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STATE OF HEAVY METAL CONTAMINATION IN WATER, FOOD; COMMUNITY PEOPLE'S HEALTH IN THE COASTAL AREA OF THUYNGUYEN DISTRICT, HAIPHONG AND RESULTS OF AN EXPERIMENTAL INTERVENTION

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SUMMARY OF DOCTORAL THESIS

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LIST OF ABREVIATIONS

AC	Activated carbon
ADD/ADI	Average daily dose/ Acceptable Daily Intake
ALA	Delta-aminolevulinic dehydratase
BW	Body weight
CR	Cancer risk
CSF	Cancer slope factor
ED	Exposure dose
EF	Exposed frequency
ML	Maximum level
HI	Hazard index
HQ	Hazard quotient
HM	Heavy metal
Min	Minimum
Max	Maximum
RfD	Reference dose
USEPA	United State Environmental Protection Agency
WHO	World Health Organization

INTRODUCTION

According to the World Health Organization (WHO), globally, there were 12.6 million deaths (23%) caused by environmental pollution in 2012.[1]. One of the major threats to ecological and human health is environmental contamination and pollution by heavy metals. Among the environmental pollutants, there is an increasing need for research on heavy metals because they are toxic, easily bioaccumulate, difficult to decompose and therefore persistent, and can pose risks to ecological and human health.[2,3] The Minamata disaster caused by organic mercury pollution in Chisso Bay, Japan is the classic evidence of coastal water pollution with serious consequences on the ecosystem and community health.[4]. The results of some studies showed that heavy metal contamination in water, vegetables and seafood was detected in some areas of Vietnam. Cd and Pb were detected as the main pollutants in surface sediments, Red River basin by Nguyen Thi Thu Hien (2016), Testuro Agusa (2014) [5,6] while As, Cr and Hg were higher than the permissible limit in the Mekong Delta [7]. High concentrations of heavy metals (As, Cd, Cr, Pb) in oyster tissue and green mussels were seen in coastal Can Gio và Do Son-Dinh Vu [8, 9].

With a 3200 km long coastline and 28 coastal provinces, the marine environment plays an important role for the socio-economic development of Vietnam [10]. Thuy Nguyen, Hai Phong is a coastal district that has been interested in exploiting geographical advantages in socio-economic development with the construction and expansion of factories and production enterprises. Currently, only limited data on the levels of heavy metal contamination in food, especially heavy metal contamination in vegetables and seafood in Thuy Nguyen, Vietnam, are available.

Based on the evidence described above, the study ***State of heavy metal contamination in water, food; community people's health in the coastal area of Thuynguyen District, Haiphong and results of an experimental intervention*** was caried out with following objectives:

1. *To identify the state of heavy metal pollution in water and food in two coastal communes of Thuy nguyen District, Haiphong city in 2017-2018.*
2. *To describe the pattern of disease and the risk due to exposure to heavy metal contamination among community residents in the study area.*
3. *To evaluate the effectivenss of removing heavy metals from water with castor activated carbon in 2018-2019.*

THE NEW CONTRIBUTION OF THE THESIS

This is one of the first studies in Vietnam which describes heavy metal contamination in water and food, and calculates the estimation of human health risk from heavy metal exposure in a particular coastal area in Vietnam.

A slow filtration tank was developed and used to remove heavy metals from water with castor activated carbon. The results showed that castor activated carbon was highly effective in the laboratory and in the field.

THESIS STRUCTURE

There are 120 pages in the main part of the thesis, which consists of the following sections: Introduction: 2 pages, Chapter 1 - Literature review: 34 pages, Chapter 2 - Materials and Methods: 26 pages, Chapter 3 - Results: 28 pages, Chapter 4 - Discussion: 27 pages, Conclusions and recommendations: 3 pages. There are 40 tables, 12 figures, and a total 7 related Appendices of 19 pages in the thesis. 149 references in which 29 Vietnamese and 120 English, were cited.

Chapter 1 : LITERATURE REVIEW

1.1. Heavy metal pollution in water and food in coastal areas

1.1.1 The source, metabolism in nature and effect of heavy metals

Heavy metals (HMs) are metals that have a density greater than 5g/cm^3 in comparison to water. HMs can be released from both natural and artificial activities. Based on the level of immediate threat to human health and the environment, As, Pb, Cd, Cr and Hg are the HMs that most concern the community and WHO.[13]

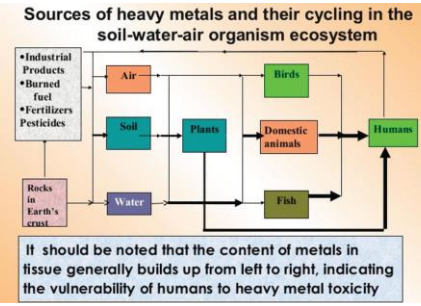

Figure 1.1. Source of heavy metals and their cycle in the environment **[26]**

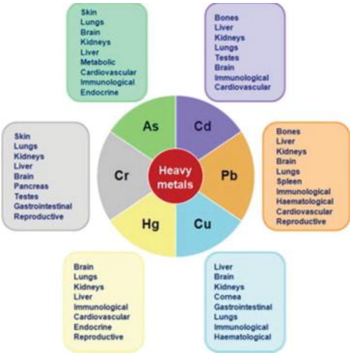

Figure 1.2. Impact of heavy metals on the environment **[26]**

1.1.2. Current state of heavy metal contamination in water and food in Vietnam and globally

1.1.2.1 Global

The concentration of HMs in seafood, especially in in the muscle and liver of the organisms, has been studied by many Asian authors.

Some studies have found that the concentration of HMs in fish and shrimp commonly consumed in the Arabian Gulf and Malaysia met the national permitted limits [28, 29]. However, one study in Jizan, Saudi Arabia, Red Sea, 2013, found that the average concentration of HMs in the country exceeded the recommended value of WHO/USEPA and decreased gradually in the order of Cr> Pb> As > Cd [30]. Oteef et al. (2015) detected Pb and Cd in leafy vegetables, (arugula and spinach) in Saudi Arabia, [38]; Husain, 2020 had identified relatively high concentrations of Cr in spinach, lettuce and carrots in the United Arab Emirates [39].

