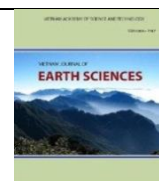




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Assessment of heavy metal concentrations and its potential eco-toxic effects in soils and sediments in Dong Cao catchment, Northern Vietnam

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ABSTRACT

The environmental risks associated with the concentration of metals in soils and sediments due to their toxicological properties on living organisms are not yet sufficiently studied in North Vietnam. Soil samples and sediments collected from three weirs (W1, W2 and W4) of the Dong Cao catchment (49.7 ha) and from the downstream Cua Khau reservoir (CK) were analyzed for heavy metal concentrations and geochemical parameters. Bioassays were then applied to assess the toxicity of these soils and sediments based on a test of phytotoxicity with garden cress (*Lepidium savitum*) and the BioTox test for toxicity to bacteria, using *Allivibrio fischeri*. Metal concentrations in sediments (Cr and Cu) were significantly higher in the Dong Cao catchment (W1 and W4) in comparison with the reservoir area. The toxicity of soils and sediments of W1 and W4 was detected at a low level by the two bioassay tests. Inhibition of light emission by *Allivibrio fischeri* was slightly reduced for soils and sediments of W1 and W4 after 15-min of the contact. Similarly, this slight impact has been reflected in the growth and seed germination of *Lepidium savitum* in the sediment samples collected from the weirs of Dong Cao catchment. The major pollutant metals were Cr, Cu and Zn. Cr contamination is undoubtedly derived from rocks whereas Cu and Zn are most likely associated with human activities (local agricultural inputs and atmospheric fallout).

Keywords: Cu; Cr; Zn; ecological risk; upland region; soil; sediment toxicity.

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1. Introduction

Heavy metal pollution has become a worldwide environmental problem (Garnier et al., 2008). Environmental pollution by heavy metals has been accelerated in Vietnam in the last two decades due to rapid economic

development, land-use changes, and intensification of agricultural practices (Huong et al., 2010). Key monitoring pollutants, including heavy metals of Cd, Pb, Hg, Cr, Ni, Cu, Zn, and As, are listed by the Ministry of Natural Resources and Environment of Vietnam (MONRE, 2015). Environmental Protection Agency of the United States reported that Cr is classified as a

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priority pollutant in Category A (human carcinogen), while Cd and Pb are classified in Category B (probable human carcinogen) (US EPA, 1999). Waste disposal is an anthropogenic activity that contributes to increasing levels of heavy metals, including copper (Cu) and zinc (Zn) in soils (Ngole and Ekosse, 2012). Cu and Zn concentrations are often influenced by leachate from the landfill of municipal waste rich in these heavy metals and those heavy metals eventually contaminate surrounding environments (Zhai et al., 2003; Chuangcham et al., 2008).

Pollution can have also natural origin due to heavy metals contents in parent material of soils. These are the most important reservoir of heavy metals in the terrestrial ecosystem, and the concentration of heavy metals in soils is, therefore, an important indicator of environmental quality (Franco-Uria et al., 2009; Li et al., 2013). In addition, we must also consider the impact of wind and water erosion. Wind erosion is responsible for the detachment and transport over large distance of dust, which may contain heavy metals (Cohen et al., 2010). Similarly, water erosion favors detachment, transport, and often a concentration of water-borne sediments in lakes and reservoirs (Kikuchi et al., 2010). Soil erosion is particularly important in this region of Vietnam exposed to severe monsoon periods and on steep slopes (Valentin et al., 2008).

The catchment of the Red River Delta is dominated by Paleozoic sedimentary rocks together with metamorphic and igneous rocks distributed along the mainstream (Borges and Huh, 2007). Driven by the intensified use of agrochemical and land use in the region, a large amount of wastewater containing heavy metals is discharged in the water systems and then accumulated in the sediments (Thuong et al., 2013). Heavy metals pollution is,

therefore, becoming a critical issue in the environmental management of catchments in the Red River Delta (Phuong et al., 2010, Thuong et al., 2013, Tra Ho and Egashira, 2000). The Dong Cao catchment (538 ha), which is a small tributary to the Red River, has been equipped for sediment yield and hydrological monitoring to assess the interaction between rainfall, runoff, groundwater, topography, soil quality, and land use and predict the impact of land use and land management on soil losses, soil fertility, and solute transport in and through the watershed (Valentin et al., 2008).

Heavy-metal pollution studies usually focus on concentrations either in aerosols, soils, or sediments, but do not attempt to relate soils and sediment concentrations. This is why our study attempted to develop an integrated pollution evaluation method for assessing ecological risk and toxicity level to organisms of heavy metal pollution within two nested catchments. We hypothesized that the combination of chemical analysis with toxicity bioassays is a valid approach for identifying the most toxic fractions and toxic compounds present in the environment. Among different toxicity bioassays, phytotoxkit and microtox seemed to be appropriate ecotoxicological screening tools for toxicity assessments, for regulatory compliance, and for use in a battery of tests to rapidly monitor the health hazards and risks of chemicals that enter the environment (De Zwart and Slooff, 1983, Morales Ruano et al., 2019). The main aim of this study was: (1) to assess heavy metal pollution in soils and sediments in Dong Cao catchment and in the downstream Cua Khau reservoir in a rural area, 40 km for Hanoi; (2) to differentiate the anthropogenic and natural origins of these heavy metals; (3) to analyze the potential

ecological risk and toxicity to organisms through chronic bioassays.

2. Material and methods

2.1. Site description

Dong Cao catchment and Cua Khau reservoir, located in the Quoc Oai district, Hanoi, approximately 40 km SW of Hanoi (20°57"N, 105°29"E, Fig. 1), were selected because of their agricultural activities. The soils and sediments were collected from different sub-catchments of Dong Cao catchment and the downstream Cua Khau reservoir (16.6 ha) down to a large catchment of 538 ha (Fig. 1). The Dong Cao catchment covers 49.7 ha of cultivated sloping lands, surrounded by hills, with average and steepest slopes of 40% and 120%, respectively. Cua Khau reservoir has a size of 4 ha. Sub-catchments of W1 (44 ha) and W2 (7.7 ha) were equipped with sediment traps and weirs before they intersect with the mainstream. W4 (8.4 ha) is on the upper part inside the catchment, W3 is no longer in use. Each sub-catchment has the same hydrological network and are thus comparable. In the upland area of Dong Cao village, crops such as cassava, arrowroot, taro, and maize were cultivated in association with some trees (*Venitia Montana*, *Acacia mangium*) from the mid-1970s (Clement and Amezaga, 2008). However, plant trees have been then chosen to cultivate from the mid-1990s as reforestation for this area and stopping crops (Clement and Amezaga, 2008).

