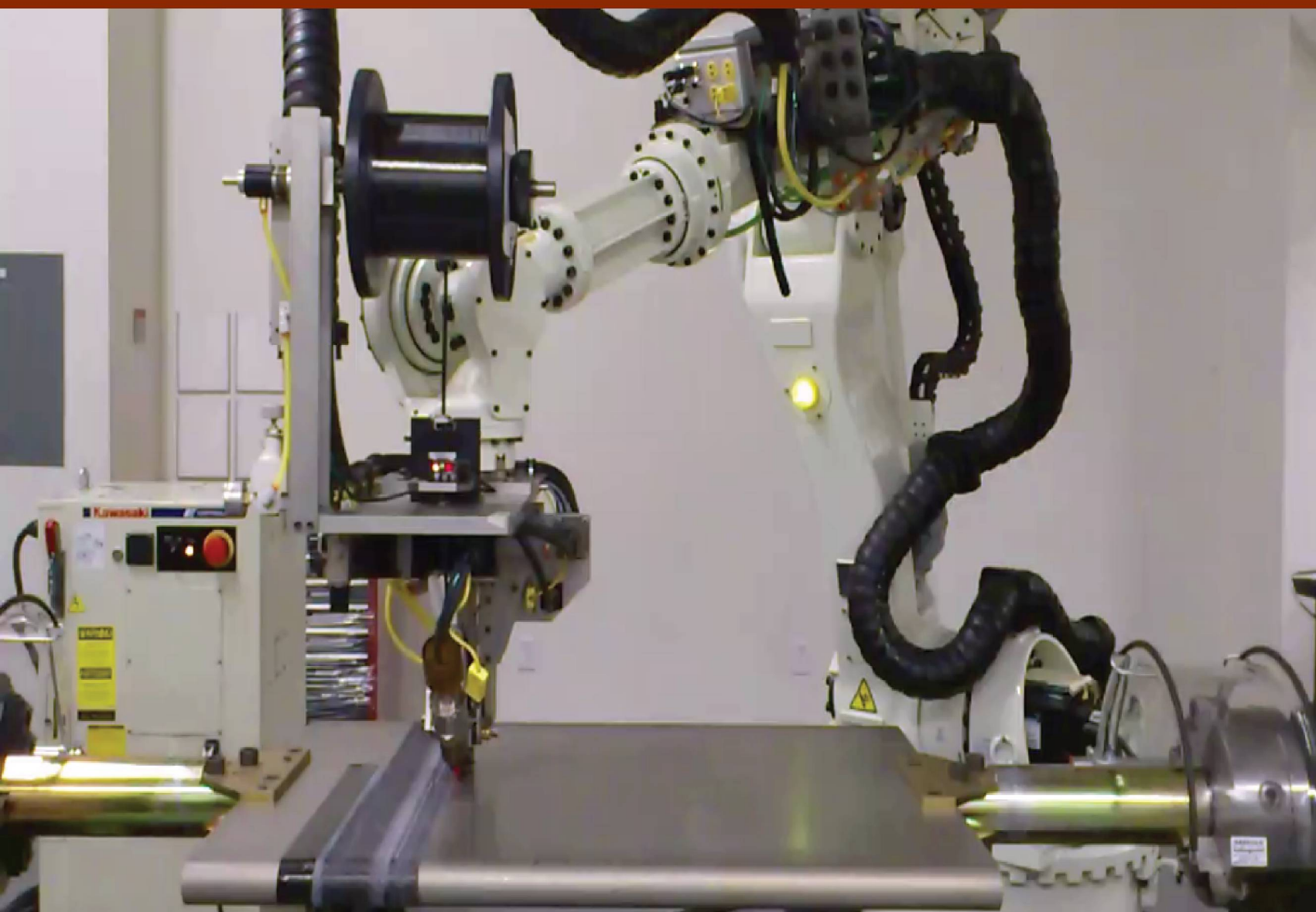


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Automated manufacturing of composites

