Water contamination and health risks in the Nhue River, Red River Delta, Vietnam: seven years of reconnaissance

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Abstract

The concentrations of nutrients (NH$_4^+$, NO$_2^-$, NO$_3^-$ and PO$_4^{3-}$), COD, BOD$_5$, coliform, turbidity and eight metals (As, Cd, Ni, Hg, Cu, Pb, Zn and Cr) were investigated in surface water of the Nhue River and To Lich River, Vietnam for 7 years (2010-2017, except 2014). The results from 505 samples demonstrated that concentrations of all these contaminants showed significant spatial and temporal variations. The Nhue River water was seriously polluted by NH$_4^+$ (0.025-11.28 mg/L), PO$_4^{3-}$ (0.17-1.72 mg/L), BOD$_5$ (5.8-179.6 mg/L), COD (1.4-239.8 mg/L) and coliform (1540-326470 CFU/100L); moderately polluted by As (0.2-131.15 μg/L) and Hg (0.11- 4.1 μg/L); and slightly polluted by NO$_2^-$ (0.003-0.33 mg/L) and Cd (2.1-18.2 μg/L). The concentrations of NH$_4^+$, PO$_4^{3-}$, COD, BOD$_5$ and coliform exceeded the drinking water guidelines at all sites and exceeded the irrigation water standards at some locations. Regarding heavy metals, only As, Cd and Hg contents were higher than the permissible limits at some locations while others were below the guideline values. Risks of metals on human health were evaluated by using hazard index (HI) and cancer risk through ingestion and dermal contacts for adults and children. It indicated that As was the most important pollutant leading to non-carcinogenic and carcinogenic concerns. The non-carcinogenic risks of As (HI 1.83-7.4 for adults and 2.6-10.5 for children) were higher than the acceptable values of 1.0 at all sites for both adults and children, while As posed significant carcinogenic risks for adults (1x10$^{-4}$ - 4.96x10$^{-4}$) but not for children (0.27x10$^{-4}$ - 1.6x10$^{-4}$). The study indicated that metals posed hazards mainly by oral intake in drinking water pathway.

Keywords: Water pollution; Nhue River; Nutrients; Heavy metals; Human health risk
1. Introduction

Nutrients play an essential role in plant growth, however, they are also considered as the major pollutants when wastewater from anthropogenic activities such as irrigation practices, mining, industries and urbanization is often discharged either untreated or partially treated into surface water. Eutrophication is caused by high levels of nutrient concentrations in rivers, resulting in the disruption of the ecological balance (Pathak et al., 2018). Nitrate and phosphate are the nutrients required for the plant growth and animal life (Hee et al., 2018; Luu et al., 2012; Zhang et al., 2015). Due to receiving wastewater from household, industries, agriculture and hospitals in high-density urban areas (MONRE, 2007), the key nutrients (N and P) are considered as priority contaminants in surface water in the United States (Carpenter et al., 1998). High concentration of nutrients in surface water may affect human health and livestock (Do and Nishida, 2014). For example, ammonia may become the toxic ions in alkaline water and poses threat for fish populations (Kannel et al., 2007). Although phosphorus is not toxic to human adults in moderate concentrations, high levels of nitrate in drinking water (≥ 10 mg/L) can cause adverse effect or even death to livestock or infants.

Chemical oxygen demand (COD) and 5-day biochemical oxygen demand (BOD₅) have been widely used to quantify organic pollution in surface water. Saksena et al. (2008) suggested that river water is free from organic pollution when the concentration of BOD₅ is low, whilst high concentration of BOD₅ is caused by high organic enrichment, decay of plants and animal matter. High levels of BOD₅ and COD in water reduce the concentration of dissolved oxygen (DO), and adversely affecting healthy fish and other aquatic life (Kannel et al., 2007). Xu et al. (2007) explained that submersed plants can be damaged by lipid peroxide and toxic conditions in water due to high COD concentration.

Microbial contaminants may pose human health risk, particularly in rural catchments or peri-urban areas of developing countries (Xue et al., 2018). For example, microbiological substance in water can cause disease such as hepatitis A and giardiasis for consumers (Momba et
al., 2000). High concentrations of total coliform causes health risk for local people, particularly farmers who are in direct contact with polluted water in the field (Pham et al., 2014). Besides a wide variety of adverse effects on the ecosystems and human health such as diarrhoea, pollutants from untreated wastewater also may pose cancer to people (Avigliano and Schenone, 2015).

Dissolved heavy metals may cause chronic disease in human when they consume contaminated vegetable (Nguyen et al., 2015). Exposure to heavy metals from water bodies may occur in human bodies via consumption of contaminated food and water (Qu et al., 2018). Dissolved heavy metals in polluted water also induce bioaccumulation in plants and aquatic life. As a result, increasing number of investigations have been carried out to assess the potential risk of heavy metals for human health and the ecosystem, using risk assessment method (Adamu et al., 2015; Alves et al., 2014; Li and Zhang; 2010, Qu et al., 2018; Saha et al., 2017) and potential ecological risk assessment (Rehman et al., 2018; Varol and Şen, 2012).