2.2. Soil and sediment sampling

Soils and sediments were sampled in October 2017, April, and August 2018. Samples were collected from the directly adjacent soils, few meters from the stream of each sub-catchment (triplicate sampling for

each site). Surface soil samples (0-25 cm) and sediment samples (5 cm) were collected with a stainless steel auger because of the most reactive to predominant biological, physical and chemical activities in these layers (Boyd et al., 1999). The sediment and soil samples were placed in sealable plastic bags and stored in the freezer at -20°C until required for analysis (Kandeler, 2007). Soil and sediment samples were then allowed to thaw at 4°C before analyzing.

2.3. Laboratory analyses of soil and sediment samples for Physico-chemical properties

Soil and sediment samples were analyzed for moisture content using the gravimetric method and pH was measured using pH meter (1:2.5 soil/sediment: water suspension). Soil and sediment samples were also air-dried at room temperature (Jackson 2005). Dried soil and sediment samples were then homogenized and gently crushed using an agate mortar and pestle. Following, a standard sieve of 2 mm mesh size was used to sieve the homogenized soils and sediments (Gelderman and Mallarino, 1998). The total organic carbon (TOC) was analyzed using chromic acid wet digestion method (Walkley and Black, 1934). Total nitrogen (TN) was measured using the Macro-Kjeldahl method. Soil available phosphorus was determined using sodium bicarbonate extraction method (Olsen et al., 1954). Total bacterial loads in the soil and sediment samples were analyzed using series dilution and standard plating techniques. Serial dilution was prepared by mixing 10 grams of soil/sediment in 95 mL of Mili-Q water and was shaken for 24 hours at 180 rpm using IKA KS 4000i control equipment. The dilution (0.1 mL) was followed spread on Petri plates which contained nutrient agar. These Petri plates were incubated at 37°C for 36 hours. Quebec Colony Counter was used to count the number of colonies on nutrient agar.

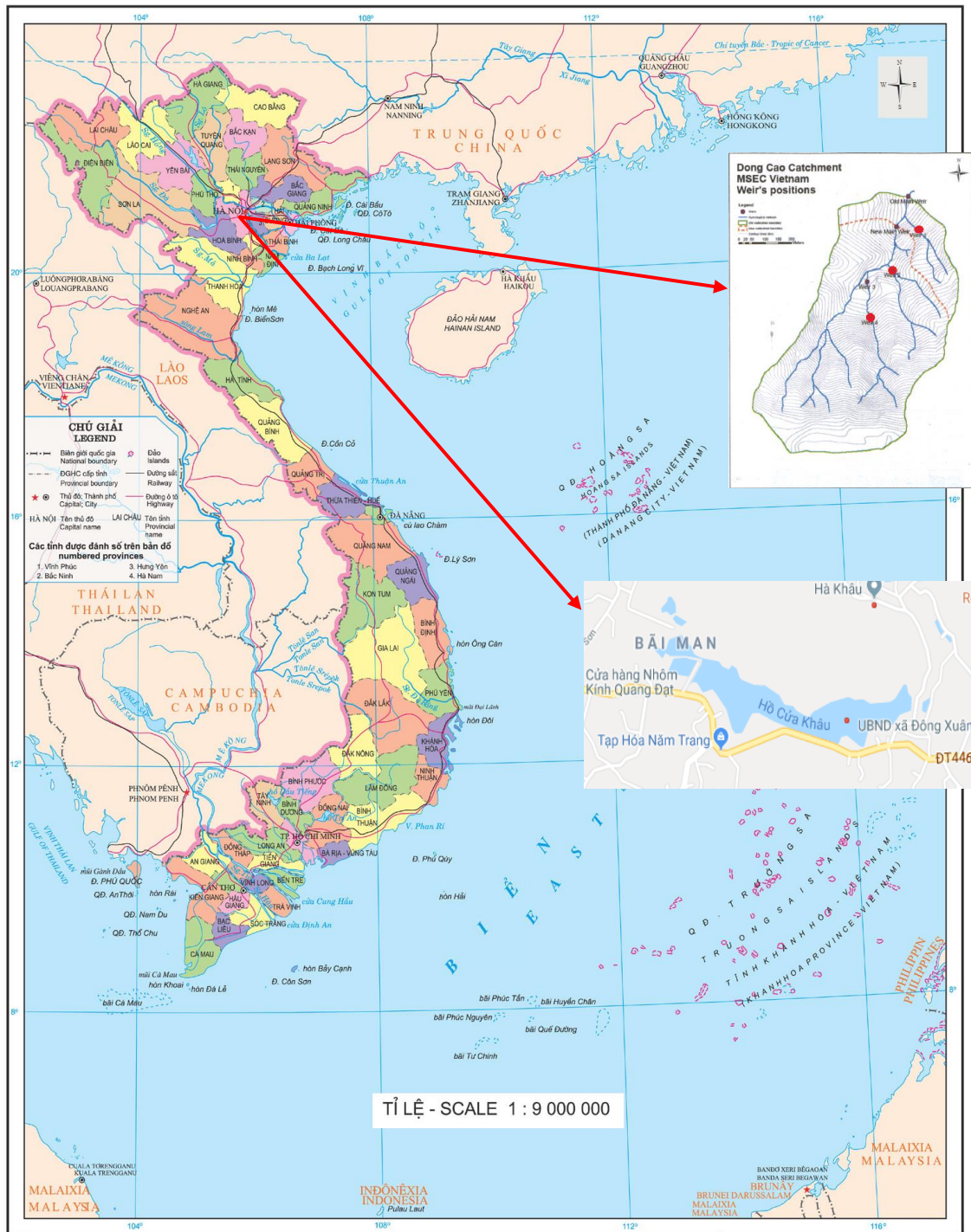


Figure 1. Study area and soil and sediment collection sites in the Dong Cao catchment

2.4. Heavy metal analyses

Soils and sediments were chemically analyzed before the toxicity test for confirmation of pollutant concentrations. Eight heavy metals (As, Pb, Hg, Cd, Cr, Cu, Zn, and Ni) were analyzed for soils and sediments. A homogenized soil and sediment samples (from 0.01 to 0.5 g) were weighed into an appropriate vessel equipped with a controlled pressure relief mechanism. Nine mL of concentrated nitric acid (HNO₃) and 03 mL of concentrated hydrochloric acid (HCl) was added into soil and sediment vessels and using microwave heating for the extraction process. Each sample in vessels has risen to 175 ± 5°C in 4.5 min for the digestion period in the microwave unit. At the end of the microwave period, the soil and sediment vessels were cooled for 5 min before moving them from the microwave unit. After cooling, the vessels were centrifuged and then diluted to volume for heavy metal analysis using ICP-MS equipment (Inductively coupled plasma mass spectrometry) with the method of SMEWW 3125:2012. The detection limit was 0.001 mg L⁻¹ for As, Cu, Ni and Zn, 0.0002 mg L⁻¹ for Cd and Hg, 0.003 mg L⁻¹ for Cr, and 0.0001 mg L⁻¹ for Pb.