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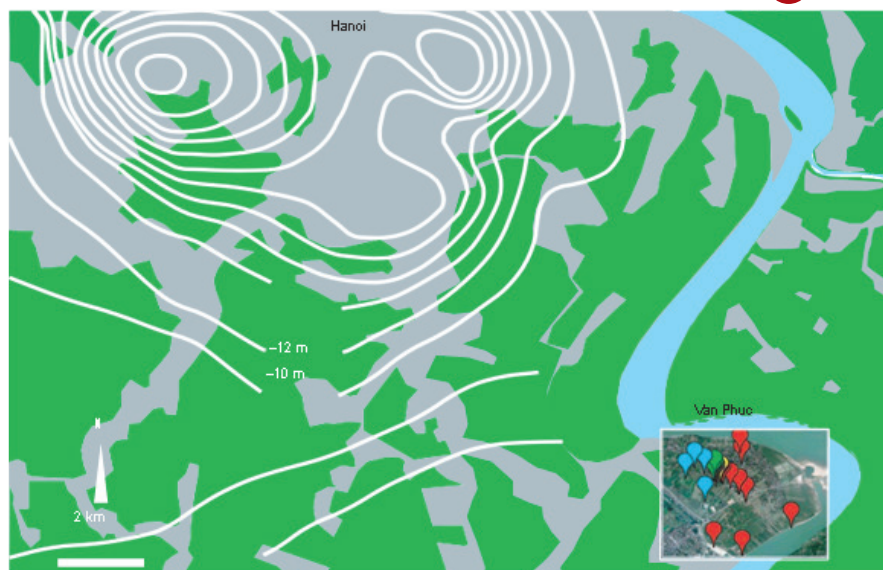
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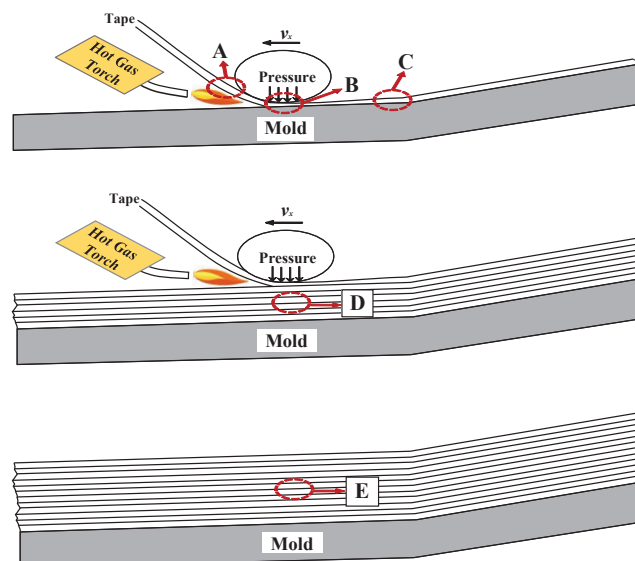
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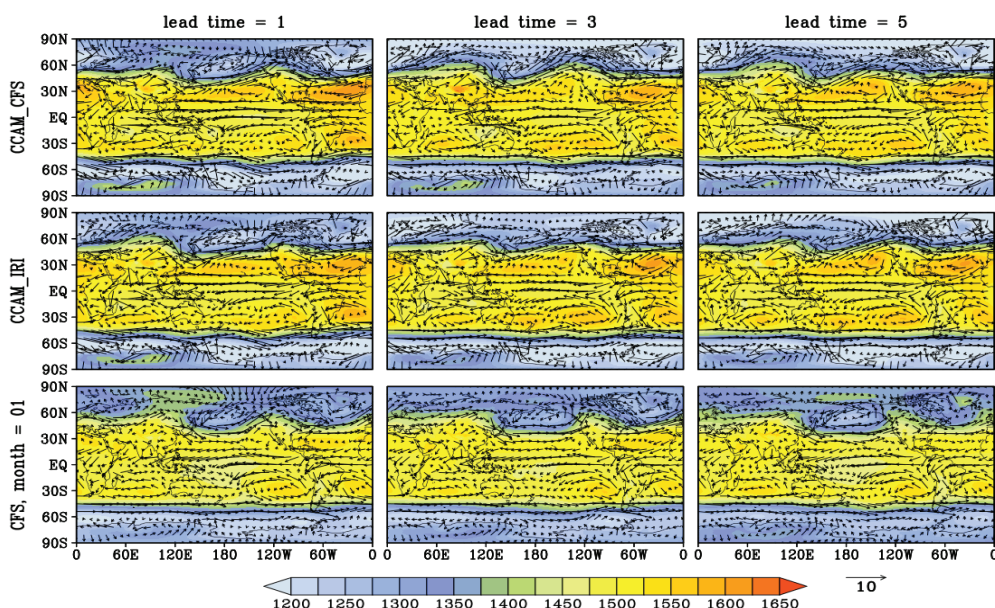
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On the determination of the Singer transfer

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Abstract:

Let P_k be the graded polynomial algebra $\mathbb{F}_2[x_1, x_2, \dots, x_k]$ with the degree of each generator x_i being 1, where $\mathbb{F}_2$ denote the prime field of two elements, and let GL_k be the general linear group over $\mathbb{F}_2$ which acts regularly on P_k .

