

Innovative Cleaning Technologies for Production of Drinking Water during Flooding Episodes (A-WATER)

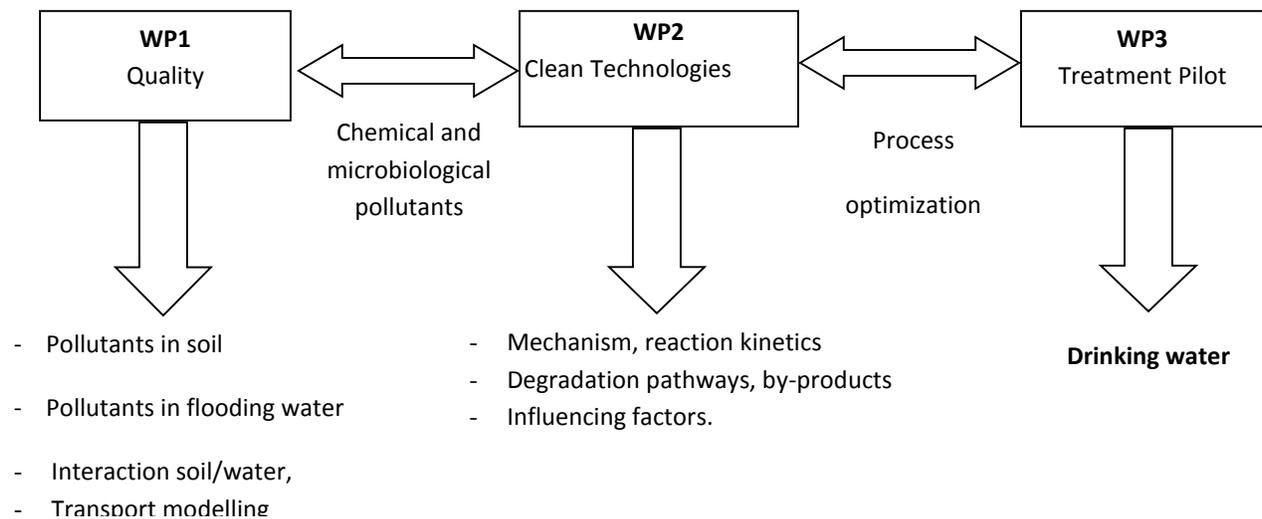
Introduction

Climate change (CC) is no longer a risk as its impact already exists; the effects of climate change can be seen every day. Storms, floods, droughts and uneven and highly variable production have become more and more frequent in Vietnam. During the flooding period, people's lives become very difficult, especially after the flood water has receded. A large area was contaminated by polluted flood water and in particular the lack of clean water for drinking and cooking is a huge problem. Many studies have shown that climate change induces freshwater pollution, and also it will increase salinity when sea levels rise. Hence, activities to improve protection of water resources, sustainable use of freshwaters including water re-use are very urgent. In addition to regulative measures to facilitate sustainable water use, research on adaptive technology, energy optimization in water treatment systems, water recycling and reuse of water are important aspects of future water handling and management.

In Vietnam, many areas still do not have regular water supply systems but obtain drinking water from common water well. In other cases communities do have water supply systems, but these systems are disabled or destroyed during flood disasters. Unfortunately, it takes long time to re-launch these systems after a flooding, and also has substantially costs. Hence, the current solution to temporarily produce water for drinking and cooking during a flooding disaster is to add alum for coagulation and precipitation of pollutants followed by disinfection by chloramines [1]. This is expensive, and the waters produced are not healthy and may contain pollutants even after treatment [1]. Thus, supply with freshwater during flood and post-flood periods are of special importance. In Vietnam, more than 80% of the population works in agriculture, comprising both crop and animal production as well as production in aquaculture. Use of fertilizers, insecticides, herbicides, and antibiotics are critical to production costs and to safeguard production yield; use of agrochemicals has been increasing over the last 20 years and it is still increasing. However, agrochemicals are also a major source of pollution to water resources. During periods of flash floods or inundation, flooding water brings nutrients and sediments to soils which in general can increase soil quality. Unfortunately, the flooding water causes dispersion of the contaminants present in soil, pesticides in plants, and antibiotics present in aquaculture ponds. The situation is aggravated as agrochemicals are often overdosed, and as soils and sediments still contain persistent pollutants such as dioxins originating from the war. In addition some soils have high natural contents of toxic trace elements, most seriously arsenic which is highly toxic to humans [2,3]. Pollutant release and spreading is highly variable depending on soil properties, pollutant chemical characteristics and loads, the hydrological regime and flow

pathways. Hence, there is a strong need to investigate how toxic soil pollutants are released and spread during flooding disasters.