2.5. Toxicity studies

To determine the toxicity of soil and sediment samples, two different ecotoxicological assays were used: (1) a Phytotoxkit test with the seeds of plant-*Lepidium sativum* to measure seed germination and root growth inhibition of plant after contacting with soils and sediments; and (2) Microtox toxicity test using marine bioluminescent bacteria *Allivibrio fischeri* to measure the inhibition of the luminescence of bacteria after contacting with soils and sediments.

2.5.1. Plant toxicity test

The toxicity of soils and sediments was assessed with the plant toxicity test. The test

was based on the measurement of germination and growth of the garden cress *Lepidium sativum* after 21 days of exposure to the soils and sediments. The test was conducted following the procedure recommended by the manufacturer (Phytotoxkit, 2004) with some minor modifications. Seeds were rinsed and imbibed with distilled water for 8 hours prior to planting in 300 mL pots with moist samples of soils and/or sediments which were sieved to less than 2 mm. Twenty seeds were planted per pot, evenly cultivated over the surface of the soils and/or sediments. Each pot was then placed on the Petri plate and was daily added with distilled water. The temperature was kept at 24°C during cultivation. Samples were provided the warm fluorescent light for 12 hours per day. The plant toxicity test was performed in three replicates for each soil and sediment samples and reference soil. The reference soil was prepared as the OECD Guideline 207 (OECD, 1984). The reference soil was moistened with deionized water at least 48h before applying the test in order to equilibrate its acidity. The inhibition percentages of seed germination (SGI) and root growth (RGI) were measured after 21 days of exposure of *Lepidium sativum* seeds to soils and sediments in comparison to the reference soil as formula below.

$$SGI \text{ or } RGI = \frac{A - B}{A} * 100 \quad (1)$$

where: A means seed germination and root length in the control; B means seed germination and root length in the test (Adamcova et al., 2016).

2.5.2. Microtox test

The sediments and soils were sieved to remove debris and native wildlife before placing in a 1-L glass beaker. Sediments and soils were freeze-dried using Cryotec V8.11. Suspending freeze-dried sediments and soils were then prepared in Milli-Q water at concentration of 100 g L⁻¹ to extract the elutriates for Microtox test with bacteria

Allivibrio fischeri. The glass bottles were shaken for a minimum of 24 hours using IKA KS 4000i control equipment. Following, the samples were centrifugated to separate the solid and liquid phases. The elutriates were filtered by a syringe filter with a porosity of 0.45 µm. Sodium chloride (NaCl) was added into the elutriates to adjust acidity to 2%. Elutriates were stored at 4°C up to the testing time (maximum of 2 days). Microtox toxicity test was used to investigate the luminescence inhibition in the marine bacteria *Allivibrio fischeri* (SDI, 1992). A negative control sample consisting of bacterial suspension in 2% NaCl was prepared along with the test samples. The light emission was read after 5 and 15 min of exposure.

Positive reference toxicant (ZnSO₄.7H₂O) was also used as a positive control using standard diluent for liquid samples (NaCl 2%) (Azur Environmental, 1998). The reference toxicant test was conducted ranging from 0 to 500 mg L⁻¹ during the study period of the Microtox test, which should be at an acceptable range for the species and reference material. The percentage of bioluminescence inhibition of *Allivibrio fischeri* was calculated as follows:

$$INH\% = 100 - \frac{IT_t}{KF * IT_0} * 100 \quad (2)$$

$$KF = \frac{IC_t}{IC_0} \quad (3)$$

where: KF = correction factor, IC_t = luminescence intensity of control solution after exposure time (5 and 15 min), IC₀ = initial luminescence of control sample, IT_t = luminescence intensity of test sample after exposure time (5 and 15 min), IT₀ = initial luminescence intensity of test sample.

2.6. The assessment of Nemerow's integrated pollution index (NIPI) and potential ecological risk (RI)

To assess the level of heavy metal contamination, Pollution Index (PI) for all studied metals were calculated for each soil

and/or sediment sample. The calculation of PI is based on analyzed trace element concentrations and standard threshold values. The PI is defined as follow:

$$PI = \frac{C_i}{S_i} \quad (4)$$

where C_i is the measured concentration of each metal in this study;

S_i is the background value in this research;

The PI of each metal is classified as non-pollution with PI < 1, low level of pollution with 1 ≤ PI < 2, moderate level of pollution with 2 ≤ PI < 3, strong level of pollution (3 ≤ PI < 5), very strong level of pollution (PI ≥ 5) (Yang et al., 2011, Wu et al., 2014).

Furthermore, to present an evaluation of the general contamination degree for each sample, the Nemerow integrated pollution index (NIPI) can be defined for each metal as formula follow (Yang et al., 2011).

$$NIPI = \sqrt{\frac{PI_{ave}^2 + PI_{max}^2}{2}} \quad (5)$$

where PI_{ave} is the mean PI value of each heavy metal and PI_{max} is the maximum PI value of each heavy metal. The NIPI is classified as non-pollution (NIPI ≤ 0.7), warning line of pollution (0.7 < NIPI ≤ 1), low level of pollution (1 < NIPI ≤ 2), moderate level of pollution (2 < NIPI ≤ 3) and high level of pollution (NIPI > 3) (Yang et al., 2011).

2.7. Statistical analysis

Statistical analysis was performed using GraphPad 6.01 statistical software. Data were analysed by one-way ANOVA followed by T-Test's test for mean comparison of the significant differences between sampling sites (p < 0.05).

3. Results

3.1. General soil and sediment characteristics and heavy metal concentrations in soil and sediment samples

In Table 1, statistically significant differences (p < 0.05) were found among soils

and sediments for clay and gravel but not for the other physical-chemical parameters (pH, moisture, soil P and total nitrogen, total organic carbon) of soils and sediments in Dong Cao catchment. However, soil P, total nitrogen, and total organic carbon in the sediment of Cua Khau lake were significantly higher than that in Dong Cao catchment ($p < 0.05$). Significant differences were found for total bacteria count

in soil and sediment samples in weirs (W1 and W4) of Dong Cao catchment, with varied concentrations of $58\text{--}61 \text{ cfu} \times 10^3 \text{ g}^{-1}$ for soil samples and $12\text{--}13 \text{ cfu} \times 10^3 \text{ g}^{-1}$ for sediment samples. The concentrations of total bacteria in W2 and Cua Khau reservoir were significantly higher than that in W1 and W4, with $104\text{--}138 \text{ cfu} \times 10^3 \text{ g}^{-1}$ for soils and $111\text{--}126 \text{ cfu} \times 10^3 \text{ g}^{-1}$ for sediments.