We study the algebraic transfer constructed by Singer [1] using the technique of the Peterson hit problem. This transfer is a homomorphism from the homology of the mod-2 Steenrod algebra $\mathcal{A}$, $\text{Tor}_{k,k+d}^{\mathcal{A}}(\mathbb{F}_2, \mathbb{F}_2)$, to the subspace of $\mathbb{F}_2 \otimes_{\mathcal{A}} P_k$ consisting of all the GL_k -invariant classes of degree d .

In this paper, by using the results on the Peterson hit problem we present the proof of the fact that the Singer algebraic transfer is an isomorphism for $k \leq 3$. This result has been proved by Singer in [1] for $k \leq 2$ and by Boardman in [2] for $k = 3$. We show that the fourth Singer transfer is also an isomorphism in certain internal degrees. This result is new and it is different from the ones of Bruner, Ha and Hung [3], Chon and Ha [4], Ha [5], Hung and Quynh [6], Nam [7].

Keywords: algebraic transfer, polynomial algebra, steenrod algebra.

Classification number: 1.1

1. Introduction

Denote by $P_k := \mathbb{F}_2[x_1, x_2, \dots, x_k]$ the polynomial algebra over the field of two elements, $\mathbb{F}_2$, in k generators $x_1, x_2, \dots, x_k$, each of degree 1. This algebra arises as the cohomology with coefficients in $\mathbb{F}_2$ of an elementary abelian 2-group of rank k . Therefore, P_k is a module over the mod-2 Steenrod algebra, $\mathcal{A}$. The action of $\mathcal{A}$ on P_n is determined by the elementary properties of the Steenrod squares Sq^i and subject to the Cartan formula $Sq^k(fg) = \sum_{i=0}^k Sq^i(f)Sq^{k-i}(g)$, for $f, g \in P_k$ [8].

The *Peterson hit problem* is to find a minimal generating set for P_k regarded as a module over the mod-2 Steenrod algebra. Equivalently, this problem is to find a vector space basis for $QP_k := \mathbb{F}_2 \otimes_{\mathcal{A}} P_k$ in each degree d . Such a basis may be represented by a list of monomials of degree d . It is completely determined for $k \leq 4$, unknown in general.

Let GL_k be the general linear group over the field $\mathbb{F}_2$. This group acts naturally on P_k by matrix substitution. Since the two actions of $\mathcal{A}$ and GL_k upon P_k commute with each other, there is an inherited action of GL_k on QP_k .

Denote by $(P_k)_d$ the subspace of P_k consisting of all the homogeneous polynomials of degree d in P_k and by $(QP_k)_d$ the subspace of QP_k consisting of all the classes represented by the elements in $(P_k)_d$. In [1], Singer defined the algebraic transfer, which is a homomorphism

$$\varphi_k : \text{Tor}_{k,k+d}^{\mathcal{A}}(\mathbb{F}_2, \mathbb{F}_2) \longrightarrow (QP_k)_d^{GL_k}$$

from the homology of the Steenrod algebra to the subspace of $(QP_k)_d$ consisting of all the GL_k -invariant classes. It is a useful tool in describing the homology groups of the Steenrod algebra, $\text{Tor}_{k,k+d}^{\mathcal{A}}(\mathbb{F}_2, \mathbb{F}_2)$. This transfer was studied by Boardman [2], Bruner, Ha and Hung [3], Ha [5], Hung [9], Chon and Ha [4, 10, 11], Minami [12], Nam [7], Hung and Quynh [6], the present author [13] and others.

Singer showed in [1] that φ_k is an isomorphism for $k = 1, 2$. Boardman showed in [2] that φ_3 is also an isomorphism. However, for any $k \geq 4$, φ_k is not a monomorphism in infinitely many degrees (see Singer [1], Bruner, Ha and Hung [3], Hung [9]). Singer made a conjecture in [1] that *the algebraic transfer φ_k is an epimorphism for any $k \geq 0$* . This conjecture is true for $k \leq 3$. It can be verified for $k = 4$ by using the results in [14, 15]. The conjecture for $k \geq 5$ is an open problem.