1.1.2.2. In Vietnam

Pham Long Hai et al. (2016) found that the As concentration in 83% of groundwater samples in Hanam exceeded WHO's recommended drinking water limits (10 µg/L) [43]. As, Pb and Cd in vegetables, especially in water spinach and lettuce, in Hanoi, Thai Nguyen, Bac Kan provinces were detected at higher levels in comparision to permissible standards [51, 52].

1.2. Disease pattern and human health risk of heavy metal exposure in coastal areas

1.2.1. Risk Assessment

1.2.2. *Disease pattern in coastal areas in Vietnam and in the world*

According the Institute of International Health Assessment and WHO, the leading causes of death globally shows an increasing trend of morbidity and mortality from non-communicable diseases (NCDs) while infectious diseases have been decreasing. In particularly, NCDs remain the biggest burden globally, especially in low and middle-income countries, including Vietnam. [58, 59].

In Vietnam, causes of morbidity are classified into three main groups: infectious diseases, non-communicable diseases and accidental poisoning. According to statistics from the Ministry of Health in 2016, the group of non-communicable diseases accounted for the highest proportion with 69.1%, an increase of 65.6% compared to 2015. In the past 5 years, the disease pattern has evolved with the trend that the non-communicable disease accounts for 2/3 of the total disease causes while contagious diseases account for about a quarter of the remaining diseases; the remainder result from accidents, poisoning, injury.[58, 60]

1.2.3. Human health risk due to exposure to drinking water, vegetable and seafood contaminated with heavy metals

- *Risk assessment method*

Hazard = Risk factor + exposure.[62]

- *Human health risk from exposure water, vegetable and seafood contaminated with heavy metals*

In Vietnam, the data for estimating the human health risk from exposure of HMs from consuming vegetables and seafood is limited. The cancer risk of As contaminated groundwater ranged from 5 x 10^{-4} in Ha Nam to 8.26 × 10^{-2} in An Giang [73], [77]. The human health risk of As contaminated vegetable was investigated in Vinh Quynh, Hanoi (2015) [74].

- *Current state of heavy metal exposure measured in biological samples*

16% of urine samples were found to have higher concentrations of HMs than the normal limit in some studies done in HaNam province [79], [80].

1.3. Strategies to remove heavy metals from water

Worldwide, the removal of heavy metals is an important step to ensure safe drinking water. Some of the common methods used to remove heavy metals include chemical precipitation, flocculation-forming, membrane filtration, ion exchange, electrochemical and adsorption.[85]. In Vietnam, some authors have researched solutions for removing heavy metals in water, however, mainly focusing on arsenic removal in groundwater because it is a common water pollutant in rural areas. Adsorption with a variety of materials (mineral coal, fiber/coconut shell) in conjunction with filtration is used to remove arsenic from the water.

Chapter 2. MATERIALS AND METHODS

2.1. Study subjects, study area and study time

*Study subjects: *(1) Water samples*: 54 surface water samples and 222 drinking (well) water samples; *(2) Food samples:* 40 seafood samples (10 for each seafood [tiger shrimp, stuffed snails, snake-head fish, and catfish]) were collected at the 2 biggest open markets and the residents' fish ponds in the study area; The most commonly grown and consumed vegetables including 12 leafy vegetables, 4 pea plants, 4 tuber vegetables, and 7 herbs were collected; *(3) Study population:* Residents who were at least ≥18 years old and had been living ≥3 yrs in the study area, which is 1500 m distance from the industry plants.

*Study location and time: Study was conducted in Tam Hung and Minh Duc communes, Thuynguyen district, Haiphong city, from December 2016 to May 2019.

2.2. Research methods

2.2.1. Study design: 2 periods

- *1st stage:* From December 2016 to May, 2017: Cross-sectional descriptive study
- *2nd stage:* From May 2017 to May 2019 conducting experimental intervention study comparing the results of removing heavy metals by using a slow filtration tank with castro tree activated carbon in the laboratory (6 months) and in field (Tam Hung commune in 18 months).

2.2.2. Sample size and sampling methods

** Sample size and sampling for the 1st objective:* Applying the formula of one proportion and mean value estimation to calculate the sample sizes we need for analysis, a total of 54 surface water samples, 222 drinking water (well) samples) and 135 vegetable samples and 40 seafood samples, which were larger than theorical sample sizes were selecleted. All samples were selected by the poroportion sampling methods in the study areas.

**Sample size and sampling for the 2nd objective: Applying* the formula to estimate one proportion to determine the sample sizes needed for interviews and biological samples, the quantities of selected samples of community residents (1010 people and 450 urine, 450 blood samples) were larger than the calculated sizes.

For sampling to investigate the disease pattern, 1010 community residents (522 persons from TamHung and 490 persons from Minh Duc) were randomly selected from the list of residents who meet the inclusion criteria community people.

For urine and blood sampling: 450 people who have symptoms and signs of heavy metal exposure were selected from 1010 local people during medical examinations and interviews.

2.2.3. Study contents, Study variables and indicators

- 1st objective:

+ The heavy metal concentration in surface water, well water (mg/l), vegetable and seafood samples (mg/kg)

- 2nd objective*:*

+ Blood heavy metals (µg/dl), and Urine heavy metals (µg/l)

+ The rate of commmunity residents who suffer from the disease by ICD 10 classification

+ Distribution of heavy metal exposure by gender

+ Distribution of common disease proportion by heavy metal exposure

+ The proportion of people having with poisoning symptoms by heavy metal exposure

+ The risk quotient due to HMs contaminated vegetables and seafood consumption

+ Hazard index (HI) for each type of vegetables and seafood

+ Estimated human risk of HMs contaminated water

+ Estimated human health risk from HMs contaminated vegetable and seafood

- 3rd objective:

+ Intervention effectiveness: Heavy metal removing indicator before and after using castro activated carbon filtration in laboratory and in the field

+ Efficiency indicator

2.4. Data collection techniques and tools

*******Techniques of collecting information on environmental samples (agricultural land, surface water and well water) and blood and urine samples:* complied with the Technical Regulation on Environmental and Occupational Health, Institute of Occupational and Environmental Health)[99]. Environmental samples, blood and urine samples, after being collected, will be analyzed and assessed for concentrations of As, Pb, Cd, Cr and Hg at the Military Medicine Research Center, the Military Medical Academy according to the corresponding technique as follows:

*****Samples of surface water, well water, vegetables, seafood: the HM concentration were determined with atomic absorption spectroscopy.