The main objective of the project is to carry out research on water cleaning methods which can be used to treat polluted water rendering it available for human consumption. The research will be followed by method optimization and development of a pilot plant for water treatment. The pilot system will be applied to provide clean water for households during flooding disasters and to treat sewage water from agricultural production in order to reuse the water. The new water treatment technology should be robust, fast, and it should respond to many different types of pollutants present at variable concentrations. Also, the water treatment systems should be highly flexible, applicable at different scales, and be energy and cost efficient and producing low emissions. A second objective of the project is to obtain knowledge on flooding water quality, and in particular how the flooding water pick up contaminants from inundated soils and sediments. A third objective comprise the food safety aspects of the water treatment process.



Background

Task 1a: Flooded water quality

In order to obtain baseline data for water quality and composition of flooding water, as well as to get insight in contaminant transfer, different sampling methods was used. Monitoring was gone on for a period of 2 years (2012 and 2013), in two sites typical for the lowland, frequently inundated area. Two locations in the center of Vietnam, Thang Long (19° 35'24" N, 105° 38' 22" E) and Huong Toan (16° 30' 52" N, 107° 32' 12" E) in Thanh Hoa and Thua Thien Hue province, respectively (Fig. 1), were selected for this study.

Monitoring was conducted before, during, and after flood. Water samples were taken at 16 locations in canals, paddy fields and rivers before and during the flood. In total, 940 organic micro-pollutants in the water samples were determined simultaneously by GC-MS method with automatic identification and quantification system (AIQS), while ICP-MS was used for determination of ten trace elements in the samples. Some parameters as physico-chemical properties (temperature, pH, Dissolved Oxygen, salinity, turbidity, conductivity, redox potential) will be measured in the field. E. coli and total coli-form will be counted by fluorescence scanning method.



Fig. 1 Location of 17 sampling sites in Thanh Hoa [TR: Muc River; TL1, TL2, TL3, TL4, TL5 and TL6: canals surrounding the study field; TC1, TC2, TC3 and TC4: canals in the paddy field; T1, T2, T3, T4, T5, T6 and T7: paddy fields] and 16 sampling sites in Hue [HR1, HR2: Bo River; HC1, HC2, HC3, HC4, HC5, HC6, HC7: canals in the field; H1, H2, H3, H4, H5, H6, H7: paddy fields]

Task 1b: Experiments of Insecticide and element release from submerged soils

Intact soil columns collected from paddy fields in the Hue province in Vietnam was submerged with 100 mm artificial floodwater. Experiments were performed under aerobic and anaerobic conditions with and without addition of dissolved organic carbon (DOC). The intact soil columns were spiked with the insecticides fenobucarb, endosulfan and dichlorodiphenyltrichloroethane (DDT), and later flooded. After 24, 48 and 72 hours, the floodwater samples were collected to analyze release of elements and insecticides.



Fig 2. Experiment of release of elements and insecticides



Fig 3. Experiment of release of elements and insecticides in Glove box

Task 1c: Experiments of individual and simultaneous effect of concentrations of DOC, surfactant sodium dodecyl sulfate (SDS), and oxalate (Oxa) on desorption of pesticides from soil to water