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In this paper, by using the results on the Peterson hit problem we present the proof of the fact that the Singer algebraic transfer is an isomorphism for $k \leq 3$. Recall that this result has been proved by Singer in [1] for $k \leq 2$ and by Boardman in [2] for $k = 3$. To prove this result, Boardman [2] computed the space $QP_3^{GL_3}$ by using a basis consisting of the all the classes represented by certain polynomials in P_3 . We also compute this space, however we use the admissible monomial basis for QP_3 that is different from the one of Boardman in [2]. By applying this technique for $k = 4$, we show that the fourth Singer transfer is also an isomorphism in certain internal degrees. This result is new and it is different from the ones of Bruner, Ha and Hung [3], Chon and Ha [4], Ha [5], Hung and Quynh [6], Nam [7]. In those works it is shown only that the fourth Singer transfer detects certain families of elements in $\text{Ext}_{\mathcal{A}}^{4,*}(\mathbb{F}_2, \mathbb{F}_2)$, and fails to detect others.

This paper is organized as follows. In Section 2, we recall some needed information on the lambda algebra and the Singer algebraic transfer. In Sections 3, we present the determination of the algebraic transfer for $k \leq 3$. Finally, in Section 4, we show that the fourth Singer transfer is an isomorphism in certain internal degrees.

2. The Singer algebraic transfer and the lambda algebra

First of all, we briefly recall the definition of the Singer transfer. Let $\hat{P}_1$ be the submodule of $\mathbb{F}_2[x_1, x_1^{-1}]$ spanned by all powers x_1^i with $i \geq -1$. The usual $\mathcal{A}$ -action on $P_1 = \mathbb{F}_2[x_1]$ is canonically extended to an $\mathcal{A}$ -action on $\mathbb{F}_2[x_1, x_1^{-1}]$ (see Singer [1]). $\hat{P}_1$ is an $\mathcal{A}$ -submodule of $\mathbb{F}_2[x_1, x_1^{-1}]$. The inclusion $P_1 \subset \hat{P}_1$ gives rise to a short exact sequence of $\mathcal{A}$ -modules:

$$0 \longrightarrow P_1 \longrightarrow \hat{P}_1 \longrightarrow \Sigma^{-1}\mathbb{F}_2 \longrightarrow 0.$$

Let e_1 be the corresponding element in $\text{Ext}_{\mathcal{A}}^1(\Sigma^{-1}\mathbb{F}_2, P_1)$. By using the cross and Yoneda products, Singer set

$$e_k = (e_1 \times P_{k-1}) \circ (e_1 \times P_{k-2}) \circ \dots \circ (e_1 \times P_1) \circ e_1 \in \text{Ext}_{\mathcal{A}}^k(\Sigma^{-k}\mathbb{F}_2, P_k).$$

Then, he defined $\hat{\varphi}_k : \text{Tor}_k^{\mathcal{A}}(\mathbb{F}_2, \Sigma^{-k}\mathbb{F}_2) \longrightarrow \text{Tor}_0^{\mathcal{A}}(\mathbb{F}_2, P_k) = QP_k$ by $\hat{\varphi}_k(z) = e_k \cap z$. Its image is a submodule of $(QP_k)^{GL_k}$. So, $\hat{\varphi}_k$ induces the homomorphism

$$\varphi_k : \text{Tor}_k^{\mathcal{A}}(\mathbb{F}_2, \Sigma^{-k}\mathbb{F}_2) \longrightarrow QP_k^{GL_k}.$$

Denote by $(P_k)^*$ the dual of P_k and by $P((P_k)^*)$ the primitive subspace consisting of all elements in $(P_k)^*$ that are annihilated by every positive degree operations in the mod-2 Steenrod algebra. The dual of φ_k :

$$Tr_k := (\varphi_k)^* : \mathbb{F}_2 \otimes_{GL_k} P((P_k)_d^*) \longrightarrow \text{Ext}_{\mathcal{A}}^{k,k+d}(\mathbb{F}_2, \mathbb{F}_2)$$

is also called the k -th Singer transfer.

