb, 596–21,198 μg/L for Fe and 194–788 μg/L for Mn were selected. In all of the treated canal water samples, the concentrations of Cr(III), Pb, Fe and Mn were decreased to below the guideline values of US-EPA. In the case of Cr(VI), 8 out of 10 water samples had concentrations lower than the guideline value of US-EPA, while the other two samples showed decreases to 6% and 17% (from 336 μg/L and 115 μg/L to 21 μg/L and 19 μg/L, respectively) of the initial concentrations.

3.6. Decreased pollution and hazard indexes of canal water samples after treatment with MF-HT

The 10 hazardous canal water samples after the relocation in which the pollution indexes (HPI and HEI) (Fig. 6A and B) and hazard indexes (HIC and HIA) (Fig. 6C and D) exceeded the safety thresholds were treated with 1% (w/v) MF-HT for 1 h. All calculated values of the indexes in all of the water samples treated with MF-HT were decreased to the values lower than their safety thresholds.

4. Discussion

In this study, Cr, Pb, Fe and Mn, but not As and Ba, were geographically identified as tannery-related pollutants. Cr was then focused on as a representative pollutant caused by the tanning process (Al Hossain et al., 2019; Tsuchiyama et al., 2020). Since there were approximately 97% decreased levels of t-Cr and Cr(III) in canal water samples after the relocation compared to those before the relocation and since it was shown that the percentages of sampling points where the Cr (III) concentrations exceeded the guideline value decreased to 50% after the relocation, the relocation of tanneries was partially successful from the viewpoint of Cr(III) water pollution. However, the median Cr(III) level after the relocation of tanneries remained higher than the US-EPA guideline value. The median levels of Cr(III) just after the relocation (in 2018) and 2 years after the relocation (in 2020) were comparable. These results suggest not only continuous water pollution of Cr(III) after the relocation but also no further improvement of the Cr(III) pollution for 2 years after the relocation due to the remaining tanneries.

The situation of Cr(VI) pollution after the relocation was more serious than that of Cr(III). While the median levels of Cr(VI) in canal water samples before the relocation of tanneries (in 2014 and 2017) and just after the relocation (in 2018) were lower than the US-EPA guideline value, unexpectedly, the median Cr(VI) level 2 years after the relocation

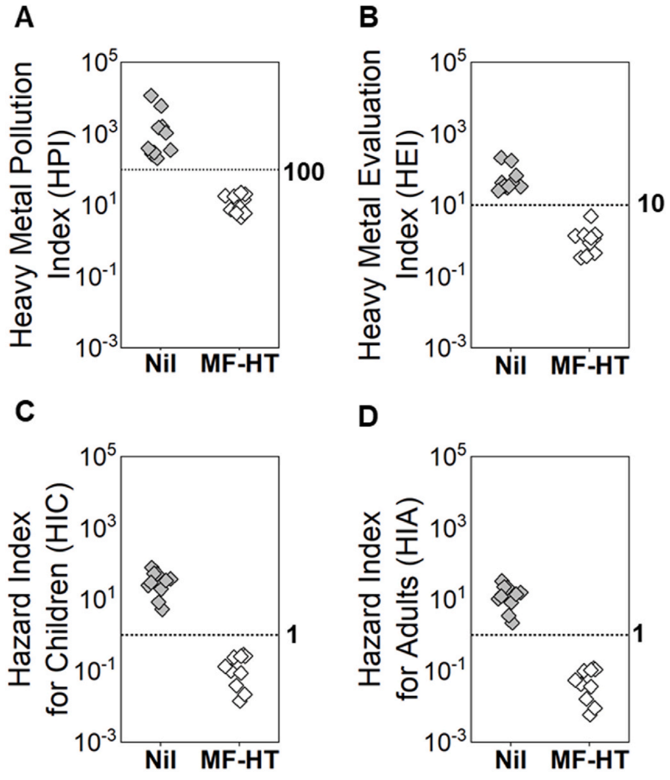

Fig. 6. Decreased levels of indexes for environmental pollution and human health risk in canal water after the relocation of tanneries by treatment with MF-HT. (A–D) HPI (A), HEI (B), HIC (C) and HIA (D) of canal water samples after the relocation of tanneries without (gray dots; $n = 10$) or with (white dots; $n = 10$) treatment with 1% (w/v) MF-HT for 1 h are presented. Safety thresholds of HPI and HEI have been set at 100 and 10, respectively, following previous studies (Prasad and Bose, 2001; Prasanna et al., 2012). Safety thresholds of both HIA and HIC have been set at 1 based on a previous study (Ojemaye et al., 2020).

was 2.8-fold higher than the guideline value. Furthermore, the percentages of polluted sampling points also increased by 3-fold (in 2018) and 7.9-fold (in 2020) after the relocation. Thus, pollution of Cr(VI) in canal water after the relocation progressed over time despite the decrease in about 70 percent of the tanneries (New Age, 2019). These results suggest the conversion of Cr(III) to Cr(VI) in nature.