✓ Evaluate the results of As, Pb, Cd, Cr and Hg contents in surface water and well water respectively according to QCVN 08 MT: 2015/BTNMT and QCVN 01: 2009/BYT [101,102].

✓ Evaluate results of As, Pb, Cd and Cr, Hg content in vegetables according to Decision No. 99/2008/ QD-BNN & PTNT [103]

✓ Evaluate results of As, Pb, Cd, Cr and Hg content in seafood according to National Standards on food according to QCVN 8-2: 2012 /BYT [104]

** Blood Pb and Cd were examined with atomic absorption spectroscopy*

*24 hour urinary As, ALA, Cr and Hg concentations were determined with atomic absorption spectroscopy and plasma mass spectrometry.

Data collection techniques and tools for health status, risks and signs of heavy metal poisoning (As and Pb contamination), frequency of vegetables and seafood consumption***

✓ Study subjects were examined and interviewed using the health examination form of the Ministry of Health and previous studies on signs and symptoms of HM poisoning. (Appendix 1)

✓ Questionnaire of daily consumption frequency and human health risk of chemical exposure from food (vegetables, seafood) during the last 7 days (Appendix 2)

***** *The evaluation methods for the human health risk of consuming HM contaminated wellwater, seafood (fish, shrimp, snail) and vegetables*: applying US.EPA and WHO guidelines to calculate the hazard quotient (HQ), hazard index (HI), cancer risk [105, 106].

$$HQ = [(C \times FIR \times ED \times EFr)/ (BW \times AT \times RfD)] \times 10^{-3}$$

$$HI = \sum HQi = HQKLN1 + HQKLN2 + HQKLN3 + \ldots + HQn$$

$$CR = [(EF \times ED \times FIR \times C \times CSF_0)/(BW \times AT)] \times 10^{-3}$$

In which:

C: HM concentrations in vegetables, fish tested (mg/kg). According to the survey, the average fish consumption for male and female is 0.02 kg/day and 0.0165 kg/day, respectively; The amount of vegetables consumed was 0.065 g/person/day in both genders.

RfD is referance dose (As = 0,0003, Cd = 0,001, Pb = 0,0035, Cr = 1,5 (mg/kg/day)).

BW is the body weight (kg). Our survey results showed the average weight of study subjects is 55.86 kg for men and 44.26 kg for women.

i is the different heavy metals

CSF_0: Potential oral carcinogenicity coefficient (mg/kg bw/day)

Results evaluation: HQ > 1: potential risk to human health
HI > 1: high risk to consumers' health
CR = 10^{-6} - 10^{-4}: acceptable cancer risk level

****Data collection for experiment intervention period***

Testing of heavy metal removal by the slow filter tank model in the laboratory with 2 types of filtation materials: (*1)* with coconut shell/skull activated carbon with As, Pb, Cd and Cr contaminated hypothetical samples at 9 volumes (from 1-48 liters); *(2)* with castor plant activated carbon at 10 volumes of water (from 20 - 2600 liters).

Tested removal of heavy metal with a slow filter tank model with castor activated carbon filter material) at 4 wells in the field for 18 months. Water samples were collected at the test tank daily for the first month and every Sunday in plastic bottles and stored at 4^0C, and transported weekly to the laboratory at the Military Institute of Medicine and Pharmacy, Military Medical University to determine the concentration of HMs

- ***Intervention supervision:***

The content and procedure of the experiment intervention in the laboratory (6 months) and in the field (18 months) were supervised by principal researchers and researchers of the Military Medical Research Institute, Military Medical Academy.

- Tool for assessing the concentration of HMs in the water: testing the concentration of HMs in the water according to the technique used in the pre-intervention stage
- *Evaluation of filtration results and efficiency index*
- Comparison of HMs content in water samples tested in the laboratory and in the field (after 18 months) with QCVN 01: 2009/BYT
- Calculate the efficiency indicator after filltration intervention

2.5. Data analysis

The collected data were entered in Excel and analysed by SPSS 22.0.

2.6. Ethical approval

The study followed and complied with the study protocol approved by the Approval Council of Hai Phong University of Medicine and Pharmacy. The consent form was collected from all study subjects, Thuy Nguyen District Medical Center, the People's Committee and people of Minh Duc, Tam Hung, Thuy Nguyen district, Hai Phong. The purpose, content and meaning of the study were clearly explained to community people who signed voluntary consent to participate in research. All personal information is kept confidential and used only for research purposes. The research results are aimed to improve the drinking water quality and the communities health in Tam Hung and Minh Duc communes, Thuy Nguyen district, Hai Phong city.

Chapter 3. RESEARCH RESULTS

3.1. Current state of heavy metal contamination in water and food in the coastal area of Thuy Nguyen district, Hai Phong in 2017-2018

Table 3.1. The concentration of heavy metals in surface water (n=54)

Concentration (mg/L) **HMs**	**Min**	**Max**	**Mean**	**No sample over MLs (n, %)**	**MLs QCVN 08:2015**
As	0.02	0.42	0.19	54 (100)	≤ 0.01
Pb	0.03	0.39	0.17	54 (100)	≤ 0.02
Cd	0.00	0.03	0.02	53 (98.15)	≤ 0.005
Cr	0.32	4.32	2.56	53 (98.15)	≤ 0.050
Hg	KPH	-	-	0 (0.00)	≤ 0.001

Table 3.2. The concentration of HMs in well water (n=222)

Concentration (mg/L) **HMs**	**Min**	**Max**	**Mean**	**No sample over MLs (n, %)**	**ML National Standards** 01:2009/MOH
As	0.01	0.48	0.06	185 (83.33)	≤ 0.01
Pb	0.01	0.42	0.12	210 (94.59)	≤ 0.01
Cd	0.00	0.15	0.03	188 (84.68)	≤ 0.003
Cr	0.02	0.82	0.25	166 (74.77)	≤ 0.05
Hg	KPH	-	-	0 (0.00)	≤ 0.001

The percentage of well water samples which did not meet the national standard in HMs were highest with Pb (94.59%), then followed by As, Cd, and Cr.