The algebra $\text{Ext}_{\mathcal{A}}^{*,*}(\mathbb{F}_2, \mathbb{F}_2)$ is described in terms of the mod-2 lambda algebra Λ (see [16]). Recall that Λ is a bigraded differential algebra over $\mathbb{F}_2$ generated by $\lambda_j \in \Lambda^{1,j}, j \geq 0$, with the relations

$$\lambda_j \lambda_{2j+1+m} = \sum_{\nu \geq 0} \binom{m-\nu-1}{\nu} \lambda_{j+m-\nu} \lambda_{2j+1+\nu}, \quad (2.1)$$

for $m \geq 0$ and the differential

$$\delta(\lambda_i) = \sum_{\nu \geq 0} \binom{i-\nu-1}{\nu+1} \lambda_{i-\nu-1} \lambda_{\nu}, \quad (2.2)$$

for $i > 0$, $\delta(\lambda_0) = 0$ and that $H^{k,d}(\Lambda, \delta) = \text{Ext}_{\mathcal{A}}^{k,k+d}(\mathbb{F}_2, \mathbb{F}_2)$.

For example, the elements $\lambda_{2^i-1} \in \Lambda^{1,2^i-1}$, $i \geq 0$, and $\bar{d}_0 = \lambda_6 \lambda_2 \lambda_3^2 + \lambda_4^2 \lambda_3^2 + \lambda_2 \lambda_4 \lambda_5 \lambda_3 + \lambda_1 \lambda_5 \lambda_1 \lambda_7 \in \Lambda^{4,14}$ are the cycles in the lambda algebra Λ . So, $h_i = [\lambda_{2^i-1}]$ and $d_0 = [\bar{d}_0]$ are the elements in $\text{Ext}_{\mathcal{A}}^{*,*}(\mathbb{F}_2, \mathbb{F}_2)$. Note that h_i is the Adams element in $\text{Ext}_{\mathcal{A}}^{1,2^i}(\mathbb{F}_2, \mathbb{F}_2)$.

There is a homomorphism $\widetilde{Sq}^0 : \Lambda \rightarrow \Lambda$ determined by

$$\widetilde{Sq}^0(\lambda_{j_1} \lambda_{j_2} \dots \lambda_{j_k}) = \lambda_{2j_1+1} \lambda_{2j_2+1} \dots \lambda_{2j_k+1}, \quad k \geq 0.$$

This homomorphism respects the relations in ((2.1)) and commutes the differential in ((2.2)). Therefore, it induces a homomorphism

$$Sq^0 : \text{Ext}_{\mathcal{A}}^{k,k+d}(\mathbb{F}_2, \mathbb{F}_2) = H^{k,d}(\Lambda) \longrightarrow H^{k,k+2d}(\Lambda) = \text{Ext}_{\mathcal{A}}^{k,2k+2d}(\mathbb{F}_2, \mathbb{F}_2).$$

A family $\{a_i : i \geq 0\}$ of elements in $\text{Ext}_{\mathcal{A}}^{k,k+*}(\mathbb{F}_2, \mathbb{F}_2)$ is called a Sq^0 -family if $a_i = (Sq^0)^i(a_0)$ for every $i \geq 0$. It is well known that $\text{Ext}_{\mathcal{A}}^{3,3+*}(\mathbb{F}_2, \mathbb{F}_2)$ contains the Sq^0 -family of indecomposable elements $\{c_i\}$ and $\text{Ext}_{\mathcal{A}}^{4,4+*}(\mathbb{F}_2, \mathbb{F}_2)$

contains seven Sq^0 -families of indecomposable elements, namely $\{d_i\}, \{e_i\}, \{f_i\}, \{g_{i+1}\}, \{p_i\}, \{D_3(i)\}$, and $\{p'_i\}$. Note that $\{h_i\}$ is also a Sq^0 -family in $\text{Ext}_{\mathcal{A}}^{1,1+*}(\mathbb{F}_2, \mathbb{F}_2)$.

The algebra $\{\text{Ext}_{\mathcal{A}}^{k,k+*}(\mathbb{F}_2, \mathbb{F}_2) | k \geq 0\}$ has been explicitly computed by Adem [17] for $k = 1$, by Adams [18] and Wall [19] for $k = 2$, by Adams [18] and Wang [20] for $k = 3$ and by Lin [21] for $k = 4$.