It has been theoretically shown that Cr(III) in soil polluted by tannery wastewater represented as tannery sludge could be oxidized through interaction with MnO_2 in an aerobic condition (Apte et al., 2005; Shi et al., 2020). Since the converted Cr(VI) is highly soluble, it could migrate into aqueous environments from the soil (Liang et al., 2021). It has been experimentally shown that Cr(III) in tannery sludge could be converted to Cr(VI) under various conditions pertaining to the natural environment (Apte et al., 2006). Alternatively, soil polluted by unsaturated oils derived from the fat-liquoring step of the pre-tanning process could also accelerate the oxidation of Cr(III) to Cr(VI) (Xu et al., 2021b). These previous studies theoretically and experimentally indicate that Cr (III) effused from tanneries can be converted to Cr(VI) in nature. The oxidization of Cr(III) in the bed and bank soils of canals via increased aeration of the soils by the decreased canal water level through the decreased number of tanneries associated with the relocation may actually increase the level of Cr(VI) in the hydrosphere of Hazaribagh.

Pb, Fe and Mn were then focused on as representative pollutants caused by the pre- and post-tanning processes (Dixit et al., 2015; Hashem et al., 2017; Sarwar et al., 2018). Median levels of these elements were temporarily decreased just after the relocation due to the decrease in about 70% of the tanneries (New Age, 2019). These results suggest that the decreased levels of tannery-related elements (Pb, Fe, and Mn) were caused by their decreased emissions from tanneries. However, the median levels of Pb and Fe 2 years after the relocation were about 3.5–4.5-fold higher than those just after the relocation. Correspondingly, there was a report of an increase in tanneries handling the processes other than tanning after the relocation (in 2019) (Uddin, 2019). These results suggested that recent elemental pollution caused by the pre- and post-tanning processes was exacerbated after the relocation of tanneries.

Finally, remediation of polluted canal water was attempted by using MF-HT. Quite high adsorption capacities of MF-HT for Pb, Fe and Mn as well as Cr(III) and Cr(VI) in comparison with adsorption capacities of other adsorbents with the top 10 adsorption qualities were found in this study (Supplemental Tables 3-5) and previous studies (Kumasaka et al., 2013; Yoshinaga et al., 2018). The MF-HT could also remediate all of the tannery-related toxic elements in the raw canal water samples to levels lower than the US-EPA guideline values. Additionally, the levels of environmental and hazard indexes (HPI, HEI, HIC and HIA) in canal water samples in which the levels exceeded their safety thresholds were all decreased to levels lower than their safety thresholds by treatment with MF-HT. These results suggest that the MF-HT can decrease environmental pollution as well as health hazards for humans. In previous studies, the price for the hydrotalcite consisting of magnesium and aluminum (MA-HT) was estimated to be 0.7 cent per kilogram (Gillman, 2006; Kato et al., 2016). Despite the difference between aluminum and iron, the price of MF-HT is assumed to be similar to the price of MA-HT. If the maximum concentrations of Cr(III) (18,713 μg/L), Cr(VI) (480 μg/L), Pb (340 μg/L), Fe (21198 μg/L) and Mn (2215 μg/L) in the canal water samples in this study are applied to the usual amount (22,000 L/day) of tannery wastewater before the relocation in Hazaribagh (Kibria et al., 2016), all of the tannery-related elements in the wastewater could theoretically be remediated by about 2300 g of MF-HT. As shown in Supplemental Table 2, the daily expense of raw materials for remediating most of the elements from the wastewater could be estimated as less than 2 cents per day. Thus, not only the remediation ability but also the price could be benefits of MF-HT. Furthermore, the MF-HT could bind not only the tannery-related inorganic matter (toxic elements) but also the tannery-related organic matter (total phenolic compounds) (Yuan et al., 2021). Since a plan for the establishment of residential land in Hazaribagh is progressing (The Daily Star, 2019), the MF-HT could be a powerful tool for decreasing the health risk through environmental remediation in a vacant lot after the relocation of tanneries.

5. Conclusions

The drastically decreased level (about 97%) of Cr(III) after tannery relocation indicates a beneficial effect of tannery relocation. In contrast, the strikingly increased (about 30-fold) level of Cr(VI) indicates a harmful effect of the relocation. Our fieldwork study newly suggests promotion of the conversion of anthropogenic Cr(III) to Cr(VI) in practice as predicted in previous experimental studies (Apte et al., 2005, 2006). The discharge of Cr(III) to nature might be a reality-based hazard for human health through the chemical conversion, despite the fact that Cr(III) is believed to be a safe element. Considering the toxicities caused by Pb, Fe and Mn in addition to Cr, health hazards in tannery built-up areas remain even after the relocation of tanneries. This study suggested that the use of MF-HT could be effective for solving the problems of environmental pollution and health hazards remaining after the relocation of pollutant sources. Since MF-HT could theoretically remediate various chemicals at a low cost, the use of MF-HT could be a potential countermeasure for not only tannery-related pollution but also various types of environmental pollution worldwide.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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