The Nhue River basin is located in highly urbanised area, which covers an area of 107.530 ha (MONRE, 2007) and has a population of 4,696,700 of which 4,378,200 living in Hanoi Capital (HPA, 2017) and 318,500 living in Hanam Province (MPI, 2018). Pham et al. (2010a) reported that an estimated 450 m$^3$/day of the capital’s wastewater was discharged without being treated into the Lu, Set, To Lich and Kim Nguu Rivers, in which To Lich River receives about two third of this wastewater (Nguyen et al., 2013). Nhue River had an average discharge of 26.2 m$^3$/s and received about 5.8 m$^3$/s of untreated domestic water from the To Lich River (Trinh et al., 2006a). Another major pollution source comes from runoff, which carries with a great amount of chemical fertilizers rich in ammonium, nitrate and phosphate (MONRE, 2007). As a result, the Nhue River is one of the three most polluted rivers in Vietnam (Do et al., 2014). Contaminated water from the Nhue River, however, is mainly used for irrigation with major crops of paddy rice and various types of vegetables in peri-urban areas and for fishponds (Do et al., 2011; Pham et al., 2011; Pham et al., 2014). Fuhrimann et al. (2016) concluded that large numbers of farmers in Hanoi faced with
a public health threat due to the wastewater from To Lich River being directly discharged to the Nhue River without treatment.

Several studies have investigated water quality in Nhue River or To Lich River. For example, Giang et al. (2015) tried to assess the impact of agricultural activities on nutrient pollution in surface water, while the studies of Duong et al. (2012) and Pham et al. (2010b) presented the variations and levels of nutrient pollution. Other studies concentrated on assessment of heavy metal concentrations in surface water (Kikuchi et al., 2009), the sediments (Nguyen et al., 2012) or both sediment and water (Nguyen et al., 2013). Furthermore, the studies of Trinh et al. (2006a), Trinh et al. (2006b) and Trinh et al. (2012) used models to evaluate and predict nutrient concentrations in surface water of the Nhue River and To Lich River. Regardless, those investigations have been limited to comparison of metal concentrations with respective standard limits and/or focused mostly on the defining possible sources, particularly for nutrient components while estimation of carcinogenic and non-carcinogenic health risks caused by dissolved heavy metals in water have not been conducted. Therefore, a detailed estimation of two these types of health risks is necessary to better inform the local residents and decision makers in relation to metal contaminations in rivers in Vietnam.

Thus, this paper aims to (i) assess the concentrations of nutrients, COD, BODs, coliform and eight heavy metals in the Nhue River and its tributary (To Lich River), (ii) compare their levels with guideline values prescribed by various agencies, and (iii) evaluate the non-carcinogenic and the carcinogenic risk caused by heavy metals posed for two groups of local residents via ingestion and dermal pathways of river water.

2. Materials and methods

2.1. Study area

The study was conducted in the Nhue River, which is located in the Hanoi and Hanam Province of the Red River Delta, Vietnam (Fig. 1). The Nhue River is a tributary of the Red River,
which is the largest river in the Northern Vietnam with 74 km length and covers a total catchment area of 107,503 ha of which 81,480 ha is irrigated (Do et al., 2011; MONRE, 2007). The Nhue River originates from the Red River at the Lien Mac Sluice, runs through the Hanoi area and Hanam Province and finally flows into the Chau Giang River at the Luong Co Sluice (Trinh et al., 2006b). Hanoi’s wastewater from domestic, industrial and hospital sources is directly released into water body of the To Lich River without treatment (MONRE, 2007). As a result, To Lich River receives about two third of the capital’s wastewater and discharges average volumes of 5.8 m$^3$/s of its water to Nhue River (Trinh et al., 2006a). Although To Lich River has not been a direct sources of water supply for irrigation and aquatic life, water of the Nhue River is the main source for these activities (Nguyen et al., 2013). The runoff of the river was reported to have large amount of chemical fertilizers (Do et al., 2011). Climate in this area is sub-tropical with two main seasons of dry and cold winter (from November to May) and rainy and hot summer (June to October) (Hansen et al., 2017; MONRE, 2007; Pham et al., 2010b; Raghavan et al., 2016).