Table 1. Soil and sediment characteristics in the study sites

Studies site	Clay (%)	Silt (%)	Sand (%)	Gravel (%)	pH	Moisture (%)	Soil P ($\mu\text{g/g}$)	TOC (%)	TN (%)	TBC ($\text{cfu} \times 10^3 \text{ g}^{-1}$)
Soil samples										
W1	48.3 ^a	43.3 ^a	4.3 ^a	4.1 ^a	7.4 ^a	32.0 ^a	0.62 ^a	3.7 ^a	1.18 ^a	58 ^a
W2	56.1 ^a	17.4 ^a	12.4 ^b	14.1 ^b	7.1 ^a	34.8 ^a	0.69 ^a	2.9 ^a	1.14 ^a	138 ^b
W4	59.0 ^a	22.9 ^a	7.5 ^a	10.6 ^b	7.3 ^a	31.9 ^a	0.70 ^a	3.4 ^a	1.51 ^a	61 ^a
CK	55.5 ^a	35.1 ^a	4.6 ^a	4.8 ^a	7.1 ^a	35.0 ^a	0.56 ^a	4.5 ^a	1.50 ^a	104 ^b
Sediment samples										
W1	27.8 ^b	NA	8.3 ^a	72.2 ^c	8.4 ^a	19.7 ^a	0.04 ^b	1.3 ^b	0.49 ^b	13 ^c
W2	28.6 ^b	NA	7.3 ^a	71.4 ^c	7.2 ^a	21.8 ^a	0.01 ^b	1.1 ^b	0.13 ^b	111 ^b
W4	37.3 ^b	NA	6.2 ^a	62.7 ^c	7.2 ^a	21.4 ^a	0.03 ^b	1.7 ^b	0.74 ^b	12 ^c
CK	57.4 ^a	42.6 ^a	NA	NA	7.0 ^a	30.0 ^a	0.32 ^a	3.6 ^a	1.46 ^a	126 ^b

Note: (Soil P = available soil phosphorus; TOC = Total organic carbon; TN = Total nitrogen; TBC = Total bacterial count). NA = Not Available. For each parameter, different letters mean statistically significant differences between sampling sites ($p < 0.05$)

The concentrations of the eight studied elements varied widely in soil and sediment samples, especially for Cr and Cu (Table 2). All the sampled soils and sediments in Weirs (W1, W2, W4) had high concentrations of Cr and Cu in comparison to soils and sediments of Cua Khau reservoir (CK). The results showed that CK sediments had low concentration of Cr, with only 73.5 mg kg^{-1} in sediment and 183.7 mg kg^{-1} in soil sample. The highest concentration was recorded for Cr in soil sample of W1 and followed by soil sample of W4, with 1191.3 and $1114.7 \text{ mg kg}^{-1}$, respectively. For sediment samples, the concentrations of Cr were high in W1, W2 and W4, with 930 , 813 and 933.3 mg kg^{-1} , respectively. Importantly, the concentrations of Cr were recorded in excess in soils and sediments in comparison to the permissible levels in the guidelines of WHO, US, Ontario and Vietnam (Table 2).

There was no significant difference between concentrations of Cu in soils of Dong Cao catchments and Cua Khau reservoir ($p > 0.05$). It was detected about $123.7\text{--}169.9 \text{ mg kg}^{-1}$ of Cu in soil samples. In contrast, the concentration of Cu (197.8 mg kg^{-1}) in the sediment of CK was significantly higher than that of Weirs ($139\text{--}156.3 \text{ mg kg}^{-1}$) ($p < 0.05$). Particularly, the concentrations of Cu in both soils and sediments of studied areas slightly exceeded the permissible levels for agriculture soil and sediment in Vietnam and other guidelines of international agencies (MONRE, 2015, MONRE, 2017, Provoost et al., 2006, US EPA, 2006).

The Zn concentrations for all samples ranged from 98.2 to 148 mg kg^{-1} for soils and from 117 to 195.3 mg kg^{-1} for sediments. Although sediments had a higher concentration of Zn than that of soils, all values fell within the permissible levels for soils or sediments

according to the Vietnamese guideline (MONRE, 2015). However, the Zn concentrations in soils exceeded 2–5 fold the permissible level for Zn of WHO and US Ontario (Ontario, 2004). (Provoost et al., 2006, US EPA, 2006). For sediment samples, Zn concentrations were also found in excess according to the guideline of Ontario (Ontario, 2004).

Table 2. Heavy metal concentration in soils and sediments (mg kg⁻¹ dried wt)

Site	As	Cd	Pb	Hg	Cr	Ni	Cu	Zn
Soil samples								
W1	12.6 ± 2.6 ^a	0.05 ± 0.02 ^a	21.7 ± 1.3 ^a	0.06 ± 0.03 ^a	1191.3 ± 38.9 ^a	32.3 ± 0.9 ^a	168.3 ± 16.6 ^a	126 ± 9.5 ^a
W2	5.0 ± 0.6 ^a	0.03 ± 0.01 ^a	39.3 ± 2.3 ^a	0.08 ± 0.03 ^a	189 ± 18.2 ^b	22.5 ± 1.6 ^a	181.3 ± 10.3 ^a	148 ± 13.1 ^a
W4	8.3 ± 0.6 ^a	0.13 ± 0.04 ^a	15.6 ± 1.1 ^a	0.07 ± 0.03 ^a	1114.7 ± 23.9 ^a	18.6 ± 1.4 ^a	123.7 ± 12.5 ^a	141.3 ± 13.1 ^a
CK	2.6 ± 0.7 ^b	0.06 ± 0.02 ^a	11.4 ± 0.8 ^a	0.07 ± 0.01 ^a	183.7 ± 16.0 ^b	59.3 ± 4.8 ^b	169.9 ± 10.1 ^a	98.2 ± 2.7 ^a
FAO/WHO ¹	20	3.0	100	-	100	50	100	300
US ²	10	4	50	0.3	1	30	100	50
Otarino ³	14	1.0	55	0.16	67	43	56	150
MONRE ⁴	15	1.5	70	-	150	-	100	200
Sediment sample								
W1	10.9 ± 0.4 ^a	0.05 ± 0.02 ^a	22.9 ± 1.5 ^a	0.03 ± 0.02 ^a	930.0 ± 36.1 ^a	24.5 ± 1.3 ^a	139 ± 7.0 ^a	177.3 ± 10.5 ^a
W2	12.3 ± 1.1 ^a	0.08 ± 0.02 ^a	11.1 ± 0.9 ^a	0.04 ± 0.01 ^a	813.0 ± 16.5 ^a	27.4 ± 1.7 ^a	156.3 ± 7.8 ^a	195.3 ± 5.5 ^a
W4	9.5 ± 0.9 ^a	0.06 ± 0.01 ^a	8.5 ± 1.1 ^a	0.05 ± 0.01 ^a	933.3 ± 32.1 ^a	22.2 ± 1.3 ^a	147.3 ± 7.5 ^a	117 ± 6.2 ^a
CK	2.3 ± 0.5 ^b	0.13 ± 0.05 ^a	14.5 ± 0.8 ^a	0.15 ± 0.04 ^a	73.5 ± 4.4 ^b	30.0 ± 1.3 ^a	197.8 ± 2.9 ^a	173.8 ± 3.5 ^a
Canada ⁵	20	4.2	57	0.3	56	-	120	200
Ontario ³	6	0.6	31	0.2	26	16	16	120
WA ⁶	11	2.2	57	0.3	56	-	120	200
MONRE ⁷	17	3.5	91.3	0.5	90	-	197	315

