HEAVY METALS IN FLOODED PADDY SOIL IN CENTRAL VIETNAM

Đến tòa soạn 25-03-2021

Ha Thu Trinh, Cuc Thi Dinh
Institute of Chemistry, VAST
Hanh Thi Duong
Institute of Environmental Technology, VAST
Giang Truong Le
Institute of Chemistry, VAST

TÓM TẮT

KIM LOẠI NẶNG TRONG ĐẤT NGẬP LỤT Ở MIỀN TRUNG VIỆT NAM

Để đánh giá tác động môi trường do lũ lụt gây ra đối với ruộng lúa, chín kim loại nặng (As, Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn) đã được phân tích trên cho mẫu đất trồng lúa ở Thanh Hóa và Huế, Việt Nam. trước và sau khi lũ lụt. Các kim loại nặng trong đất được xử lý chiết tách bằng hệ vi sóng trong bình kín, và sau đó được xác định bằng thiết bị khối phổ plasma liên kết cảm ứng (ICP-MS). Nồng độ của bảy (Cu, Pb, Zn, Cr, Co, Cd và As) trong số chín kim loại nặng được phân tích trong đất trồng lúa sau khi ngập lụt đều giảm so với trước khi ngập lụt ở tất cả các mẫu ở Thanh Hóa và Huế; có thể là do sự rửa giải các nguyên tố này từ đất vào nước. Tuy nhiên, việc giảm nồng độ Fe và Mn trong đất lúa sau khi ngập lụt có thể là do các phản ứng oxy hóa khử và sự khử Mn (III / IV) thành Mn (II) và Fe (III) thành Fe (II) . Nhìn chung, mức phát hiện của 9 kim loại nặng trong đất trồng lúa trong nghiên cứu này thấp hơn giá trị quy định được ban hành bởi Quy chuẩn kỹ thuật quốc gia về giới hạn cho phép của kim loại nặng trong đất và hướng dẫn chất lượng môi trường của Canada về bảo vệ đời sống thủy sinh, điều đó cho thấy rằng không có nguy cơ tiềm ẩn về kim loại nặng đối với môi trường nước trong khu vực nghiên cứu.

Từ khóa: *kim loại nặng, đất, nước lụt.*

1. INTRODUCTION

Rice farming is one of the main forms of agricultural cultivation in Hue and Thanh Hoa province in central Viet Nam [5]. Every summer, storms with heavy rainfall leads to flooding of the area with water levels of up to 2 meters [5]. Floodwater contains suspended solids, heavy metals and organic compounds (e.g. surfactants and organic acids) that effect on the desorption of organic pollutants, especially pesiticides, and heavy metals in the soil [1]. When paddy fields are flooded, heavy metals [1], nutrients and pesticide were released from the soil into the water [2, 3], resulting the changes of soil quality. The adsorption and chelation of heavy metals by organic matter depends on the redox conditions and pH, which is similar to the adsorption of iron oxide and manganese oxide. The changes in the redox conditions lead to the decomposition of organic matters and therefore cause the dissolution of dissolved organic matter and heavy metals [4, 5].

Ten heavy metals (As, Cu, Cd, Cr, Co, Pb, Zn, Fe, Mn, Al) were detected in floodwater in paddy field in Hue and Thanh Hoa in our previous study [6], with total concentration ranged from 0.1 to 3170 μg L^{-1}. The results demonstrated that floodwater was contaminated by heavy metals released from soil.

According to our knowledge, there is little research that has been carried out on heavy metals in flooded paddy soils in Vietnam, especially in central area of Vietnam. Therefore, the aim of this study is to: (1) clarify the contamination status for heavy metals in the paddy soils before and after flooding, and (2) initial study the potential risks of detected heavy metals in paddy soils to aquatic environment.

2. EXPERIMENTAL

2.1. Chemicals and materials

Sample collection: Surface soil samples before flooding were collected in the paddy field in June and July, 2012 in Thanh Hoa and Hue, respectively, and the samples were collected in September and November, 2012, respectively after flooding. Cultivation characteristics, weather conditions, flooding during sampling were presented in our previous study [6]. A total of 28 paddy soil samples were collected in both locations, surface soil (0-15 cm) was sampled using a stainless steel shovel. Samples were transported to a laboratory in boxes packed with ice and kept at -20°C until analysis.