Fig. 1. Locations of sampling sites along the Nhue River and To Lich River, Vietnam.
2.2. Sample collection and methods

2.2.1. Sampling

Ten sampling locations were chosen along the Nhue River and its tributary (Fig. 1) including Lien Mac Sluice (site 1), Dien Bridge (site 2), Ha Dong Dam (site 3), To Bridge (site 4), Xem Bridge (site 5), Dong Quan Dam (site 6), Nhat Tuu Dam (site 7), Luong Co Sluice (site 8) and Phu Van Bridge (site 9). Site 10 was Thanh Liet Dam situated at the downstream of To Lich River near the junction with the Nhue River. The sampling of water was conducted by the Institute of Irrigation Planning, Hanoi, Vietnam over a 7-year period (2010-2013, 2015-2017). The water samples were collected at a depth of 0.5 m below surface in the midstream. Samples were preserved according to standard methods for the examination of water (Rice et al., 2012). Specifically collected water samples were preserved at 2-5 °C by placed in the cooler boxes, and transported to the Laboratory of Institute of Irrigation Planning, Hanoi, Vietnam immediately for analysis.

2.2.2. Chemical and microbiological analysis

The chemical and microbiological measurements were undertaken according to standard methods for the examination of water and wastewater (Rice et al., 2012). Ammonia (NH₄⁺), nitrite (NO₂⁻), nitrate (NO₃⁻) and phosphate (PO₄³⁻) concentrations were measured by spectrometric method (Rice et al., 2012). BOD₅ was determined after 5 days of incubation in the dark at 20 °C, and COD was analysed following standard method (Rice et al., 2012). Total coliform was identified by membrane filtration method (Dean, 1990). The concentration of all heavy metals (As, Cd, Ni, Hg, Cu, Pb, Zn, Cr) were analyzed by flame atomic absorption spectrometry (Dean, 1990).

2.2.3. Human health risk assessment from exposure to heavy metals

According to Saha et al. (2017), dissolved heavy metals in surface water may threat human health associated with two main pathways including the ingestion and dermal absorption. In turn, the studies of Alves et al. (2014), De Miguel et al. (2007) and Saha et al. (2017) used the equations (2) and (3), which were introduced by the US Environmental Protection Agency (USEPA), to
calculate the average daily dose (ADD) for two subpopulation groups separately via these two pathways. This work only assessed the health risk for two subpopulation groups of adults (as the general population) and children (as a sensitive group) by each metal in surface water using Equations (1) and (2):

\[
ADD_{\text{ing}} = \frac{C_w \times RI \times EF \times ED}{BW \times AT} \quad (1)
\]
\[
ADD_{\text{derm}} = \frac{C_w \times SA \times K_p \times EF \times ED \times ET \times CF}{BW \times AT} \quad (2)
\]

where \(ADD_{\text{ing}}\) and \(ADD_{\text{derm}}\) are ingestion average daily dose (mg/kg/day) by ingestion and dermal absorption pathways; \(C_w\) is the metal concentrations (mg/L) in water; \(IR\) is the ingestion rate (day\(^{-1}\)) of water; \(EF\) and \(ED\) are the exposure frequency (day/year) and duration (year); \(BW\) is the body weight (kg); \(AT\) is the averaging time (day); \(SA\) is the exposed skin surface area (m\(^2\)); \(K_p\) is the dermal permeability constant (cm/h); \(ET\) is the exposure time (h/day); and \(CF\) is the unit conversion factor.

The potential health risk of each metal was expressed in terms of a non-carcinogenic and a carcinogenic ways. The risk characterization of the potential non-carcinogenic human health risks are usually defined by hazard quotient (HQ), which was calculated by using Equation (3):

\[
HQ = \frac{ADD}{RfD} \quad (3)
\]

where HQ is unit less and RfD is the corresponding reference dose (mg/kg-day). When the value of HQ exceeds 1.0, non-carcinogenic risk might be posed to human health (USEPA, 2004).

The sum of HQs from all metals used to evaluate the total potential non-carcinogenic risks was introduced by Equation (4):

\[
HI = \sum_{i=1}^{n} HQ_i \quad (4)
\]

where HI is hazard index; \(i\) is the exposure pathway of each metal. When \(HI > 1\), it indicates that human health may be adversely effected by heavy metals (Qu et al., 2018; Rehman et al., 2018; Fakhri et al., 2018; Saha et al., 2017).

The carcinogenic risk (CR) was calculated by Equation (5) to express the level of potential cancer risk of heavy metal for human health (Fakhri et al., 2018; Saha et al., 2017):
\[ CR = ADD \times CSF \]  

where CSF is the cancer slope factor (mg/kg-day\(^{-1}\)). The cancer risk was only calculated for As from two exposure pathways of ingestion and dermal. Then the sum of both values was calculated to obtain the total carcinogenic risk. According to Qu et al. (2018), carcinogenic risks acceptance by the USEPA ranged from \(1 \times 10^{-6}\) to \(1 \times 10^{-4}\), in which risks exceeding \(1 \times 10^{-4}\) are considered as unacceptable while the risks below \(1 \times 10^{-6}\) are not likely pose significant health hazards.