Table 3.3. The concentration of HMs in vegetable samples (n=135)

Concentration **HMs**	**Min**	**Max**	**Mean**	**No sample over MLs (n, %)**	**Decision 99/2008/MARD**
As	0.17	1.69	0.87	52 (38.52)	≤ 1.0
Pb	0.11	1.96	0.80	123 (91.11)	≤ 0.3
Cd	0.00	3.27	0.82	95 (70.37)	≤ 0.1
Cr	0.02	1.57	0.51	107 (79.26)	≤ 0.1
Hg	0.00	0.04	0.01	0	≤ 0.05

The percentage of vegetable samples with concentrations of HMs higher than the permitted standard for Pb (91.11%), followed by Cr (79.26%) and Cd (70.37%) and lowest in As (38.52%).

Table 3.4. The concentration of heavy metals in seafood samples (mg/kg)

Seafood / HMs	Snake-head fish		Catfish		Stuffed Snail		Tiger Shrimp	
	Mean (Min, Max)	N^* (n, %)	Mean (Min, Max)	N^* (n, %)	Mean (Min, Max)	N^* (n, %)	Mean (Min, Max)	N^* (n, %)
As	1.18 (1.18-1.19)	-	1.66 (1.56-1.80)	-	0.80 (0.77-0.81)	-	0.80 (0.77-0.81)	-
Pb	0.08 (0.07-0.09)	0	0.10 (0.08-0.12)	0	1.24 (0.72-1.76)	10 (100)	1.24 (0.72-1.76)	10 (100)
Cd	2.30 (1.91-2.74)	10 (100)	1.06 (0.94-1.18)	10 (100)	1.62 (1.35-1.97)	10 (100)	1.62 (1.35-1.97)	10 (100)
Cr	2.12 (1.96-2.31)	-	2.25 (2.04-2.47)		1.46 (1.03-1.87)	-	1.46 (1.03-1.87)	-
Hg	ND	0	ND	0	ND	0	ND	0

N^*: No sample over MLs;   ND: not detected

3.2. State of disease structure and the human health risk due to heavy metal contamination and exposure in the study area

Table 3.5. The distribution of common diseases by gender

Disease group	**Male (n =447)**		**Female (n= 563)**		**Total (n=1010)**		**p**
	n	**%**	**n**	**%**	**N**	**%**	
Circulatory system	179	40.04	240	42.63	419	41.49	0.41
Respiratory system	136	30.43	166	29.48	302	29.90	0.75
Digestive system	223	49.89	264	46.89	487	48.22	0.34
Urinary system	35	7.83	37	6.57	72	7.13	0.44
Motor System	196	43.85	236	41.92	432	42.77	0.54
Endocrine system-metabolism disease	82	18.34	98	17.41	180	17.82	0.69
Ear - Nose - Throat	155	34.68	143	25.40	298	29.50	<0.01
Tooth - Jaw - Face	373	83.45	477	84.72	850	84.16	0.58
Eye disease	107	23.94	141	25.04	248	24.55	0.68
Skin disease	152	34.00	244	43.34	396	39.21	<0.01
Nervous system	215	48.10	280	49.73	495	49.01	0.61
Infectious disease	273	61.07	330	58.61	603	59.70	0.43

The rate of common diseases in adults is quite high, with the highest rates of diseases of the teeth - jaw - face, infectious, digestive diseases, circulatory diseases and skin diseases.

3.2.2. HM concentrations in blood and urine samples of study subjects

Table *3.6.* HM concentrations in blood and urine samples *(n=450)*

Concentration HMs	TB ± SD	Min – Max	N^* (n, %)	Normal value
Blood_Pb *(µg/dL)*	9.06 ± 0.99	6.23-11.35	96 (21.33)	< 10
Blood_Cd *(µg/l)*	KPH		(0.0)	-
Urine_As *(µg/l)*	69.96 ± 23.38	44.65- 43.32	174 (38.67)	< 60
U_ALA (mg/l)	4.50 ± 1.59	2.16 - 11.24	96 (21.33)	< 5
U_ Cr (µg/l)	40.04 ± 6.97	21.38 - 86.56	-	-
U_Hg (µg/l)	1.32 ± 0.51	0.37 -3.50	(0.0)	-

N^*: Samples exceeded normal level

21.33% of samples had blood Pb, urinary ALA and 38.67% had urinary As higher than the normal threshold.

Table 3.7. Distribution of HM exposure by gender (n=450)

Gender HMs exposure	Male (n=225)		Female (n=225)		Total (n=450)		p
	No	**%**	**No**	**%**	**No**	**%**	
Yes*	86	38.20	99	44.00	185	41.10	0.213
No	139	61.80	126	56.00	265	58.90	

: B_Pb $\geq$ 10 µg/dL or U_As > 60 or U_ALA $\geq$ 5 mg/L*

41.10% of local people had HM exposure, however there was no difference in HM exposure rate by gender (p>0.05).

3.2.3. The assocation between HM exposure and health indicators among study subjects

Table 3.8. The assocation between poisonous symptoms and HM exposure among study subjects

HMs exposure / **Symptoms**	**Yes (n= 185)**		**No (n =265)**		**p**	**OR (95%CI)**
	n	**%**	**n**	**%**		
Asthenia	133	71.89	88	33.21	< 0.01	5.14 (3.41 - 7.75)
Neurasthenia	126	68.11	107	40.38	< 0.01	3.15 (2.13 - 4.68)
Hair loss	74	40.00	30	11.32	< 0.01	5.22 (3.23 - 8.44)
Sensory disorder	65	35.14	29	10.94	< 0.01	4.41 (2.70 - 7.19)
Vasomotor disorder	118	63.78	70	26.42	< 0.01	4.91 (3.27 - 7.36)
Thick horn/nails	11	5.95	1	0.38	< 0.01	16.69 (2.14-130.43)
Skin pigmentation disorders	18	9.73	4	1.51	< 0.01	7.03 (2.34 - 21.14)
Tumor	16	8.65	0	0.00	< 0.01	-
Pregnancy disease	5/22	22.73	1/29	3.45	0.03	8.24 (0.89 - 76.59)

The morbidity rate of some poisonous symptoms/diseases in the exposed group were significantly higher than the non-exposed (p<0.05). Specifically, the highest prevalence of diseases/symptoms was keratosis, skin pigmentation disorder.