Desorption of pesticides (fenobucarb, endosulfan and dichlorodiphenyltrichloroethane (DDT)) from soil to aqueous solution with the simultaneous presence of dissolved organic carbon (DOC), sodium dodecyl sulfate (SDS) and sodium oxalate (Oxa) was investigated in batch test by applying a full factorial design and the Box-Behnken response surface methodology (RSM). The statistical software Modde 8.0.2 (Umetric, Sweden) was used to create the experimental design, statistical analyses, and regression model. Response surface methodology (RSM) based on quadratic and cubic models with central composite circumscribed design (CCC) is composed of a full factorial design and star points. It has been used to study the simultaneous effects of independent variables (DOC (mg L^{-1}), SDS (CMC), and Oxa (M) in the solution) on response functions (pesticides were desorbed from soil into desorption solution). The three independent variables (DOC, SDS and Oxa) were coded with x_1 , x_2 and x_3 , respectively, the response functions (Y_1 , Y_2 and Y_3) are the concentrations of fenobucarb, endosulfan and DDT, respectively, in the desorption solution: $Y = \beta_0 + \beta_i \sum x_i + \beta_{ij} \sum x_i^2 + \beta \sum x_i x_j$. where β_0 is a constant; and β_i , β_{ii} , and β_{ij} are linear, quadratic, and interactive coefficients, respectively. Fourteen combinations along with 3 replicates of the central point were formed, corresponding to 17 experiments

Task 2: Water Treatment Technology – Advanced Oxidation Processes (AOPs)

Task 2a: Degradation of fenobucarb by electrolysis

The degradation of BPMC using an electrolysis unit at a laboratory scale. The degradation was mainly done by a direct oxidation and briefly by an indirect oxidation which consists in generating strong oxidants (radicals, peroxides...) that can degrade the insecticide. This part of the project was done in three steps: first, the optimization and study of the generation of disinfectants by the electrolysis unit, then the optimization of methods for BPMC analyses and finally, BPMC degradation studies using the electrolysis unit. The electrolysis unit consists of a reactor cell with a volume of 70 cm³, iridium oxide coated-titanium electrodes purchased from Adept Water Technologies (Denmark) and Tygon[®] E-3603 tubing for the inlet and the outlet of the system (Figure 5).

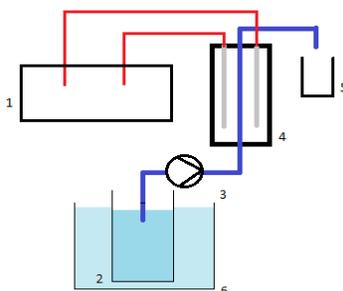


Fig 5: Schema of the electrolysis unit. 1. Adjustable DC power supply, 2. Reservoir (inlet), 3. Peristaltic pump, 4. Electrolysis cell with electrodes inside, 5. Samples (outlet), 6. Thermostatic water bath

Experiment of Direct oxidation: Different initial concentration of the BPMC in the reservoir was tested (5 mg/l, 10 mg/l). Tests were run at different currents (0.5 A, 1.0 A, 1.5 A, 2.0 A and 2.5 A) when it was possible and samples were collected at the outlet for HPLC analyses. Initial run was done at 0.0 A to check if any degradation or loss of the pesticide happened without the electrolysis process. Tests were also run at a fixed current to study the degradation ratio of the BPMC in the time by connecting the outlet to the inlet reservoir (cycle). Samples were collected at different moment at the outlet (from 0 to 240 min). The influence of the flow rate was also studied by varying it at 50 ml/min, 100 ml/min and 200 ml/min. After being collected, samples were used to measure the pH and to be analyzed by HPLC (see HPLC optimization).

Experiment of indirect oxidation: The electrolyte was a solution with NaCl ($[Cl^-] = 50 \text{ mg/l}$) in 1L of MilliQ water. Since NaCl is already a salt, other neutral salts are not needed. Parameters for the electrolysis was a flow rate of 5 mg/l a current of 1.5 A. The initial concentration of BPMC was 5 mg/l.

Task 2b: Studies on the electrochemical disinfection of water containing microbial pollution

To determine the inactivation of spores by the electrochemical unit, immediately and after storage. Concentration of active chlorine produced by electrolysis and the time needed to inactivate 100% of *Bacillus cereus* spores .

Collect samples in the tank over time: 0, 10, 20, 30 min, 1hour. Samples were withdrawn from the reactors and quenched of residual disinfectant by the addition of an equal volume of 1%, wt./vol sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). Sample size volume: 100ml to determine viability of spores, 10ml sample to analyze active chlorine, 20ml sample to measure pH, EC, temperature, 3 ml sample to analyze Cl^- , ClO_3^- .