3. Results and discussion

3.1. Nutrients, COD and BOD\(_5\) concentrations

3.1.1. Nutrients concentrations

Nutrient concentrations in surface water samples of the Nhue River were presented in Fig. 2 and Table 1. The mean \(\text{NH}_4^+\) concentrations followed a decreasing order as: site-10 (5.061 mg/L) > site-4 (4.118 mg/L) > site-5 (3.896 mg/L) > site-3 (3.830 mg/L) > site-6 (3.228 mg/L) > site-2 (3.018 mg/L) > site-7 (2.646 mg/L) > site-8 (2.422 mg/L) > site-1 (2.116 mg/L) > site-9 (1.42 mg/L). Fig. 2a showed that \(\text{NH}_4^+\) concentrations in 2017 were higher than other years at all sites except site 8. The mean concentrations of \(\text{NH}_4^+\) in the Nhue River were higher than those of Saigon River in both dry and rainy seasons (Strady et al. 2017), which receives large amount of urban domestic and industrial wastewater from the largest city (Ho Chi Minh) in Vietnam. Compared with other urban rivers globally, the highest \(\text{NH}_4^+\) concentration in Nhue River were dramatically higher than those rivers in China (Wang et al., 2018), India (Saksena, 2018) and Spain (Vega et al., 1998), suggesting that high intensity and contamination levels wastewater were discharged into the Nhue River. Furthermore, compared to the national guideline values (MONRE, 2015), 93% and 78% of surface water samples exceeded the permissible limits of \(\text{NH}_4^+\) for drinking water and irrigation purposes, respectively.

Mean \(\text{NO}_2^-\) concentrations followed a decreasing order: site-9 (0.1282 mg/L) > site-8 (0.096 mg/L) > site-4 (0.086 mg/L) > site-7 (0.076 mg/L) > site-5 (0.073 mg/L) > site-6 (0.071 mg/L) >
site-2 (0.054 mg/L) > site-10 (0.049 mg/L) > site-3 (0.045 mg/L) > site-1 (0.027 mg/L). The high mean NO$_2^-$ concentrations in Nhue River were found at the downstream sites, suggesting that agricultural activities such as using pesticides and fertilizers are likely the major contributors leading to NO$_2^-$ pollutants. Fig. 2b also presented sharply high concentrations of NO$_2^-$ at sites 4 and 5 in 2013 and sites 6 and 9 in 2011. Compared to the previous studies and other rivers, the NO$_2^-$ concentrations were similar with the data ten years ago (Duong et al., 2007) and were lower than that of Luoc River, Vietnam (Ta et al., 2018). This study found that 33% of NO$_2^-$ samples exceeded the drinking water and irrigation guidelines (MONRE, 2015).

Mean NO$_3^-$ concentrations decreased as: site-2 (0.819 mg/L) > site-4 (0.728 mg/L) > site-3 (0.668 mg/L) > site-5 (0.63 mg/L) > site-9 (0.613 mg/L) > site-7 (0.611 mg/L) > site-10 (0.577 mg/L) > site-6 (0.55 mg/L) > site-8 (0.52 mg/L) > site-1 (0.421 mg/L). The results indicated that the mean NO$_3^-$ concentrations in 2016 were dramatically higher than those in other years (Fig. 2c). Mean concentration of NO$_3^-$ were in accordance with other studies, except the Nairobi River, Kenya (Njuguna et al., 2017). Moreover, NO$_3^-$ concentration at all sites were below the permission limits for both drinking water and irrigation guidelines prescribed by MONRE (2015) with only 6% and 2% of total samples exceeding these levels (Table 3).

Fig. 2d indicated that average PO$_4^{3-}$ concentrations followed the order: site-10 > site-4 > site-3 > site-5 > site-6 > site-2 > site-7 > site-8 > site-1 > site-9. Mean concentrations of PO$_4^{3-}$ in surface water varied from 0.170 to 1.720 mg/L, which was lower than that of Pisuerga River, Spain (Vega et al., 1998), but higher than Gomti River, India (Singh et al., 2004). Regarding the temporal distributions, PO$_4^{3-}$ concentrations in 2017 at the sites of 1, 2, 3, 4, 5 and 10 were remarkably higher than other years of the investigated period, while other sites showed a roughly constant trend. Concentrations of PO$_4^{3-}$ exceeded the prescribed limits of drinking water and irrigation guidelines by MONRE (2015) with the percentages of 100% and 93%, respectively.
Table 1. Concentrations of Nutrients, BOD\textsubscript{5}, COD and coliform in surface water of the Nhue River in comparison to other rivers