Note: For each heavy metal, different letters mean statistically significant differences between sampling sites (p < 0.05).

¹(Provoost et al., 2006), ²(US EPA, 2006) ³(Ontario, 2004), ⁴(MONRE, 2015), ⁵(CANADA, 2014), ⁶(WA, 2010), ⁷(MONRE, 2017)

The concentrations of Ni in soils and sediments from CK were high 59.3 and 30 mg kg⁻¹, respectively. Soils and sediments in weirs (W1, W2 and W4) had lower Ni concentrations, ranging from 18.6 to 32.3 mg kg⁻¹ and from 22.2 to 27.4 mg kg⁻¹, respectively. Ni values did not exceed permissible level in soils and/or sediments (MONRE, 2015, MONRE, 2017) However, according to the guideline of Ontario (Ontario, 2004), sediments of both Weirs and CK were found in excess of permissible level.

The Pb concentrations for all samples ranged from 8.5 to 39.3 mg kg⁻¹. The concentrations of Cd and Hg were about 0.03–0.13 mg kg⁻¹ and 0.03–0.15 mg kg⁻¹, respectively. Most concentrations were within permissible levels for soils and sediments according to the guidelines of WHO, US and Vietnam (70 mg kg⁻¹) (MONRE, 2015, MONRE, 2017, Provoost et al., 2006, US EPA, 2006).

Soil As concentrations ranged from 2.8 to 12.2 mg kg⁻¹ and sediment As concentration

from 2.6 to 11.3 mg kg⁻¹. Almost all samples had As concentration within the permissible levels for soils in Vietnam (12 mg kg⁻¹), except for W1 (soil with 12.2 mg kg⁻¹) and for W2 (sediment with 12.3 mg kg⁻¹). However, As was found in excess according to the Ontario guideline (Ontario, 2004).

3.2. Ecological risk assessments for soils and sediments in Dong Cao catchment

Pollution severity and its variation along the sites was determined with the use of pollution load index (PI) and Nemerow's integrated pollution index (NIPI). Based on the monitoring data of soil and sediment quality in the study area, a quantitative analysis of heavy metal pollution in soil and sediment in Dong Cao catchment was conducted using the method of PI and NIPI (Yang et al., 2010).

The values of pollution index for studied heavy metals varied greatly among heavy metals (Table 3). The PI values of As, Cd,

Pb, Hg, Ni and Zn in ranged from 0.02 to 0.75 for soil samples and from 0.02 to 0.98 for sediment samples in Dong Cao weirs and CKL, indicating that the soils and sediments can be considered as uncontaminated by those heavy metals. The PI values of Cu in soils and sediments was around 1.24–1.95, indicating that the soils and sediments were contaminated by Cu. Especially, the copper risk of contamination was recorded ($1 < PI \leq 3$) for all samples both soil and sediment at the studied sites. Soils in W1 and W4 sites had high values of PI for Cr, with 5.91 and 7.71 respectively, indicating that W1 and W4 were strongly contaminated by Cr. Referring to the classification of Cheng et al. (2014), the degree of contamination risk by chromium is very high for soil samples at W1 and W4, where $PI > 5$. Similarly, sediment samples at the sites of W1, W2 and W4 had moderate contamination by chromium ($3 < PI < 5$), with PI values of 4.7, 4.01 and 4.55, respectively.

Table 3. Pollution index (PI) of studied heavy metals in soils and sediments

Site	As	Cd	Pb	Hg	Cr	Ni	Cu	Zn
Soil samples								
W1	0.61	0.02	0.21	0.14	5.91	0.63	1.53	0.64
W2	0.26	0.01	0.40	0.20	0.84	0.43	1.70	0.75
W4	0.43	0.04	0.14	0.20	7.71	0.37	1.24	0.70
CK	0.14	0.02	0.11	0.23	0.84	1.30	1.60	0.48
Sediment samples								
W1	0.52	0.02	0.21	0.14	4.70	0.52	1.31	0.89
W2	0.57	0.03	0.10	0.14	4.01	0.56	1.54	0.98
W4	0.49	0.02	0.08	0.14	4.55	0.42	1.40	0.60
CK	0.13	0.03	0.14	0.46	0.37	0.60	1.95	0.87

The Nemerow integrated pollution index (NIPI) of heavy metal in soils and sediments was calculated (Table 4). Fig. 2 shows the NIPI values of soil metals. The pollution levels varied widely among different soil samples. The NIPI values in soils ranged from 0.001 to 34.29. The soils showed a high content of Cr at the studied sites of W1 and W4, and moderate content of Cu in all studied

sites. All sediments collected from weirs in Dong Cao had high concentration of Cr, with NIPI ranged from 16.75 to 19.43 (Fig. 3), whereas high content of Cu was recorded in Cua Khau reservoir (NIPI > 3). The risk of contamination of sediments was low for Cu ($1 < NIPI < 2$) and on the warning line of pollution for Zn ($0.7 < NIPI < 1$).