Task 2c: Studies on the electrochemical disinfection of water containing *Cryptosporidium*

To determine the current and the time needed to inactivate 3log of freshly *Cryptosporidium* oocysts in calf faeces when the sample run through the the electrolysis unit (A-cell). Electrolyte is Chlorine (50mg/L) in deionize water: Experiments were performed at $24,5^\circ\text{C}$ with a sodium

chloride at a target concentration of 50 mg/liter Cl^- in 0.01 M phosphate-buffered water, pH 7.1 (EW). Samples were withdrawn from the reactors at 0, 60, 120, 240 minutes and quenched of residual disinfectant by the addition of an equal volume of 1%, wt./vol, sodium thiosulfate

Task 3: Building water treatment pilot and application

Based on the data collected during mainly Task 1, 2, the process studies and optimization parameters, a modularized water treatment pilot plant was build. The pilot involve three main modules: coagulation/flocculation, mineralization reactor and disinfection module. The mineralization reactor was constructed based on ozonation, photo-Fenton, electro-Fenton or a combination of these processes, which is the heart of the pilot plant. This modular reactor is responsible for degradation of organic compounds as well as disinfection. Other pilot operation parameters such as water flows, energy, stirring, etc. was tested. the quality of the produced water ensure. The pilot plant should be able to produce 1000 liter per 24 hours. After optimization in the laboratory and tested with real samples, all component will be built as a mobile system and transportable.

Result

Screening of inorganic and organic contaminants in floodwater in paddy fields of Hue and Thanh Hoa in Vietnam

Flood water quality database: the concentrations of 277 organic micro-pollutants and ten elements (As, Cu, Cd, Cr, Co, Pb, Zn, Fe, Mn, Al) ranged from 0.01 to 7.6 $\mu\text{g L}^{-1}$ and 0.1 to 3170 $\mu\text{g L}^{-1}$, respectively, in the floodwater. Contaminants originated from industrial sources (e.g. PAH) were detected at low concentrations, ranged from 0.01 to 0.18 $\mu\text{g L}^{-1}$, while concentrations of pollutants originated from domestic sources (e.g. sterols, pharmaceuticals and personal care products and pesticides) were ranged from 0.01 to 2.12 $\mu\text{g L}^{-1}$. The results indicated that contaminants in floodwater come from untreated wastewater from villages, and the agricultural activities are the major sources of increased pesticides resuspended in the floodwater.

Pesticide and element release from a paddy soil in central Vietnam: Role of DOC and oxidation state during flooding

Insecticide release into floodwater depends on their initial concentration in the soil and was enhanced by the presence of DOC under aerobic conditions more than under anaerobic conditions. Release of Al, Cu, Ni and Pb increased in the presence of DOC in floodwater under aerobic conditions. Meanwhile As, Co, Fe, Mn, Sb and Zn release only increased under anaerobic conditions with highest release without DOC added. Several elements and all three insecticides studied show increased release to floodwater in response to DOC and reducible elements respond to the anaerobic conditions in the soil source.

Simultaneous effect of dissolved organic carbon, surfactant, and organic acid on the desorption of pesticides investigated by response surface methodology

The individual effects and interaction of DOC, SDS, and Oxa were evaluated through quadratic regression equations. When the aqueous solution includes 50 mg L⁻¹ DOC, 3.75 CMC SDS, and 0.1 M Oxa, the maximum desorption concentrations of fenobucarb, endosulfan, and DDT were 96, 80, and 75 µg L⁻¹, respectively. The lowest concentration of SDS, DOC, and Oxa caused the minimum desorption. This point at conditions of concern for flooding water is high content of organic compounds causing potentially high contamination by desorption, and the remarkably lower desorption at organic matter-free conditions. The suspended organic matter is one of the common characteristics of flooding and irrigation water in rice fields, and surfactants from pollution increase the problem with desorption of legacy pesticides in the rice fields. The quadratic regression equations of response functions for fenobucarb (Eq. 6), endosulfan (Eq. 7), and DDT (Eq. 8) with the R² values for fenobucarb, endosulfan, and DDT were 0.990, 0.976, and 0.984, respectively.