<table>
<thead>
<tr>
<th>River</th>
<th>Nutrients (mg/L)</th>
<th>BOD\textsubscript{5} (mg/L)</th>
<th>COD (mg/L)</th>
<th>Coliform (CFU/100mL)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH\textsubscript{4}+</td>
<td>NO\textsubscript{2}−</td>
<td>NO\textsubscript{3}−</td>
<td>PO\textsubscript{4}−</td>
<td>Mean ± SD (Min-Max)</td>
</tr>
<tr>
<td>Nhue River</td>
<td>3.17±2.46 (0.025-11.28)</td>
<td>0.07±0.11 (0.003-0.33)</td>
<td>0.614±1.54 (0.005-6.91)</td>
<td>0.60±0.30 (0.17-1.72)</td>
<td>55.04±39.69 (5.8-179.6)</td>
</tr>
<tr>
<td>Nhue River</td>
<td>5.9 (2.2-7.8)</td>
<td>0.05 (0.01-0.08)</td>
<td>1.2 (0.9-1.7)</td>
<td>1.7 (0.96-2.66)</td>
<td></td>
</tr>
<tr>
<td>Thames River</td>
<td>0.187</td>
<td>8.49</td>
<td>30.94±4.51 (0.21-40.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nairobi River, Kenya (Dry season)</td>
<td>0.10</td>
<td>0.98</td>
<td>0.038</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daugava River, Latvia</td>
<td>2.40</td>
<td>1.69</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sai Gon River, Vietnam (Dry season)</td>
<td>0.14±0.01</td>
<td>1.83±0.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Luoc River, Vietnam</td>
<td>0.24±0.02</td>
<td>0.22±0.16</td>
<td>0.14±0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huanghe River, China</td>
<td>0.98 (0.2-5.78)</td>
<td>4.84</td>
<td>(2.03-16.56)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indian River, USA</td>
<td>0.22±0.11</td>
<td>0.22±0.16</td>
<td>0.14±0.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Overall, the nutrient concentrations, particularly $\text{NH}_4^+$ in the Nhue River and To Lich River were very high due to urban wastewater discharges, which could result in an excessive growth of algae in the decomposition process causing the depletion of dissolved oxygen (Kannel et al., 2007). It is evident that surface water in the Nhue River was heavily enriched with nutrient components, particularly $\text{NH}_4^+$ because its concentrations were above the acceptable values for any category of surface water quality guidelines or standards.

3.1.2. $\text{BOD}_5$ and COD concentrations

Fig. 3a illustrated average concentrations of $\text{BOD}_5$ followed a decreasing order: site-10 > site-4 > site-3 > site-6 > site-2 > site-7 > site-8 > site-9 > site-1. The highest $\text{BOD}_5$ concentration was 179.8 mg/L at site-4, which was 31 times higher than the lowest value (5.8 mg/L at site-1). Ranging between 17.52 and 107.87 mg/L, the average concentrations of $\text{BOD}_5$ in the Nhue River were at least double than those of the previous study (Duong et al., 2006). These degrees, however, were similar to the Old Brahmaputra River, Bangladesh (Bhuyan et al., 2018), and significant higher than those other studies of Hafni (2015), Sánchez et al. (2007), Singh et al. (2004) and Wang et al. (2018). Table 3 showed that 100% samples of $\text{BOD}_5$ in surface water exceeded the permission limits of drinking water guidelines while the percentage of samples exceeding the $\text{BOD}_5$ concentration for irrigation purpose was 89% (MONRE, 2015).
Figure 2. Contaminant concentrations for different years (average values with standard deviation (SD)) at ten different sites of the Nhue River and its tributary To Lich River in Vietnam: NH$_4^+$ (a), NO$_2^-$ (b), NO$_3^-$ (c), PO$_4^{3-}$ (d), and compared with National water quality guidelines (drinking water-red line and irrigation-black line).
Fig. 3b illustrated that the highest COD concentration in the Nhue River occurred at site 10 followed by site 4, due to wastewater discharge from tributary. Average concentrations of COD followed the order: site-10 > site-4 > site-5 > site-3 > site-6 > site-2 > site-7 > site-8 > site-9 > site-1, and ranged from 25.67 to 119.07 mg/L. The mean concentrations of COD at sites 1, 2, 6 and 10 increased from 25.67 mg/L to 145.09 mg/L, which are significantly higher than the results by Duong et al. (2006). COD concentrations in the Nhue River were higher than in the Gambulawung River, Indonesia (Hafni, 2015), the Guadarrama River, Spain (Sánchez et al., 2007), Gomti River, India (Singh et al., 2004), the Haihe River, Huai River, Huanghe River and Pear River in China (Wang et al., 2018). Compared to the guideline values, 99% and 82% of samples exceeded the drinking water and irrigation guidelines recommended by MONRE (2015), respectively.
**Figure 3.** Contaminant concentrations for different years (average values with SD) at ten different sites of the Nhue River and its tributary To Lich River in Vietnam: BOD$_5$ (a), COD (b) and coliform (c) and compared with National water quality guidelines (drinking water–red line and irrigation – black line).

The results showed that the COD and BOD$_5$ concentrations varied slightly during the period 2010-2013. After that, the concentrations significantly increased during 2015-2017. It is likely that significant increase in wastewater volume from domestic and industrial sources of Hanoi resulted in worsening pollution in surface water.