2.2. Analysis

Soil samples were dried until no further weight loss occurred, and then passed through a 2 mm stainless steel sieve and pulverized in an agate mortar. About 0.25g dry soil was digested using a closed vessel microwave assisted system (Anton Paar GmbH, Multiwave 3000) according to the USEPA 3052 method (USEPA, 1996). After digestion, the digested sample was fixed at a volume of 50ml with reagent water (Milli Q Integral). Heavy metals in the soil samples were determined by an inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500CX, Agilent Technologies, UK). Polyatomic interferences were removed with an octopole reaction system (ORS) pressurized with He or H_2.

Quality controls were performed by blank analysis and the analysis of a soil certified reference material for trace metals (National Institute of Standards and Technology - NIST 2711). Montana Soil (NIST 2711) were included in every digestion. The recovery of the heavy metals As, Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn were within 85-108% of the certified values. Results of blank sample showed that there is no contamination by the targets during extraction and analysis procedure.

The physicochemical characteristics of soil such as cation exchange capacity (CEC), pH, organic carbon content (OC), nitrogen (TN), density, sand, silt and clay also determined for soil samples in Thanh Hoa and Hue.

3. RESULTS AND DISCUSSION

3.1. Physisco-chemical properties of paddy soil

Selected physicochemical characteristics of the soil samples are shown in Table 1. The result shown that no change about the physisco-chemical properties of soil in Thanh Hoa and Hue before and after flooding. Soil texture in Thanh Hoa is clay loam and in Hue is silt clay loan.

Concentration of nine heavy metals in paddy soil at the two study sites in Thanh Hoa and Hue before and after flooding was presented Fig.1

3.2. Elemental content in paddy soil

Average concentration of arsenic in soil were 0.09 mg kg-1 d.w. and 0.06 mg kg-1 d.w. in Thanh Hoa before and after flooding, respectively, and 0.13 and 0.06 mg kg-1 d.w. in Hue before and after flooding. These values were below limitation value regulated by National technical regulation on the allowable limits of heavy metals in the soils (15 mg kg-1 d.w.) [7] and Canadian environmental quality guidelines for protection of aquatic life (12 mg kg-1 d.w.) [7].

Table 1. The physisco-chemical properties of soil in Thanh Hoa and Hue

No	Parameter	Unit	Thanh Hoa	Hue
1	pH_KCl	-	4.44	4.24
2	CEC	meq/100g	16.2	11.8
3	Organic carbon content	%	2.21	1.85
4	Total nitrogen	%	0.254	0.211
5	Sand (2-0.02)	%	21.3	6.86
6	Silt (0.02-0.002)	%	49.6	65.1
7	Clay (< 0.002)	%	28.9	28.1
8	Texture	-	Clay loam	Silt clay loam

These concentrations were also below arsenic concentrations of (9.11-18.7 mg kg^{-1} d.w.) observed in agricultural soils in Hanoi [8]. The results indicated that the paddy soil in Thanh Hoa and Hue has not been polluted with arsenic. Cadmium concentration in soil was less than 0.58 mg kg^{-1} d.w. and 0.35 mg kg^{-1} d.w. in Thanh Hoa before and after flooding, respectively. Concentration of cadmium in Hue before and after flooding

was below 0.52 mg kg^{-1} d.w. and 0.14 mg kg^{-1} d.w., respectively. The concentration of cadmium in the soil in Thanh Hoa and Hue were lower than limitation value regulated by National technical regulation on the allowable limits of heavy metals in the soils (1.5 mg kg^{-1} d.w.) [7] and lower than regulation value issued by CCME (1.4 mg kg^{-1} d.w.) [7]. The detected levels of Cd in this study was similar to those observed in Hanoi's peri-urban agricultural soils (0.33-0.67 mg kg^{-1} d.w.) [8]. Overall, the investigated paddy soils in this study were not polluted with cadmium.

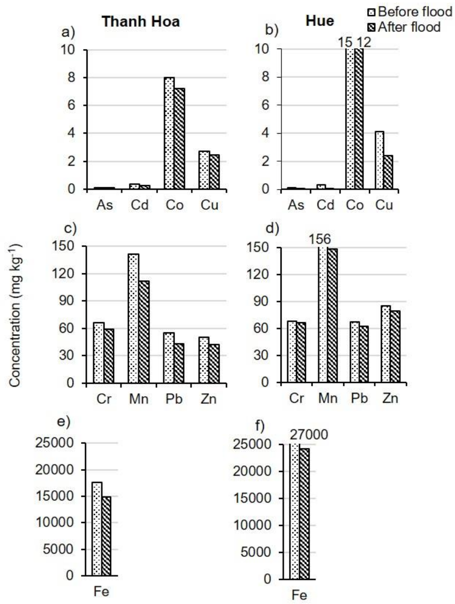

Fig.1. Concentration of nine heavy metals in paddy soil in Thanh Hoa and Hue before and after flooding

Chromium in paddy soil in Thanh Hoa before and after flooding were 59.3-76.6 mg kg^{-1} d.w. and 53.5-67.3 mgkg^{-1} d.w., respectively, and concentration in Hue were 58.6-75.2 mg kg^{-1} d.w. and 60.6-72.3 mg kg^{-1} d.w., respectively. These levels were nearly 3 times lower than the regulated values issued by the National technical regulation on the allowable limits of heavy metals in the soils (150 mg kg^{-1} d.w.) [7], while it was close to the limitation value issued by CCME (64 mg kg^{-1} d.w) [7].