Table 4. The Nemerow's integrated pollution index (NIPI) of heavy metals in soil and sediment samples

Site	As	Cd	Pb	Hg	Cr	Ni	Cu	Zn
Soil samples								
W1	0.46	0.001	0.17	0.18	34.29	0.33	2.88	0.37
W2	0.25	0.002	0.46	0.38	0.85	0.29	2.64	0.82
W4	0.37	0.004	0.14	0.27	29.45	0.17	2.55	0.66
CK	0.11	0.004	0.17	0.23	0.84	1.41	2.30	0.55
Sediment samples								
W1	0.24	0.0002	0.11	0.08	16.75	0.30	1.76	0.79
W2	0.31	0.001	0.07	0.05	20.06	0.23	1.74	0.86
W4	0.18	0.0008	0.02	0.03	19.43	0.24	1.53	0.69
CK	0.08	0.001	0.11	0.39	0.23	0.26	3.92	0.93

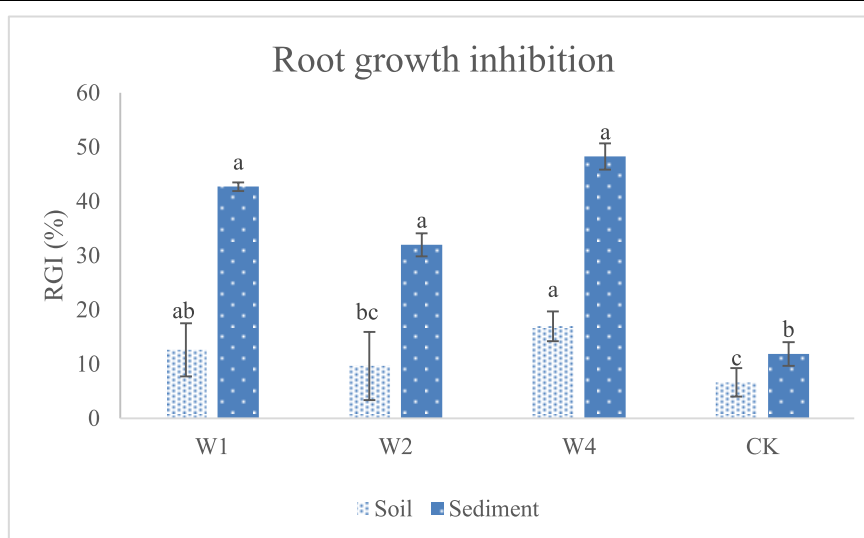


Figure 2. Roots growth inhibition of *L. savitum* (%) in soils and sediments of weirs in Dong Cao catchment and Cua Khau reservoir. Analysis were performed in triplicates and errors bars present standard deviation (n=3). Different letters mean statistically significant differences between sampling sites ($p < 0.05$).

3.3. Toxicity studies

3.3.1. Plant toxicity test

Figure 2 and 3 present the effect of soils and sediments in Dong Cao catchment on the inhibition of seed germination and root growth of the test plant *L. savitum*. In the plant toxicity test with *L. savitum*, the plants cultivated in the soils and sediments of Cua Khau reservoir had a significant lower root growth inhibition than those grown in the soils and sediments in Dong Cao weirs ($p < 0.05$). The inhibition of root growth of

L. savitum was in the range of 6.6–13% for soils and 11.9–48.3% for sediment samples. However, the inhibition of seed germination varied greatly between sampling sites of Dong Cao weirs and Cua Khau reservoir. The seed germination inhibition of samples in Cua Khau reservoir was only 1.6% for soils and 13.3% for sediments, whereas, much more inhibition of seed germination was observed for soils and sediments in Dong Cao weirs, ranging from 13.3–21.7% for soils and 65–73.3% for sediments.

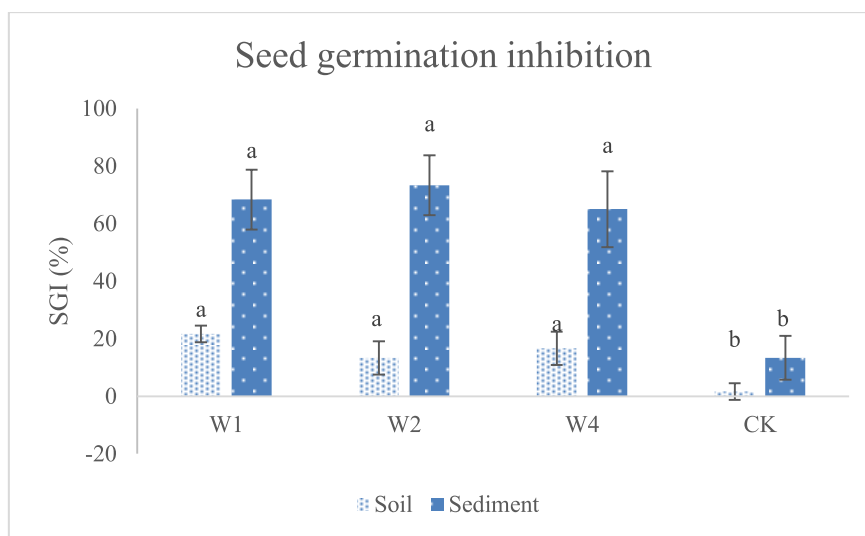
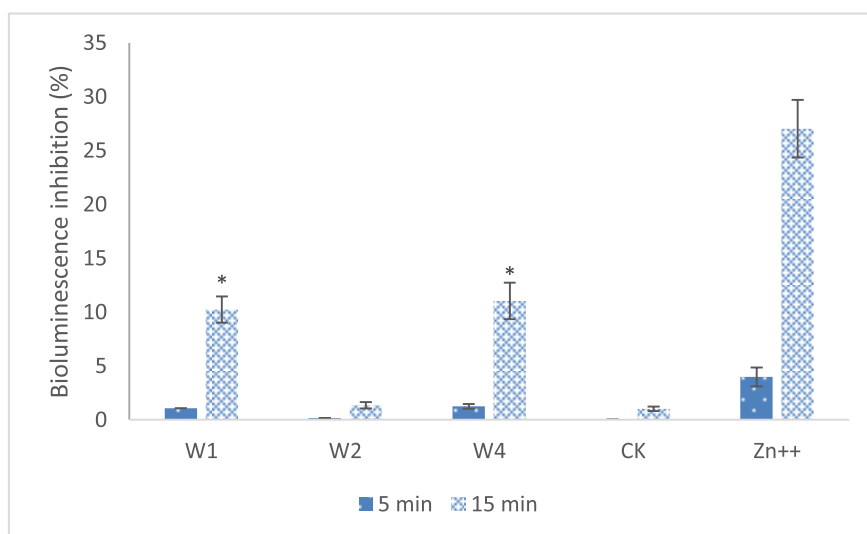


Figure 3. Seed germination inhibition of *L. savitum* (%) in soils and sediments of weirs in Dong Cao catchment and Cua Khau reservoir. Analysis were performed in triplicates and errors bars present standard deviation (n=3). Different letters mean statistically significant differences between sampling sites (p < 0.05)

3.3.2. Microtox test

Allivibrio fischeri emits light as a result of normal metabolic processes. A reduction in luminescent ability during exposure to contaminants or pollutants is taken as a measure of toxicity. The elutriates from both soils and sediments exposed very low toxicity to *Allivibrio fischeri* compared to the

reference toxicant Zn⁺⁺. In soil and sediment samples, after 5 min of contact, no difference between sampling sites was observed (Fig. 4 and 5). However, after 15 min of the contact, only soils and sediments of W1 and W4 sites caused a significant inhibition of bioluminescence (p < 0.05) in comparison to its in W2 and CK sites.