* Human health risk related to HM contaminated drinking water

Table 3.9. Estimated HM doses taken into the human body through digestive route

Dose/day / **HMs**	**D (mg/kg/day)**	**TDI (mg/kg/day)**	**No sample over TDI n (%)**
Arsenic	0.0031 ± 0.0006	0.002	114 (51.35)
Lead	0.0030 ± 0.0041	0.003	144 (64.86)
Cadimium	0.0012 ± 0.0004	0.060	0 (0)
Chromium	0.0066 ± 0.0078	0.300	0 (0)

51.53% and 64.86% of households using well water which contaminated with As and Pb for drinking with D > TDI, respectively**.**

Cancer risk estimation related to HM contaminated well water

Table 3.10 Cancer risk estimation related to As contaminated well water

Variable	**Acceptable cancer risk**	**Min**	**Max**	$\bar{X}$	**SD**
R_1	$10^{-6} - 10^{-4}$	3.2×10^{-3}	5.8×10^{-3}	4.6×10^{-3}	0.9×10^{-3}
R_2		3.8×10^{-3}	6.9×10^{-3}	5.5×10^{-3}	1.1×10^{-3}
R_3		4.8×10^{-3}	8.7×10^{-3}	6.9×10^{-3}	1.4×10^{-3}
R_4		27.7×10^{-3}	50.1×10^{-3}	40.1×10^{-3}	8.2×10^{-3}

Note: R_1 : cancer risk at present with current exposure among local adults;
R_2 : cancer risk at 5 years later with current exposure among local adults
R_3 is cancer risk at 10 years later with current exposure among local adults
R_4 is cancer risk at the whole life year with current exposure among local adults

All the risk estimations were higher than the acceptable level.

Table 3.11. Cancer risk estimation related to Pb contaminated well water

Variable	**Acceptable risk level**	**Min**	**Max**	$\bar{X}$	**SD**
R_1	$10^{-6} - 10^{-4}$	$3{,}12 \times 10^{-6}$	$8{,}73 \times 10^{-5}$	$2{,}56 \times 10^{-5}$	$3{,}50 \times 10^{-5}$
R_2		$3{,}74 \times 10^{-6}$	10×10^{-5}	$3{,}07 \times 10^{-5}$	$4{,}20 \times 10^{-5}$
R_3		$4{,}68 \times 10^{-6}$	10×10^{-5}	$3{,}83 \times 10^{-5}$	$5{,}25 \times 10^{-5}$
R_4		$2{,}71 \times 10^{-5}$	80×10^{-5}	20×10^{-5}	30×10^{-5}

The estimated average cancer risks related to Pb contaminated water at any time points were under and below accetaple risk level.

Table 3.12. Cancer risk estimation related to Cd contaminated well water

Variable	**Acceptable risk level**	**Min**	**Max**	$\bar{X}$	**SD**
R_1	$10^{-6} - 10^{-4}$	3×10^{-4}	6×10^{-4}	5×10^{-4}	1×10^{-4}
R_2		3×10^{-4}	8×10^{-4}	6×10^{-4}	2×10^{-4}
R_3		4×10^{-4}	10×10^{-4}	7×10^{-4}	2×10^{-4}
R_4		$24 \times 10^{-}$	56×10^{-4}	40×10^{-4}	12×10^{-4}

The current estimated cancer risk among adults in Tam Hung and Minh Duc communes from using Cd contaminated well water for drinking at any time points were higher than the acceptable level.

Table 3.13. Estimated cancer risk related to Cr contaminated well water

Variable	Acceptable risk level	Min	Max	$\bar{X}$	SD
R_1	10^{-6} - 10^{-4}	5 x 10^{-4}	9.4 x 10^{-3}	3.3 x 10^{-3}	3.9 x 10^{-3}
R_2		6 x 10^{-4}	11.2 x 10^{-3}	4.0 x 10^{-3}	4.7 x 10^{-3}
R_3		7 x 10^{-4}	14.0 x 10^{-3}	5.0 x 10^{-3}	5.8 x 10^{-3}
R_4		41 x 10^{-4}	81.2 x 10^{-3}	28.7 x 10^{-3}	33.8 x 10^{-3}

The current estimated cancer risk among adults from using Cr contaminated well water for drinking at any time points were higher than the acceptable level.

***Cancer risk related to HM contaminated food consumption**

Table 3.14. Estimated cancer risk related to HM contaminated vegetable consumption by gender

Cancer risk HMs		Min	Max	$\bar{X}$	SD
As	Male	2,97 x 10^{-7}	2,96 x 10^{-6}	1,51 x 10^{-6}	6,03 x 10^{-7}
	Female	3,74 x 10^{-7}	3,74 x 10^{-6}	1,90 x 10^{-6}	7,61 x 10^{-7}
Pb	Male	1,09 x 10^{-9}	1,94 x 10^{-8}	7,91 x 10^{-9}	3,30 x 10^{-9}
	Female	1,37 x 10^{-9}	2,45 x 10^{-8}	9,99 x 10^{-9}	4,16 x 10^{-9}
Cd	Male	0,00	6,85 x 10^{-9}	1,72 x 10^{-9}	1,37 x 10^{-9}
	Female	0,00	8,64 x 10^{-9}	2,17 x 10^{-9}	1,72 x 10^{-9}
Cr	Male	9,89 x 10^{-9}	9,13 x 10^{-7}	2,97 x 10^{-7}	1,92 x 10^{-7}
	Female	1,25 x 10^{-8}	1,15 x 10^{-6}	3,74 x 10^{-7}	2,42 x 10^{-7}

The estimated risk of cancer due to HM contaminated vegetables consumption in both gender were highest from As. and lowest with Cd.

Table 3.15. Estimated cancer risk related to HM contaminated seafood consumption by gender

Cancer risk HMs		Min	Max	$\bar{X}$	SD
As	Male	4.37 x 10^{-7}	1.02 x 10^{-6}	6.82 x 10^{-7}	1.77 x 10^{-7}
	Female	4.37 x 10^{-7}	1.01 x 10^{-6}	6.76 x 10^{-7}	1.76 x 10^{-7}
Pb	Male	2.20 x 10^{-10}	8.63 x 10^{-9}	2.83 x 10^{-9}	2.91 x 10^{-9}
	Female	2.19 x 10^{-10}	8.56 x 10^{-9}	2.80 x 10^{-9}	2.88 x 10^{-9}
Cd	Male	6.36 x 10^{-10}	2.48 x 10^{-9}	1.39 x 10^{-9}	5.81 x 10^{-10}
	Female	6.31 x 10^{-10}	2.46 x 10^{-9}	1.38 x 10^{-9}	5.76 x 10^{-10}
Cr	Male	1.94 x 10^{-7}	4.64 x 10^{-7}	3.54 x 10^{-7}	7.70 x 10^{-8}
	Female	1.92 x 10^{-7}	4.60 x 10^{-7}	3.51 x 10^{-7}	7.64 x 10^{-8}

The estimated risk of cancer due to HM contaminted seafood consumption in both genders was highest with As > Cr > Pb > Cd, but are lower or within the acceptable level.