$$[\text{fenobucarb}] = -27.92 + 1.42[\text{DOC}] + 7.51[\text{SDS}] + 693[\text{Oxa}] + 0.008[\text{DOC}]^2 + 2.45[\text{SDS}]^2 + 2809[\text{Oxa}]^2 - 0.35[\text{DOC}] * [\text{SDS}] - 9.81[\text{DOC}] * [\text{Oxa}] - 33.49[\text{SDS}] * [\text{Oxa}] \quad (6)$$

$$[\text{endosulfan}] = -50.54 + 1.04[\text{DOC}] + 38.75[\text{SDS}] + 81.75[\text{Oxa}] - 3.85[\text{SDS}]^2 + 3925[\text{Oxa}]^2 - 0.17[\text{DOC}] * [\text{SDS}] - 4.65[\text{DOC}] * [\text{Oxa}] - 1.47[\text{SDS}] * [\text{Oxa}] \quad (7)$$

$$[\text{DDT}] = -51.35 + 0.93[\text{DOC}] + 38.09[\text{SDS}] + 324[\text{Oxa}] - 0.004[\text{DOC}]^2 - 4.45[\text{SDS}]^2 - 0.092[\text{DOC}] * [\text{SDS}] - 1.19[\text{DOC}] * [\text{Oxa}] \quad (8)$$

Subjected to $25 \leq [\text{DOC}] \leq 75$ (mg L⁻¹), $1 \leq [\text{SDS}] \leq 5$ CMC, $0.001 \leq [\text{Oxa}] \leq 0.1$ M

The flooded water clean equipment

The flood water treatment pilot was built to produce 1000 L clean water/24 hours. It was built as a mobile and transportable system. An assessment on the validity of the method, technical parameters and economic factors were used for construction the prototype. The built pilot plan was applied for on-site drinking water production during flooding periods and for treatment of effluents from agricultural or aqua cultural activities. The water-cleaning pilot was tested in the field (fish pond, and flooded location)

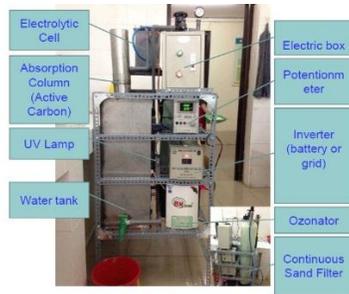


Figure 6: Equipment in Water-clean-Unit (a)



Figure 7: Water clean- Unit from Denmark (b)



Fig. 8 Testing clean water unit in Trung Van lake



Fig 9: Taking samples from water treatment pilot system

Two systems were tested in the field, water samples after treatment were taken and analyzed to determine the effectiveness of the systems by comparing the parameters of water after treatment with the parameters of standard clean water. The results of the analysis of the parameters are given in the table below:

Table 1: Analytic results of water samples from Trung Van lake

No	Parameters	Unit	Analytical results		QCVN 01:2009/ BYT
			Before treatment	After treatment	
1	pH	-	7,66	7.65	6,5– 8,5
2	TDS	mg/l	450	50	1000
3	Turbidity	NTU	18,1	0,45	2
4	Ammonium (NH ₄ ⁺)	mg/l	0,95	0,86	3
5	Nitrite (NO ₂ ⁻)	mg/l	0,50	<0,01	3
6	Nitrate (NO ₃ ⁻)	mg/l	0,22	0,17	50
7	Overall stiffness	mgCaCO ₃ /l	110	50	300
8	Cl ⁻ (Clorua)	mg/l	13,6	10	250
9	Permanganate	mg/l	5,2	1	2
10	Iron (Fe)	mg/l	0,71	<0,001	0,3
11	Mangan (Mn)	mg/l	0,152	<0,001	0,3

12	Arsenic (As)	mg/l	0,002	<0,001	0,01
13	Total Coliform	1 CFU/100ml	1500	0	0
14	Fecal E.coli	1 CFU/100ml	300	0	0
15	Aldrin + Dieldrin	µg/l	< 0.001	< 0.001	0,03
16	Endrin	µg/l	< 0.001	< 0.001	
17	BHC	µg/l	< 0.001	< 0.001	1
18	DDT	µg/l	0.001	0.001	2
19	1,2 - Dibromo - 3 Cloropropan	µg/l	< 0.001	< 0.001	1
20	Lindan	µg/l	0.001	0.001	2
21	Chlordane	µg/l	0.001	0.001	0.2
22	Heptachlor	µg/l	< 0.001	< 0.001	0.03
23	Atrazine	µg/l	< 0.001	< 0.001	2