← Figure 4. Bioluminescence inhibition of *Allivibrio fischeri* after 5 and 15 min of *Allivibrio fischeri* exposed to soils collected in weirs of Dong Cao catchment, Cua Khau reservoir and reference toxicant (Zn⁺⁺). Analysis were performed in triplicates and error bars present standard error (n=3). An asterisk denotes statistical significance (p < 0.05).

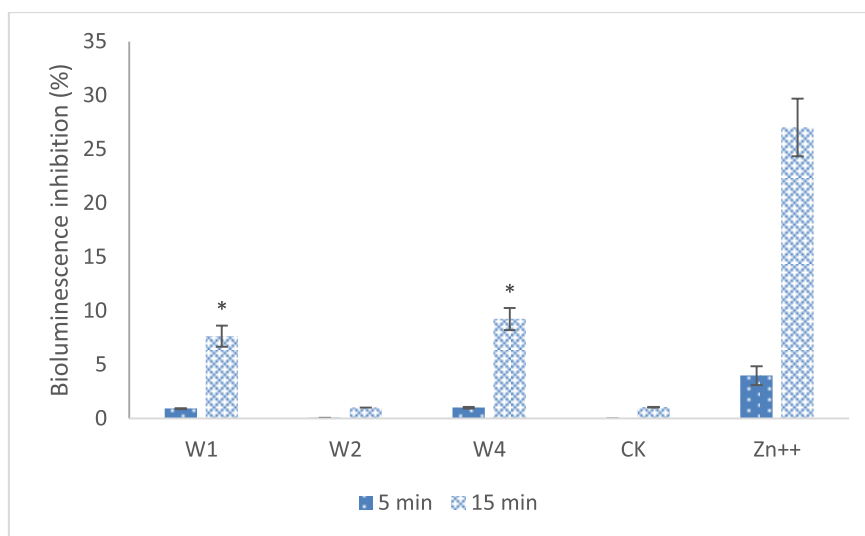


Figure 5. Bioluminescence inhibition of *Allivibrio fischeri* after 5 and 15 min of *Allivibrio fischeri* exposed to sediments collected in weirs of Dong Cao catchment, Cua Khau reservoir and reference toxicant (Zn⁺⁺). Analysis were performed in triplicates and error bars present standard error (n=3). An asterisk denotes statistical significance (p < 0.05)

4. Discussions

4.1. Heavy metal pollution in Dong Cao catchment and Cua Khau reservoir and its origins

Soils and sediments were identified as contaminated by Cr, Cu and Zn. The concentrations of Cr in soils of W1 and W4 were 5.5 fold higher than baseline level (MONRE, 2015). Similarly, in the sediments, Cr concentrations of the three weirs in Dong Cao catchment were 4–4.5 fold higher than this standard. Cr is often associated with biogeochemical process in soils (Thin et al., 2017). In fact, the heavy metals in agricultural soils of upland areas may be mostly derived from the parent rocks and strongly depend on the parent rocks, except for Cd (Tra Ho and Egashira, 2000). In addition, the distribution of Cr may vary in soils because of the greater variability caused by various pedogenetic processes and contribution of different soil types mixed with the original weathering products of rock (Chrysochoou et al., 2016).

Previously, Garnier et al. (2008) demonstrated that chemical weathering could lead to a Cr enrichment during soil genesis and increased its abundance in soils and sediments. The Cr contamination in sediment derived primarily from natural sources and can be enriched in the fine fraction of sediments (Nguyen et al., 2016) but in our study, we did not observe this concentration.

The concentrations of Cr in soils of W1 and W4 were from 7 to 12 fold higher than the one found in CK. The distribution of Cr may vary when examining the longitudinal behaviour (along a toposequence) (Chrysochoou et al., 2016). Previous studies in Italy and Brazil reported that the higher concentration of Cr was found on the summit and shoulder positions of hills (Morrison et al., 2015). Rocks have the potential to have substantially higher Cr concentrations, with concentration of 860–1100 mg kg⁻¹ (Chrysochoou et al., 2016). Similar concentrations (813–1191 mg kg⁻¹) were found in soils and sediments, which means

that chromium is very conservative from rocks to soils and sediments and can be considered in this study as of natural origin. The ratios of rocks in soils and sediments of weirs were higher than that of Cua Khau reservoir (Table 1), which tends to show that chromium concentration tends to decrease when the size of the catchment increases. In the Dong Cao catchment, soils are young and shallow due to the steep slope and their chemistry is directly derived from the parent materials. Conversely, the soils of the Cua Khau catchments are much thicker and older alluvial soils with a reduced influence of the parent material.

The results also showed that soils and sediments in Dong Cao catchment and Cua Khau reservoir were contaminated by Cu and Zn. Cu and Zn are widely used by man including the people for different purposes such as the manufacture of cleaning products, and are contained in cosmetics and shampoos, paints and pigments, and lubricants (Alloway and Ayres, 1998; European-Commission, 2001), they are found in most municipal solid waste, and consequently in leachate derived from municipal solid waste landfills in the region. Cu and Zn contamination in soils and sediments may correspond to agricultural chemicals (pesticides and fertilizers) in the region (Tra Ho and Egashira, 2000). Fang et al. (2011) also found that high heavy metal contents in soil often occurred in the peri-urban areas.

In addition to agricultural chemicals applied in Dong Cao on cassava before 2004, when cultivation was abandoned, the atmospheric deposition due to the aerosols emitted by Hanoi and other cities can be another cause of heavy metal contamination in Dong Cao catchment and Cua Khau. The high accumulation of heavy metals in soils and sediments could be due to the contribution of natural and anthropogenic dust in urban aerosols (Cohen et al., 2010, Liu et al., 2019).