3.3. Experimental results of removing heavy metals in water with activated carbon

3.3.1. Experimental results from laboratory tests

Table 3.16. Results in removing As with coconut shell &castro active carbon

Tested V (L)	**Coconut shell AC**			***Tested V(L)***	**Castro AC**		
	Input	**0.1**	**1.0**		***Input***	**0.1**	**1.0**
1	Output	0.059	0.920	***20***	**Output**	< 0.005	< 0.005
2		0.068	0.946	***300***		< 0.005	< 0.005
3		0.085	0.975	***600***		< 0.005	< 0.005
4		0.088	0.983	***900***		< 0.005	< 0.005
6		0.092	0.987	***1200***		< 0.005	< 0.005
8		0.094	0.988	***1500***		< 0.005	< 0.005
12		0.093	0.990	***1800***		< 0.005	0.015
24		0.096		***2100***		< 0.005	0.028
48		0.097		***2400***		< 0.005	0.048
				2600		< 0.005	0.062

Note: *National permissible standard: As < 0.01 ppm*

No output As concentrations met the permissible standard was seen with coconut shell material. However, with castor AC filtration, the output of As met the permissible standard in 2600 liters and 1500 litres.

Table 3.17. Results in removing Pb with coconut shell and castro active carbon

Tested V (L)	**Coconut shell AC**			***Tested V (L)***	**Castro AC**		
	Input	**0.1**	**1.0**		***Input***	**0.1**	**1.0**
1	Output	0.061	0.922	20	***Output***	< 0.01	< 0.01
2		0.070	0.948	300		< 0.01	< 0.01
3		0.087	0.977	600		< 0.01	< 0.01
4		0.090	0.985	900		< 0.01	< 0.01
6		0.094	0.989	1200		< 0.01	< 0.01
8		0.096	0.99	1500		< 0.01	< 0.01
12		0.095	0.992	1800		< 0.01	0.016
24		0.098		2100		< 0.01	0.029
48		0.099		2400		< 0.01	0.050
				2600		< 0.01	0.058

Note: National permissible standard: Pb < 0.010 ppm

Similar results were seen in removing Pb from water with coconut shell and castro activated carbon.

Table 3.18. Results in removing Cd with coconut shell and castro AC

Tested V (L)	**Coconut shell AC**			***Tested V (L)***	**Castro AC**		
	Input	**0.03**	**0.3**		***Input***	**0.03**	**0.3**
1	Output	0.018	0.276	20	***Output***	< 0.003	< 0.003
2		0.021	0.284	300		< 0.003	< 0.003
3		0.026	0.293	600		< 0.003	< 0.003
4		0.027	0.295	900		< 0.003	< 0.003
6		0.028	0.296	1200		< 0.003	< 0.003
8		0.029	0.297	1500		< 0.003	< 0.003
12		0.028	0.992	1800		< 0.003	0.008
24		0.029		2100		< 0.003	0.016
48		0.018		2400		< 0.003	0.025
				2600		< 0.003	0.046

Note: National permissible standard: Cd < 0.003 ppm

Similar results were seen in removing Cd from water with coconut shell and castro activated carbon.

Table 3.19. Results in removing Cr with coconut shell and castro activated carbon

Tested V (L)	**Coconut shell AC**			***Tested V (L)***	**Castro AC**		
	Input	**0.5**	**5.0**		***Input***	**0.5**	**5.0**
1	Output	0.310	4.615	20	***Output***	< 0.05	< 0.05
2		0.355	4.745	300		< 0.05	< 0.05
3		0.440	4.890	600		< 0.05	< 0.05
4		0.455	4.930	900		< 0.05	< 0.05
6		0.475	4.950	1200		< 0.05	< 0.05
8		0.485	4.955	1500		< 0.05	< 0.05
12		0.480	4.965	1800		< 0.05	0.059
24		0.495		2100		< 0.05	0.062
48		0.500		2400		< 0.05	0.089
				2600		< 0.05	0.091

Note: National permissible standard: Cr < 0.05 ppm

Similar results were seen in removing Cr from water with coconut shell and castro activated carbon.

3.3.2. Experiment results of removing heavy metals in the field

Table 3.20. Experiment results of removing heavy metals in the field

HMs / **Wellwater**	**As**		**Pb**		**Cd**		**Cr**	
	(1)	**(2)**	(1)	**(2)**	(1)	**(2)**	(1)	**(2)**
1st well	0.40	<0.01	0.03	<0.01	0.12	<0.003	0.25	<0.003
2nd well	0.11	<0.01	0.42	<0.01	0.15	<0.003	0.82	<0.003
3rd well	0.45	<0.01	0.32	<0.01	0.12	<0.003	0.85	<0.003
4th well	0.13	<0.01	0.18	<0.01	0.10	<0.003	0.62	<0.003
QCVN 01:2009/BYT	**≤ 0,01**		**≤ 0,01**		**≤ 0,003**		**≤ 0,05**	
Effective Index	96,33		95,79		97,55		99,53	

(1): Before filtration; (2): After filtration

The concentration of HMs in all four experimented wells met the National permissible standard QCVN 01: 2009/MOH, the filtration efficiency ranged from 95-99%, highest in Cr and lowest in Pb, in order of Cr> Cd> As> Pb.

Chapter 4. DISCUSSION

4.1. The current state of heavy metal contamination in the environment in a coastal area Thuynguyen District, Haiphong

HM concentration in water samples

Table 3.1 shows that in surface water, the order of detected HM concentrations is Cr> As> Pb> Cd. This result is similar to the study of surface water samples near the coastal thermal power plant in Taiwan.[112] Similar to surface water sources, Cr and Cd were determined to have the highest and lowest values in well water sample (Table 3.2). However, in well water, the Pb content is higher than As. These results are consistent with the study done in Southeastern coastal India when reporting similar trends with Pb and Cd even though the Pb and Cd content in our study is much higher than in India [113]. The As concentration found in our study was higher than in Ha Nam, which was identified as a hot spot for As in groundwater in the North of Vietnam, with the As content ranging from 8-579 ppb (Mean 301 ppb). equivalent to 0.008-0.579 mg /l. average 0.301 mg /l [120].