### 3.2. Coliform concentrations

**Fig. 3c** showed that coliform concentrations at site 10 (tributary) followed by site-4 situated downstream of To Lich River were significant higher than those at other sites due probably to municipal wastewater from the Hanoi city via To Lich River. After site-5, a dramatic decrease in coliform concentrations in downstream of the Nhue River was observed due to the decomposition. The order of coliform concentrations (CFU/100mL) was site-10 (105,252) > site-4 (102,250) > site-5 (72,271) > site-6 (56,238) > site-7 (42,907) > site-2 (26,732) > site-3 (26,459) > site-8 (18,742) > site-9 (11,757) > site-1 (5,292). The average coliform concentrations showed a decreasing trend after the investigated period (Fig. 2g).

**Table 3** compares Coliform with the surface water guidelines for drinking water and irrigation purposes (MONRE, 2015). 98% and 86% of coliform samples exceeded the drinking
water and irrigation guidelines suggested by MONRE (2015), respectively. This study agreed with Fuhrimann et al. (2017) that microbial contamination posed gastrointestinal infections to urban farmers in Hanoi due to using wastewater from the Nhue River and To Lich River in agriculture and aquaculture. Pham et al. (2014) found that 27% of diarrhoeal episodes in the dry season due to farmers exposure to wastewater from the Nhue River during agricultural activities. Although the Coliform concentrations were higher than the permission value, their figures significantly reduced to near the accepted values in the last two years of the surveyed period. It is suggested that the improvement of on-site sanitation system effluents in the studied areas, particularly in inner Hanoi city, leading to the significant change.

3.3. Heavy metal concentrations

The results obtained from the heavy metal analyses of the surface water samples in the Nhue River and its tributary – To Lich River – were graphically shown in Fig. 4 and Table 2, and were compared with the guideline values. The mean concentrations (μg/L) of eight metals followed a decreasing order as: Ni (47.18) > As (32.91) > Zn (17.43) > Cu (6.34) > Cd (6.21) > Pb (3.21) > Hg (2.03) > Cr (1.03). The highest concentrations were observed for Ni and As, while the lowest for Hg and Cr. The relatively high level of Ni and As found in this area may be due to anthropogenic sources such as industrial and municipal wastewater (Nguyen et al., 2015).
Figure 4. Heavy metal concentrations for different years (average values with SD) at ten different sites of the Nhue River and its tributary To Lich River in Vietnam: As (a), Hg (b), Pb\(^{2+}\) (c) and Cd (d) and their comparison with drinking water guidelines (WHO, 2017) (red line) and irrigation purpose (MONRE, 2015) (black line).

Compared with previous studies (Duong et al., 2006; Kikuchi et al., 2009; Nguyen et al., 2013; Nguyen et al., 2015), there was a considerable increase in the concentrations of heavy metals in surface water of the Nhue River and To Lich River (Table 2). Kikuchi et al. (2009) suggested three main sources of heavy metal contaminations in surface water of the Nhue River: (i) the Hong River, the headwater of the Nhue River; (ii) wastewater from the urbanized areas and craft villages located along the middle-stream of the river basin; and (iii) industrial and municipal wastewater in the To Lich River. For example, the high concentrations of As, Cd and Cu at sites 4, 5 and 10 may be due to the industrial and municipal wastewater discharged into To Lich River whilst sources from urban areas and craft villages seemed to account for significant concentration of Pb at site 9 (Fig. 4e). Both natural and anthropogenic sources situated along the river length may attribute to the relatively high level of Hg at sites 1, 7 and 10 (Fig. 4b). Therefore, surface water quality in the Nhue River may pose risk for irrigation and aquaculture caused by As and Hg.
The surface water of the Nhue River is the primary source for fisheries and irrigation in this area. Therefore, heavy metal concentrations were compared with the irrigation water quality guidelines prescribed by National technical regulation on surface water quality of Vietnam (Ministry of Natural Resources and Environment, Vietnam (MONRE), 2015). Fig. 4 revealed that only the median concentrations of As (at sites 3, 5 and 10), Hg (at sites 1, 3, 5, 6, 7, 9 and 10) and Cd (at site 10) exceeded the permissible limits, while As, Hg and Cd at other sites and Ni, Zn, Cu, Pb and Cr at all sites (Table 3) were within the recommended limits suggested by MONRE. The results also showed that 65% of surface water samples exceeded the permissible limits of (MONRE, 2015). The metal concentrations found in the river water samples were also compared to drinking water quality guidelines recommended by World Health Organisation (WHO, 2017) and MONRE (2015) (Table 3). 81%, 65% and 52% of surface water samples exceeded the As, Hg and Cd limits suggested by MONRE (2015), while the proportion of Cd was 92% in WHO standard.