Theorem 2.1 (see 17-21)

i) The algebra $\{\text{Ext}_{\mathcal{A}}^{k,k+*}(\mathbb{F}_2, \mathbb{F}_2) | k \geq 0\}$ for $k \leq 3$ is generated by h_i and c_i for $i \geq 0$ and subject only to the relations $h_i h_{i+1} = 0, h_i h_{i+2}^2 = 0$ and $h_i^3 = h_{i-1}^2 h_{i+1}$. In particular, $\{c_i : i \geq 0\}$ is an $\mathbb{F}_2$ -basis for the indecomposable elements in $\text{Ext}_{\mathcal{A}}^{3,3+*}(\mathbb{F}_2, \mathbb{F}_2)$.

ii) The algebra $\{\text{Ext}_{\mathcal{A}}^{k,k+*}(\mathbb{F}_2, \mathbb{F}_2) | k \geq 0\}$ for $k \leq 4$ is generated by $h_i, c_i, d_i, e_i, f_i, g_{i+1}, p_i, D_3(i)$ and p'_i for $i \geq 0$ and subject to the relations in i) together with the relations $h_i^2 h_{i+3}^2 = 0, h_j c_i = 0$ for $j = i - 1, i, i + 2$ and $i + 3$. Furthermore, the set of the elements $d_i, e_i, f_i, g_{i+1}, p_i, D_3(i)$ and p'_i , for $i \geq 0$, is an $\mathbb{F}_2$ -basis for the indecomposable elements in $\text{Ext}_{\mathcal{A}}^{4,4+*}(\mathbb{F}_2, \mathbb{F}_2)$.

It is well known that the dual of P_k is the divided power algebra generated by $a_1, a_2, \dots, a_k$:

$$(P_k)^* = \Gamma(a_1, a_2, \dots, a_k)$$

where $a_j^{(i)}$ is dual to $x_j^i \in P_k$ with respect to the basis of P_k consisting of all monomials in $x_1, x_2, \dots, x_k$ and $a_j = a_j^{(1)}$. The graded vector space $\{(P_k)^* | k \geq 0\}$ is an algebra with a multiplication defined by

$$(a_1^{(i_1)} \dots a_k^{(i_k)})(a_1^{(i_{k+1})} \dots a_m^{(i_{k+m})}) = a_1^{(i_1)} \dots a_k^{(i_k)} a_{k+1}^{(i_{k+1})} \dots a_{k+m}^{(i_{k+m})} \in (P_{k+m})^*,$$

for any $a_1^{(i_1)} \dots a_k^{(i_k)} \in (P_k)^*$ and $a_1^{(i_{k+1})} \dots a_m^{(i_{k+m})} \in (P_m)^*$. In [10], Chon and Ha defined a homomorphism of algebras

$$\phi = \{\phi_k | k \geq 0\} : \{(P_k)^* | k \geq 0\} \longrightarrow \{\Lambda^{k,*} | k \geq 0\} = \Lambda,$$

which induces the Singer transfer. Here, the homomorphism $\phi_k : (P_k)^* \rightarrow \Lambda^{k,*}$ is defined by the following inductive formula:

$$\phi_k(a^{(I,t)}) = \begin{cases} \lambda_t, & \text{if } k - 1 = \ell(I) = 0, \\ \sum_{i \geq t} \phi_{k-1}(Sq^{i-t} a^I) \lambda_i, & \text{if } k - 1 = \ell(I) > 0, \end{cases}$$

for any $a^{(I,t)} = a_1^{(i_1)} a_2^{(i_2)} \dots a_{k-1}^{(i_{k-1})} a_k^{(t)} \in (P_k)^*$ and $I = (i_1, i_2, \dots, i_{k-1})$.

Theorem 2.2 (see Chon and Ha [10]) If $b \in P((P_k)^*)$, then $\phi_k(b)$ is a cycle in the lambda algebra Λ and $Tr_k([b]) = [\phi_k(b)]$.

Note that this theorem is a dual version of the one in Hung [22].

We end this section by recalling some results on Kameko's homomorphism and the generators of the general linear group GL_k .

One of the main tools in the study of the hit problem is Kameko's homomorphism $\widetilde{Sq}_*^0 : QP_k \rightarrow QP_k$. This homomorphism is induced by the $\mathbb{F}_2$ -linear map $\psi : P_k \rightarrow P_k$, given by

$$\psi(x) = \begin{cases} y, & \text{if } x = x_1 x_2 \dots x_k y^2, \\ 0, & \text{otherwise,} \end{cases}$$

for any monomial $x \in P_k$. Note that ψ is not an $\mathcal{A}$ -homomorphism. However, $\psi Sq^{2t} = Sq^t \psi$, and $\psi Sq^{2t+1} = 0$ for any non-negative integer t .