The concentration of HMs in vegetable samples

Food consumption accounts for up to 80% to 90% of the daily doses of As, Cr, Cd. and Pb to which humans are exposed. Levels of Pb in mustard greens in this study were higher than in other studies. In general, the maximum concentration of HMs in vegetables detected in the order of Cd> Pb> As> Cr> Hg. Similarly high Cd concentrations were found in leafy vegetables sampled at Dabaoshan mine and at Bac Kan. [125],[51]. Other studies have found lower and higher Cd concentrations in vegetables compared to those found in our study. [123], [127], [128]

The concentration of HMs in seafood samples

Heavy metals, which have adverse effects on human health, can accumulate in fish and shrimp tissues. which are generally found in the last zone of the aquatic food chain. Metals are usually taken up from food and water in fish and shrimp, distributed by circulation and eventually accumulate in target organs [129],[130]. The lower concentration of Cr detected in shrimp in this study is similar to that observed in the research of Batvari et al who conducted a study in southeast coast of India; whereas the concentrations of Cd were higher than the concentrations of Pb in this study, the inverse was observed in studies of other coastal regions in Asia, India, Turkey, and Yemen.[117, 129, 137]. The trend of As levels being higher than Pb levels in fish tissues in our study is consistent with results reported from Bangladesh, which showed the mean concentration of As and Pb to be 1.59 and 1.13 mg/kg in summer and 1.81 and 1.45 mg/kg in winter, respectively.[139] The present study results, which found the order of heavy metal concentrations to be Cr > As > Pb > Cd, are different from the findings from Le Quang Dung et al. which reported the order of heavy metal concentration in oysters along the Hai Phong-Ha Long coast was As > Cd > Pb > Cr with concentrations of 10.10 to 19.33, 3.53 to 12.74, 0.79 to 6.20, and 0.81 to 4.47 mg/kg dry weight, respectively.[9]

4.2. The current disease pattern situation and human health risk related to heavy metal exposure

**Prevalence of disease symptoms in the study area*

The results in Table 3.5 show that the prevalence of symptoms/diseases among local people in the study area were in the following order: teeth-jaw-face (84.16%) > infectious (59.70%) > nervous system (49.01%) > digestion (48.22%) > motor system (42.77%)> circulation (41.49%) > dermatology (39.21%) > respiratory system (29.90%) > ENT (29.50%) > eyes (24.55%)> endocrine-metabolism (17.82%) > urinary (7.13%). The rate in men was statistically significantly higher than in women in most of the symptoms/diseases group except ENT and Dermatology ($p < 0.05$). The prevalence of gastrointestinal/digestive symptoms/diseases in the two communes in our study was 48.22%, higher than the study results of Ha Xuan Son (2005) (19.6%) and Dang Minh Ngoc and colleagues (2005) in some communes in Ha Nam and Hung Yen is 12.7%. [91, 145]

**Heavy metal concentrations in blood, urine samples among local people*

Exposure to heavy metals can be detected using biological samples (blood, urine, hair, nails, etc). Arsenic can accumulate in keratin-rich tissues such as skin, nails, hair, and in epithelial tissues and organs such as the oral mucosa, esophagus, stomach, and small intestine. Although gender may not effect the level of arsenic accumulation in the body, however, the arsenic levels increase with age or exposure duration [6]. The results in Table 3.6 show that the concentration of As, Pb in 20-38% of samples exceeded the permitted limits. There is no recommended limit of Cr among community residents or the general population at present. Cd was not detected in blood samples and Hg-urinary content was within the biological limit (1.32 ± 0.45 µg/l). In the present study, HM exposure was detected in 41.10% of the subjects (Table 3.7). This result was lower than the study from Tran Thi Khuyen (2012) but higher than findings from Ha Xuan Son in Thai Nguyen (2015). [90, 91]

***The relationship between the heavy metal contaminated environment and local human health**

The state of water, vegetables, fish, and seafood contaminated with HMs, which were released from industial activities such as mining, metallurgy, thermal power, shipbuilding and cement production. were studied in some studies in China, Taiwan, Korea and the United States. Regarding the relationship between the common morbidity rate and HM exposure, Table 3.8 shows that HM exposure increases the rate of urinary symptoms/diseases (18.96), circulatory (OR = 4.82), and digestive diseases (OR = 2.90) ($p < 0.05$).

***Human health risk related to heavy metal contaminated water and food consumption**

**Human health risk related to heavy metal contaminated water exposure*

51.53% and 64.86% of households may suffer from exposure to As and Pb contaminated water, respectively. Therefore, it is necessary to support and guide household members in implementing the strategies for removing HMs from water. (Table 3.9)

**Cancer risk estimation related to HM contaminated water consumption*

The results presented in tables 3.10-3.13 show that the cancer risk due to exposure of HM contaminated water in the study area may increase from 1.2 times to 1.5 times and 6.67-30.3 times after 5 years, 10 years, and throughout the whole lifetime exposure, respectively compared to the present. The risk correspond to the order As > Cr > Cd > Pb. Everyone has certain cancer risks. The cancer risk for tobacco smoke from secondhand smoking ranges from 10 x 10^{-5} with low exposure (not married to smoker) to 10 x 10^{-5} with high exposure (married to smoker). The cancer risk to carcinogens from indoor radon (average concentration Becquerel $50/m^3$), benzene in the exhaust gas in big cities (average concentration was from 80 $\mu g/m^3$ x 10^{-5} to 45 x 10^{-5}, respectively. [116, 147]

**Cancer risk estimation related to consuming heavy metal contaminated foods*

Cancer risk due to exposure to HM contaminated vegetables and seafood in this study was in the order As > Cr > Pb > Cd. (Table 3.14-3.15)