The concentrations of all metals were in accordance with the previous studies of Duong et al. (2006) and Kikuchi et al. (2009), while the results by Nguyen et al. (2015) showed remarkably higher concentrations of As, Pb and Zn. In comparison with Saigon River in Vietnam and other rivers around the world, the concentrations of all metals were higher.
Table 2. Concentrations of heavy metals (µg/L) in surface water of the Nhue River in comparison to other rivers

<table>
<thead>
<tr>
<th>Rivers</th>
<th>As Mean ± SD (Min-Max)</th>
<th>N</th>
<th>Cd Mean ± SD (Min-Max)</th>
<th>N</th>
<th>Ni Mean ± SD (Min-Max)</th>
<th>N</th>
<th>Hg Mean ± SD (Min-Max)</th>
<th>N</th>
<th>Cu Mean ± SD (Min-Max)</th>
<th>N</th>
<th>Pb Mean ± SD (Min-Max)</th>
<th>N</th>
<th>Zn Mean ± SD (Min-Max)</th>
<th>N</th>
<th>Cr Mean ± SD (Min-Max)</th>
<th>N</th>
<th>References</th>
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<tbody>
<tr>
<td>Nhue River</td>
<td>32.91±28.94 (0.20-131.15)</td>
<td>74</td>
<td>6.21±3.67 (2.10-18.20)</td>
<td>60</td>
<td>47.18±16.86 (25.80-93.10)</td>
<td>60</td>
<td>2.03±2.61 (0.11-4.10)</td>
<td>55</td>
<td>6.34±10.58 (0.25-60.13)</td>
<td>187</td>
<td>3.22±5.3 (0.12-7.0)</td>
<td>187</td>
<td>17.43±18.85 (1.10-72.0)</td>
<td>60</td>
<td>1.03±1.32 (0.1-6.0)</td>
<td>76</td>
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<td>4.73±1.20 (2.60-6.54)</td>
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<td>4.04±2.59 (2.13-10.2)</td>
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<td>2.26±0.91 (1.41-4.19)</td>
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<td>30.5±15.5 (11.5-61.9)</td>
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<td>3.81±1.20 (1.85-5.40)</td>
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<td>Jan. 2006</td>
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<td>11.0±5.8 (6.24-23.6)</td>
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<td>7.13±5.56 (1.79-18.8)</td>
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<td>20.9±2.4</td>
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<td>Qu et al. (2018)</td>
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Table 3. Percentage of samples that exceeded drinking water and irrigation guidelines prescribed by WHO and Vietnamese National surface water quality standards (MONRE, 2015)

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<td>Nutrient</td>
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<td>NH₄-N (mg/L)</td>
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<td>NO₂-N (mg/L)</td>
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<td>NO₃-N (mg/L)</td>
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<td>PO₄³-P (mg/L)</td>
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<td>COD (mg/L)</td>
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<td>BOD₅ (mg/L)</td>
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<td>Coliform</td>
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<td>98</td>
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<td>(CFU/100 mL)</td>
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<td>Heavy metal</td>
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<tr>
<td>As (μg/L)</td>
<td>10</td>
<td>81</td>
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<tr>
<td>Cd (μg/L)</td>
<td>5</td>
<td>52</td>
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<tr>
<td>Ni (μg/L)</td>
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<td>Hg (μg/L)</td>
<td>1</td>
<td>65</td>
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<tr>
<td>Cu (μg/L)</td>
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<td>Pb (μg/L)</td>
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<tr>
<td>Zn (μg/L)</td>
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<td>Cr (μg/L)</td>
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3.4. Human health risk assessment

3.4.1. Average daily dose

The average daily dose (ADD) values through ingestion and dermal contact were measured for eight heavy metal concentrations in surface water of the Nhue River. Two population groups of adults and children were selected to analyse. The exposure and risk assessment were carried out by the deterministic approach to estimate the mean, median, 5th and 95th percentile of ADD values. Compared within two exposure routes of water, ingestion was the dominant source, which agreed with the previous studies (Alves et al., 2014; Saha et al., 2017). Moreover, the ADD values for adults were significant less than those for children.

3.4.2. Hazard quotient

Hazard quotient (HQ) values for eight trace metals in the Nhue River through exposure to ingestion and dermal contact with adult and children were displayed in Fig. 5. Only the mean HQ of As through ingestion pathway for both groups exceeded the respective safe reference doses (HQs > 1), indicating a potential of As for a non-carcinogenic adverse health effect (Giri and Singh, 2015; Saha et al. 2017).

HQ values of all other trace metals through both ingestion and dermal pathways were below the acceptable point (HQ = 1). Therefore the exposed population is considered safe to health risk (Saha & Paul, 2018). As was the main contributor to total HQs followed by Cd and Hg, while rest of the metals accounted for marginal contribution on the total HQs (Fig. 5b).
Figure 5. Hazard quotient (HQ) by adults and children through ingestion (a), dermal (b) and their comparison with the acceptable level for non-carcinogenic effects (black line).