Average concentration of copper in soil were 2.69 mg kg^{-1} d.w. and 2.46 mg kg^{-1} d.w. in Thanh Hoa before and after flooding, respectively, and 4.13 mg kg^{-1} d.w. and 2.41 mg kg^{-1} d.w. Hue, respectively. These levels were lower than the regulated values issued by National technical regulation on the allowable limits of heavy metals in the soils (100 mg kg^{-1} d.w.) [7], and the guidelines issued by The Canadian Council of Ministers of the Environment (63 mg kg^{-1} d.w) [7]. The detected concentration of copper in this study is about 20 times lower than those found in peri-urban Hanoi agricultural soils (48.1 mg kg^{-1} d.w.) [8].

Average concentration of copper in soil were 2.69 mg kg^{-1} d.w. and 2.46 mg kg^{-1} d.w. in Thanh Hoa before and after flooding, respectively, and 4.13 mg kg^{-1} d.w. and 2.41 mg kg^{-1} d.w. Hue, respectively. These levels were lower than the regulated values issued by National technical regulation on the allowable limits of heavy metals in the soils (100 mg kg^{-1} d.w.) [7], and the guidelines issued by The Canadian Council of Ministers of the Environment (63 mg kg^{-1} d.w) [7]. The detected concentration of copper in this study is about 20 times lower than those found in peri-urban Hanoi agricultural soils (48.1 mg kg^{-1} d.w.) [8] Lead concentrations were 44.3-69.6 mg kg^{-1} d.w. and 35.1-57.4 mg kg^{-1} d.w. in Thanh Hoa before and after flooding, respectively, and 61.6-78.1 mg kg^{-1} d.w. and 58.2-72.2 mg kg^{-1} d.w. in Hue, respectively. These values were close to the regulated value issued by the National technical regulation on the allowable limits of heavy metals in the soils (70 mg kg^{-1} d.w.) [7] and lower than regulation value issued by CCME (70 mg kg^{-1} d.w.) [7]. Detected concentration of lead in this study were close to those in peri-urban Hanoi agricultural soils (32.5-67.4 mg kg^{-1} d.w.) [8]. Zinc concentrations in soil were 39.7-60.8 mg kg^{-1} d.w. and 33.6-50.1 mg kg^{-1} d.w. in Thanh Hoa before and after flooding, respectively, and 78.3-94.6 mg kg^{-1} d.w. and 71.9-85.6 mg kg^{-1} d.w. in Hue, respectively. These values were lower than the regulated value issued by the National technical regulation on the allowable limits of heavy metals in the soils (200 mg kg^{-1} d.w.) [7] and lower than regulation value issued by CCME (200 mg kg^{-1} d.w.) [7]. The concentration of zinc in this study was lower than those detected in the agricultural soils in Hanoi 90.8- 189 mg kg^{-1} d.w. [8].

Accordingly, concentration of detected heavy metals in the present study was lower than limitation values issued by QCVN 03 [9], Probable Effect Level (PEL) issued by CCME [7] and in peri-urban Hanoi agricultural soils [8]. This result demonstrated that there is no potential risk of heavy metals on paddy soils and no restriction exists towards their use [10].

The average concentration of heavy metal in the paddy soils before flooding in Hue was higher than those in Thanh Hoa. The concentration of 7 heavy metals (Cu, Pb, Zn, Cr, Co, Cd and As) in the flooded soil sample decreases compared to before floods in all samples in Thanh Hoa and Hue. This due to the release of these elements from the soil into the water. This is in accordance with our previous study, in which the concentration of these elements in floodwater after the flooding were higher than those before flooding [8].