Table 8.3: Analytic results of floodwater sample from Ha Tinh

No	parameters	Unit	Results		QCVN 01:2009/ BYT
			Before treatment	After treatment	
1	pH	-	7,66	7.65	6,5– 8,5
2	TDS	mg/l	1500	50	1000
3	Turbidity	NTU	40	0,45	2
4	Ammonium (NH ₄ ⁺)	mg/l	0,75	0,56	3
5	Nitrite (NO ₂ ⁻)	mg/l	0,43	<0,01	3
6	Nitrate (NO ₃ ⁻)	mg/l	0,26	0,13	50
7	Overall stiffness	mgCaCO ₃ /l	150	50	300
8	Cl ⁻ (Clorua)	mg/l	11,6	9	250
9	Permanganate	mg/l	4,6	1	2
10	Iron (Fe)	mg/l	0,51	<0,001	0,3
11	Mangan (Mn)	mg/l	0,16	<0,001	0,3
12	Arsenic (As)	mg/l	0,001	<0,001	0,01
13	Total Coliform	1 CFU/100ml	100	0	0

14	Fecal E.coli	1 CFU/100ml	100	0	0
15	Aldrin + Dieldrin	µg/l	< 0.001	< 0.001	
16	Endrin	µg/l	< 0.001	< 0.001	1
17	BHC	µg/l	0.001	0.001	2
18	DDT	µg/l	< 0.001	< 0.001	1
19	1,2 - Dibromo - 3 Cloropropan	µg/l	0.001	0.001	2
20	Lindan	µg/l	0.001	0.001	0.2
21	Chlordane	µg/l	< 0.001	< 0.001	0.03
22	Heptachlor	µg/l	< 0.001	< 0.001	2
23	Atrazine	µg/l	< 0.001	< 0.001	2

Water quality: Based on the results of the above analysis, the water after using pilot water treatment system has reached the standards of drinking water quality according to Vietnamese standard QCVN 01: 2009 / BYT issued given by the Ministry of Health in 2009.

Research capacity building

Capacity building

The cooperation between Vietnamese and Danish scientists increased the knowledge level of each partner, where Vietnamese scientists have experienced a lift with respect to environmental and analytical chemistry, and Danish scientists got new insight into pollutant chemistry and dynamics of subtropical/tropical areas and the application of AOP to flood water cleaning. Working together and exchanging know-how on a common research topic has helped Vietnamese researchers integrate into the global scientific community.

Equipment enhancement

New materials, equipment and instruments in this project were used to reinforce the fundamental performance and to apply the research performed by the institute. The instruments were known to be part of the infrastructure necessary for the development of the Institute of Technology adaptation to climate change.

Some material, equipment and new instruments for this project have reinforced the capacity to perform fundamental and applied research by the Institute. These instruments are seen as part of the necessary infrastructure for development of the research unit on the adaptation technologies for climate change

Education

Through the project, there were 3 master's students and 3 PhD students involved in the project activities, receiving support from the project both in terms of data and funding. Three Vietnamese PhD students were educated following the "sandwich" approach with joint Vietnamese-Danish supervisors through scientific topics of the project. Each PhD student spent 9 months in Denmark. Three PhD. Student, and three MSc. students (one Danish, two Vietnamese) finished their projects in Vietnam in related projects.

The project has given participants of the project opportunities to attend and present scientific reports at international conferences and seminars (more than five presentations given). Through field surveys and field research, research staff and local communities exchanged scientific knowledge and experience with each other. Through researchers, local authorities have improved practical skills and scientific knowledge.

Published results

The obtained results were presented at seminars, scientific workshops, conferences, and in specialized scientific reports. Three articles have been published, and one manuscript has been submitted in international journals.

Recommendations

The development and application of the water treatment system to explore the ability of equipment in new projects is also an important strategy. The advanced version not only could be used for flood water but also for polluted water, and be able to provide a clean water source for polluted areas. The project of developing a polluted river water treatment system in Hanoi is one of the next topics in our plan.

The success of the project and owning advanced technology has contributed the development of the environmental industry in Vietnam. The obtained results contributed to the development of policies responding to climate change and disaster prevention.

Based on the success of this project, we would continue our new research projects into developing the water treatment system for polluted river water in Hanoi (based on the fact that the pollution of rivers in Hanoi has always been a very hot issue to local people and Vietnamese government).