4.3. Results of removing HMs with castro activated carbon

4.3.1. HMs removal results in the laboratory

Clean water is a basic human need. Availability of clean drinking water is an important criterion for maintaining a healthy life. However, while the global demand for water increases each year. There are many types of potential pollution associated with water resources. Furthermore, climate change (rising temperature, changing water cycle) is also impacting this problem and has potential impacts such as increased flooding, drought, and intensification of toxic chemicals and pollution in the environment [148]. Vietnam is one of the developing countries affected by climate change. Therefore, it is greatly affected by the lack of clean water and water pollution caused by heavy metals. At present, no drug is effective for treating HM poisoning in people. Therefore, exposure prevention is one of the most effective strategies for for limiting exposure. Currently, in rural areas, slow filter tank technology is still commonly used, but it cannot remove arsenic. Technology is required to ensure efficient filtration of arsenic by a method that is inexpensive, easy to implement and has sufficient capacity to support the daily life and livestock breeding activities of households. From a review of the literature, we found that most of the arsenic removal methods are based on the principle of arsenic precipitation and adsorption on different materials. Each method has both advantages and disadvantages, filtration efficiency and cost depending on the type of material selected. A solution was studied and applied in order to overcome the above disadvantages. To that end, we propose a method and filter tank capable of effectively removing arsenic from domestic water by using activated carbon from castor plants. With the use of this activated carbon, the arsenic removal efficiency can be ten times higher than that of other conventional activated carbon. The cost of activated carbon from castor plants is cheap, and therefore suitable for the economic conditions of the people in rural areas. Depending on the starting material, the activated carbon has different absorption capacities for arsenic. In the research process, looking for a filter material capable of effectively removing arsenic that is cheap and suitable for conditions in rural areas, we have conducted many trials with many types of materials. Various types of activated carbon, including fossilized activated carbon, namely mineral coal (coal) and organic. inexpensive types of activated carbon such as activated carbon from agricultural by-products, agricultural processing products such as rice husks, coconut skulls, etc. The study results showed that the castor plant activated carbon/castor seed processing by-products demonstrated the ability to remove arsenic. Test results in table 3.16-3.19 show that, although coconut skull activated carbon is commonly used to filter water in the community, it is not able to remove heavy metals.

4.3.1. The experimental result of removing heavy metals in the field

The results in table 3.20 show that the slow filter tank combined with castor activated carbon was effective at removing HMs, and most effective are removing Cr after 18 months of experiments in the field. The filtration efficiency is maintained, the concentration of Cr in the filtered water is ensured according to hygienic standards after 18 months of testing. Thus, the slow filter tank model combined with castor activated carbon shows the following advantages: Easy to build, common materials and easy to buy; high flow rate (40L/h); easy to use. users who need water to cook or boil drinking water can get water directly from the tap of the filter tank; no electricity; the filtered water is colorless and odorless; moss in water can be eliminated; the price of the filter tank is much cheaper (=1/10); replaceable the filter material; all experimental households regularly use filter tanks, serving drinking water and daily life. Thus, the slow filtration tank model combines heavy metal castor activated carbon in well water with high flow rate, completely meeting the needs of people with normal income levels. Our research results are similar to the findings from other Vietnamese reseachers such as Nguyen Xuan Huan, Nguyen Khac Hai, Hà Xuân Sơn and Tran Thi Khuyen, Bui Huy Tung [81, 90, 91, 120, 149].

Some limitations of the study

To the best of our knowledge, this is the first study to measure heavy metal contamination in water, seafood, and vegetables collected from coastal communes in Northern Vietnam. However, the current data represented only a cross-sectional snapshot. There were only four filtration tanks using castro activated carbon in the field because of the limited resourses. However, effectiveness of removing HMs shown in both the laboratory and the field indicated that a similar solution should be considered and applied for other rural areas.

CONCLUSIONS

1. Current situation of heavy metal pollution in water and food in the coastal area of Thuy Nguyen district Hai Phong in 2017-2018

The high rate of samples with the concentration of HMs in water and food exceeding the permitted standards were detected:

- 90% water, shrimp and snail samples had Pb concentrations higher than the permitted standards
- 80% water and vegetable samples had higher concentrations of Cr than the permitted standards
- 70% water, vegetable and seafood samples had higher concentrations of Cd than the permitted standards
- 80% water samples and 38% vegetable samples had higher concentrations of As than the permitted standards

2. Current status of disease structure and health risks related to heavy metal exposure among local community in the study area

- The disease structure of the population in the study area includes diseases with a high rate (cardiovascula, tumor, gastroenterology ...) was consistent with the disease patterns from developed countries.
- The symptoms of poisoning are keratosis, skin pigmentation disorder, hair loss, vasomotor/sensory disturbances, body weakness. and nerves.
- The rate of people exposed to HM is 41.10%.
- The estimated cancer risk due to consumption of food contaminated with HMs in the population decreases gradually from As > Cr > Pb > Cd.

3. The results of removing heavy metal in water by castor plant activated carbon

- In the laboratory: Castor plant activated carbon helps to remove As. Pb. Cd and Cr in water efficiently at a volume of 1500l of water.
- Testing in the field: efficiency index of heavy metal filtration in well water is high from 95% -99%. highest with Cr at 99%.

RECOMMENDATIONS

1. Periodically identify the heavy metal concentrations in water sources and foodstuff (vegetables and aquatic products) in coastal areas.
2. Health exammination relating to HM exposure should be developed and implemented in coastal communities.
3. It is necessary to apply and replicate the castor activated carbon filtration tank model for similar rural areas.

LIST OF RELATED PUBLICATIONS

1. Nguyen Thi Minh Ngoc. Pham Van Han. Ho Anh Son. Nguyen Van Chuyen. *Evaluate the efficiency of arsenic removal from water with castor activated carbon*. The Journal of Vietnam Medicine. volume 484. September. 2019. pages 40-46.

2. Nguyen Thi Minh Ngoc. Nguyen Van Chuyen. Nguyen Thi Thu Thao. Nguyen Quang Duc. Nguyen Thi Thu Trang. Nguyen Thi Thanh Binh. Hoang Cao Sa. Nguyen Bao Tran. Nguyen Van Ba. Nguyen Van Khai. Ho Anh Son. Pham Van Han. Elizabeth V Wattenberg. Hiroyuki Nakamura and Pham Van Thuc. *Chromium. cadmium. lead and arsenic concentrations in water. vegetables and seafood consumed in a coastal area in Northern Vietnam.* Environmental Health Insights. Volume 14:1-9. 2020.

3. Nguyen Thi Minh Ngoc. Nguyen Van Chuyen. Ho Anh Son. Pham Van Han. *Heavy metal exposure and some health indicators among residents living in a coastal area of Haiphong city in 2017*. The Journal of Community Medicine. Volume 3 (56). May and June. 2020.