The average concentrations of ion were 175 g/kg and 148 g/kg in Thanh Hoa before and after flooding, respectively, and 271 g/kg d.w. and 241 g/kg d.w. in Hue, respectively. The average concentrations of manganese were 141mg/kg and 110 mg/kg in Thanh Hoa before and after flooding, respectively, and 160 mg/kg d.w. and 140 mg/kg d.w. for Hue before and after flooding. The average concentrations of Fe and Mn in the paddy soil after flooding were lower than those before flooding in both locations (Fig.1), perhaps due to the redox reactions occurred while flooding and the reduction of Mn(III/IV) to Mn(II), Fe(III) to Fe(II), which results in increasing the dissolution of Fe(II) - and Mn(III/ IV)-hydroxides in water and decreasing in the soil [10, 12-14]. Arsenic concentration decreased in Thanh Hoa and Hue after flooding (Fig.1), probably due to the reduction potential becomes sufficiently low when the soil was flooded. As(V) was reduced to As(III), which in turn has a lower sorption affinity to soil particles [11] resulting in partial release to the water and their concentration in soil decreased after flooding. The similar observation was seen in water where arsenic concentration in the water after flooding was higher than those before flooding [6].

4. CONCLUSION

In this study, concentration of nine heavy metals detected in the paddy soils was generally lower than regulation threshold values issued by the National technical regulation on the allowable limits of heavy metals in the soils [7] and Canadian environmental quality guidelines for protection of aquatic life [7], implying no potential risks of heavy metals to the aquatic environment and there is no restriction exists towards their use. The data obtained in this study provides the overview on status the sources of heavy metals in paddy soils before and after flooding in Vietnam.

Acknowledgements: This study was supported by the National Foundation for Science and Technology Development (NAFOSTED) - Ministry of Science and Technology, project number: 104.01-2018.318

REFERENCES

1. Allan, I.J., et al., *Measuring nonpolar organic contaminant partitioning in three Norwegian sediments using polyethylene passive samplers*. Science of The Total Environment, 2012. 423(0): p.125-131.
2. Norrman, J., et al., *Arsenic mobilisation in a new well field for drinking water production*

along the Red River, Nam Du, Hanoi. Applied Geochemistry, 2008. 23(11): p. 3127-3142.

3. Hoai, P.M., et al., *Pesticide pollution in agricultural areas of Northern Vietnam: Case study in Hoang Liet and Minh Dai communes*. Environmental Pollution, 2011. 159(12): p. 3344 - 3350.

4. Gao, J.P., et al., *Distribution of pesticides in the sediment of the small Teufelsweiher pond (southern Germany)*. Water Research, 1997. 31(11): p. 2811-2819.

5. Trinh, H.T., Giang T.L., et al., *Pesticide and element release from a paddy soil in central Vietnam: Role of DOC and oxidation state during flooding*. Geoderma, 2018. 310: p. 209-217.

6. Trinh, H.T. et al., *Screening of inorganic and organic contaminants in floodwater in paddy fields of Hue and Thanh Hoa in Vietnam*. Environmental Science and Pollution Research, 2017. 24(8): p. 7348-7358.

7. CCME, C.C.o.M.o.t.E., *Canadian environmental quality guidelines for protection of aquatic life: summary table*. In: Canadian Environmental Quality Guideline, Winnipeg, Manitoba, Canada.http://www.ccme.ca/publications>,2002

8. Marcussen, H., et al., *Element contents and food safety of water spinach (Ipomoea aquatica Forssk.) cultivated with wastewater in Hanoi, Vietnam.* Environmental Monitoring and Assessment, 2008. 139(1): p. 77-91.

9. QCVN03, *National technical regulation on the allowable limits of heavy metals in the soils*. 2008/BTNMT.

10. Swartjes, F.A.J.R.A., *Risk-Based Assessment of Soil and Groundwater Quality in the Netherlands*: Standards and Remediation Urgency, 1999. 19(6): p. 1235-1249.

11. Wilson, S.C., Lockwood, P.V., Ashley, P.M., 2010. The chemistry and behaviour of anti-mony in the soil environment with comparisons to arsenic: a critical review. Environ.
Pollut. 158 (5), 1169–1181.

12. Patrick, W.H., Jugsujinda, A., 1992. Sequential reduction and oxidation of inorganic ni-trogen, manganese, and iron in flooded soil. Soil Sci. Soc. Am. J. 56 (4), 1071–1073.

13. Miao, S., DeLaune, R.D., Jugsujinda, A., 2006. Influence of sediment redox conditions on release/solubility of metals and nutrients in a Louisiana Mississippi River deltaic plain freshwater lake. Sci. Total Environ. 371 (1–3), 334–343.

14. Guo, T., DeLaune, R.D., Patrick Jr., W.H., 1997. The influence of sediment redox chem-istry on chemically active forms of arsenic, cadmium, chromium, and zinc in es-tuarine sediment. Environ. Int. 23 (3), 305–316.