3.4.3. Hazard index

Fig. 6a showed that the non-carcinogenic risk of As concentrations combined by ingestion and dermal exposure exceeded the safety level (HI>1) for adults and children at the Nhue River area. The mean HI values of Cd were closed to 1.0. Other metals exhibited much lower values of HI for adults and children. As contributed to 80% of total HI values followed by Cd and Hg with around 11% and 6%, respectively. Other metals accounted for marginal proportion of total HI. The study also showed that HI of children was higher than that of adults, indicating that children were more susceptible to non-carcinogenic risk from heavy metals. Mean HI values of trace metals ranged from 0.0017 to 3.25 for adults and 0.0024 to 4.49 for children. HI values of As in this study were roughly similar to those of Bangshi River in Bangladesh (Saha et al., 2017) while HI values
of other metals were significantly lower. Compared to other studies, mean HI values of trace metals in this study were higher than those of the Padro River, Brazil (Alves et al., 2014) and Wen-Rui Tang River, China (Qu et al., 2018). Therefore, As was the most important pollutant which may pose health risk for local people, particularly for sensitive children in the studied area.

With regard to spatial distribution, total HI values at all sites were higher than the recommended level of 1.0, followed by a decreasing order: site-5 > site-10 > site-3 > site-4 > site-2 > site-6 > site-7 > site-8 > site-1 > site-9 (Fig. 5b). Total HI values varied from 1.83 to 7.66 for adults and from 2.62 to 10.75 for children. The results showed high HI values at the sites are closed to the urban area, suggesting that industrial and municipal wastewater are the main sources of heavy metals.

![Graph showing hazard index for metals and sites]

**Figure 6.** Hazard index (HI) for adults and children displayed by metals (a) and trace sites (b) with the benchmark values.

### 3.5.2. Total cancer risk (TCR)

The total cancer risk for adult and children were estimated by sum of cancer risks through ingestion and dermal exposure. The acceptable levels of cancer risk prescribed by USEPA varies from $1 \times 10^{-6}$ to $1 \times 10^{-4}$ (Alves et al., 2014; Fakhri et al., 2018; Qu et al., 2018; Rehman et al., 2018; Saha et al., 2017). When the carcinogenic risk values are higher than $1 \times 10^{-4}$, it indicates that heavy metals may pose adverse health hazard to local residents.
The estimated total cancer risk for adults ranged from \(1.75 \times 10^{-4}\) (95% lower) to \(6.54 \times 10^{-4}\) (95% upper), whilst the figures for children varied between \(4.79 \times 10^{-5}\) and \(7.83 \times 10^{-5}\). This study showed that the mean TCR for adults was always higher than the safety limit of \(1 \times 10^{-4}\) while the mean TCR for children was below this level. Other studies of Li and Zhang (2010) and Saha et al. (2017) also found that As was the main substance which not only caused non-carcinogenic but also carcinogenic concerns for local people, while Qu et al. (2018) indicated that the cancer risk caused by As concentration in surface water of Wen-Rui Tang River, China was below the acceptance level.

Regarding spatial distribution, Fig. 7b indicated that only TCR values of As at sites 3, 5 and 10 closed to the To Lich River were higher than recommended limits of \(1 \times 10^{-4}\), while other sites had acceptable values of TCR. Therefore, our study showed that local people using the water of Nhue River and To Lich River might have cancer risk associated with As, in which adult faced with higher risk than children. In addition, compared between ingestion and dermal contacts, the former pathway was the main factor contributed to total cancer risk with its proportion over 99%.

**Fig. 7.** Cancer risk for adults and children displayed by sites (a) and trace metals (b) with the benchmark values.
4. Conclusions
Surface water in the Nhue River was highly polluted by NH$_4^+$, PO$_4^{3-}$, COD, BOD$_5$ and Coliform, moderately polluted by As and Hg, slightly polluted by NO$_2^-$ and Cd. Concentrations of NH$_4^+$, PO$_4^{3-}$, COD, BOD$_3$ and Coliform at all site were higher than the drinking water guidelines established by WHO and MONRE and higher than the recommended limits for irrigation prescribed by MONRE, while heavy metals including As, Hg and Cd at some locations exceeded both water quality guidelines.

Exposure risk assessment tools were used to predict human risk of metals. Overall, there were high potential of non-carcinogenic human health risks for adults and children at all site due to exposure to As. In contrast, As was the only element causing potential carcinogenic risks at some urban sites for adults. Therefore, this study provides a useful guidance for surface water regulatory activities and public health surveillance actions in urban and peri-urban areas of Vietnam.

Acknowledgements
We are grateful to the staff at the Division for Water Quality and Environment Management Laboratory and Consultancy, Institute of Water Resources Planning, Vietnam for providing the data. The data was the results of the baseline survey projects "Monitoring and forecasting of water quality in irrigation system of Nhue River in service of agricultural water production" from 2010 to 2017. The project was sponsored by Directorate of Water Resources, Ministry of Agriculture and Rural Development, Vietnam.

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