The anthropogenic dust could derive from coal combustion and/or vehicle emission (Cao et al., 2006, Gatari et al., 2006). Previous studies indicated that human activities produced anthropogenic dust, which is characterized by a high concentration of toxic heavy metals (e.g. Pb, Zn, Co, Cr, Ni, and As) (Qiao et al., 2013, Lee et al., 2015, Lu et al., 2013). The recent studies in the region also demonstrated that the metals (Cr, Cu, Ni, Pb, and Zn) were emitted from urban/industrial activities (Chifflet et al., 2018). In Hanoi, Gatari et al. (2006) indicated that fuel oil and coal combustion were the major sources of fine and coarse particles that contained some hazardous trace elements such as Cr, Mn, Ni, and Pb. The local emission sources in Hanoi such as waste burning, road transport, soil/road dust, and construction activities were the main sources of particle matters containing a high level of several elements (Fe, Pb, Zn, Al, Cr, and Mn) (Hai and Kim Oanh, 2013). Moreover, dust/particle matter storm could be traveling large distances, e.g. through southern China to Vietnam and beyond (Hien et al., 2004, Lee et al., 2006) and airborne soils and desert dust can arrive at Hanoi by wind trajectories (Hien et al., 2004). These desert aerosols can contain heavy metals, including Cu and Zn (Norouzi et al., 2017). We can therefore clearly differentiate Cr derived from rocks, and Cu and Zn, which resulted from agricultural chemicals and atmospheric fallout.

Interestingly, the degree of contamination of soils and sediments in Cua Khau reservoir was considered as more slightly polluted than the Dong Cao catchment because the PI values in soil and sediment samples of Cua Khau reservoir were below 1.0 for most studied metals, except for Cu with $PI > 1$ in both soils and sediments. The analysis results showed that the average of PI descended in the order of $Cr > Cu > Zn > As = Ni > Pb = Hg > Cd$. All of the sampling points have

strong pollution of Cr, but less than in the Dong Cao catchment, and moderate pollution by Cu, whereas other heavy metal only showed non-pollution to the soils and sediments in Dong Cao.

4.2. Toxic effects of soil and sediment samples at Dong Cao catchment and Cua Khau reservoir

The results showed that both soils and sediments had a strong impact on the growth and seed germination of *L. sativum*. The growth and seed germination inhibition values were significantly higher in soils and sediments of sub-catchments (W1, W2, and W4) than that of the Cua Khau reservoir. These results are very consistent with the concentrations of heavy metals, especially Cr, Cu and Zn (Table 1), thus affecting the related bioavailability of these heavy metals to plants. The root growth of trees and crops is well-documented in decreasing because of heavy metal contamination (Godbold and Kettner, 1991, Tang et al., 2001). Plant growth and development could be adversely affected by Cr toxicity in the germination process (Shanker et al., 2005). The general response of root growth reduction due to Cr toxicity may be due to inhibition of cell division/elongation in the roots or due to the prolongation of the cell cycle in the roots (Shanker et al., 2005).

Although Zn and Cu are micronutrients for plants to grow and for various biochemical and physiological pathways of plants (Narula et al., 2005), high levels of these elements could be toxic to them (Das et al., 1997). Excess amounts of Zn may prevent plant growth and development by making an imbalance between intake and distribution of minerals or by interfering with metabolic processes and antioxidant defense systems (Xu et al., 2010). The presence of Cu or Zn inhibited seed germination of wheat plant *Triticum aestivum* (Wang et al., 2011) and

affected to relative shoot length of the *Solanum lycopersicum* plant (Wang et al., 2011, Al Khateeb and Al-Qwasemeh, 2014).

All samples have been denoted of non-toxic with bioluminescence inhibition values of 0.01–1.25%. This could be attributed to the too-short time of contact between bacteria and elutriates, to provoke the bioluminescence inhibition (Romero-Freire et al., 2014, Romero-Freire et al., 2015). After 15 min contact, much higher toxicity towards *Allivibrio fischeri* was observed for elutriates from soils and sediments of W1 and W4 (bioluminescence inhibition depending on the luminescence of bacteria after exposing elutriates for 15 min – 7.7–11%). The cause of the observed high bioluminescence inhibition was the bioavailable heavy metals in soils and sediments of W1 and W4. Because the highest concentrations of Cr were observed in both soils and sediments of W1 and W4. The main cause of the observed high level of bioluminescence inhibition was most probably the immobilization of contaminants present in soils (Koltowski et al., 2017). Relatively low values of bioluminescence inhibition (by 1.0–1.3%, after 15 min of the contact) were noted for elutriates from soils and sediments of W2 and Cua Khau reservoir, which is consistent with the heavy metal concentrations. Elutriates from samples of W2 and Cua Khau reservoir was not toxic for *Allivibrio fischeri*. This is probably due to the properties of soils and sediment in W2 and Cua Khau reservoir, particularly by total bacteria content (TBC) in samples. In this study, soils of W1 and W4 were characterized by over 2-fold higher TBC content than that of W2 and Cua Khau reservoir. TBC in sediments of W1 and W4 were recorded by over 10-fold higher than that of W2 and Cua Khau reservoir. Bacteria is a commonly known to be involved in the import and mobilization of metals (Chandrangsu et al., 2017); thus, the presence of the high total bacteria contents may

increase the toxicity of sediments. Further studies on metal-bacteria interaction are needed to clarify the response of bacteria to heavy metal concentrations.

5. Conclusions

The major pollutant metals in Dong Cao catchment were Cr, Cu, and Zn according to the international and Vietnamese guidelines for both soils and sediment. The upland areas (Weirs of Dong Cao catchment) had higher concentrations of Cr than that in CK, while CK had a high concentration of Cu for both soil and sediment in comparison to upland areas. This study clearly indicated that Cr contamination is derived from rocks whereas Cu and Zn are most likely associated with human activities (local agricultural inputs and atmospheric fallout).

The data of this study revealed that the Phytotoxkit test was effective in identifying toxic samples of sediment in comparison to the Microtox test. Growth inhibition (%) at the sediment samples was higher than that at the soils. Importantly, sediments of sub-catchments (W1, W2, and W4) had significantly higher growth inhibition values than that of the Cua Khau reservoir. For the Microtox test, the slight toxic toward *Allvibrio fischeri* was only observed after 15-min of the contact to sediments of W1 and W4 of Dong Cao catchment. Our results showed that the phytotoxicity test used to assess the toxicity of soils and sediments to biota community was more effective and efficient than the Microtox test.

Conflicts of interest

The authors declare no conflicts of interest.

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