For a positive integer n , by $\mu(n)$ one means the smallest number r for which it is possible to write $n = \sum_{1 \leq i \leq r} (2^{u_i} - 1)$, where $u_i > 0$.

Theorem 2.3 (Kameko [23]) Let m be a positive integer. If $\mu(2m+k) = k$, then $(\widetilde{Sq}_*^0)_m : (QP_k)_{2m+k} \rightarrow (QP_k)_m$ is an isomorphism of the GL_k -modules.

Definition 2.4 Let f, g be two polynomials of the same degree in P_k . Then, $f \equiv g$ if and only if $f - g \in \mathcal{A}^+ P_k$. If $f \equiv 0$, then f is called hit.

For $1 \leq i \leq k$, define the $\mathcal{A}$ -homomorphism $\rho_i : P_k \rightarrow P_k$, which is determined by $\rho_i(x_i) = x_{i+1}, \rho_i(x_{i+1}) = x_i, \rho_i(x_j) = x_j$ for $j \neq i, i + 1, 1 \leq i < k$, and $\rho_k(x_1) = x_1 + x_2, \rho_k(x_j) = x_j$ for $j > 1$.

It is easy to see that the general linear group GL_k is generated by the matrices associated with $\rho_i, 1 \leq i \leq k$, and the symmetric group Σ_k is generated by the ones associated with $\rho_i, 1 \leq i < k$. So, a class $[f]$ represented by a homogeneous polynomial $f \in P_k$ is an GL_k -invariant if and only if $\rho_i(f) \equiv f$ for $1 \leq i \leq k$. It is an Σ_k -invariant if and only if $\rho_i(f) \equiv f$ for $1 \leq i < k$.

3. Determination of Tr_k for $k \leq 3$

3.1. Determination of Tr_k for $k \leq 2$

In this subsection, we present the proof of the following.

Theorem 3.1.1 (Singer [1]) *The algebraic transfer Tr_k is an isomorphism for $k \leq 2$.*

It is well-known that

$$(QP_1)_n^{GL_1} = (QP_1)_n = \begin{cases} \langle [x^{2^u-1}] \rangle, & \text{if } n = 2^u - 1, u \geq 0, \\ 0, & \text{otherwise.} \end{cases}$$

According to Theorem 2.1, we have

$$\text{Ext}_{\mathcal{A}}^{1,t+1}(\mathbb{F}_2, \mathbb{F}_2) = \begin{cases} \langle h_u \rangle, & \text{if } t = 2^u - 1, u \geq 0, \\ 0, & \text{otherwise.} \end{cases}$$

Since $(P_1)^* = \Gamma(a)$ and $a^{(2^u-1)} \in P((P_1)^*)$, $\phi_1(a^{(2^u-1)}) = \lambda_{2^u-1}$ is a cycle in $\Lambda^{1,*}$. Using Theorem 2.2, we get $\text{Tr}_1([a^{(2^u-1)}]) = [\phi_1(a^{(2^u-1)})] = [\lambda_{2^u-1}] = h_u$, $\forall u \geq 0$. So, Tr_1 is an isomorphism.

Now, we present the proof of this theorem for $k = 2$ by computing the space $(QP_2)^{GL_2}$. From a result of Wood [24], we need only to compute this space in the degree $n = 2^{s+t} + 2^s - 2$ with s, t non-negative integers.

First, we consider the degree $n = 2^{s+1} - 2$ with $s \geq 0$. Since the iterated Kameko homomorphism $(\widetilde{Sq}_*)^s : (QP_2)_n \rightarrow (QP_2)_0$ is an isomorphism of GL_2 -modules and $(QP_2)_0^{GL_2} = \langle 1 \rangle$, hence $(QP_2)_n^{GL_2} = \langle [p_{2,s}] \rangle$ with $p_{2,s} := (x_1 x_2)^{2^s-1}$.

Next, we compute $(QP_2)_n^{GL_2}$ with $n = 2^{s+1} + 2^s - 2$, $s \geq 0$. Since the iterated Kameko homomorphism $(\widetilde{Sq}_*)^s : (QP_2)_n \rightarrow (QP_2)_1$ is an isomorphism of GL_2 -modules, we need only to compute $(QP_2)_1^{GL_2}$.

According to Peterson [25], $(QP_2)_n$ is the vector space of dimension 2 with a basis consisting of 2 classes represented by the following monomials:

$$v_{s,1} = x_1^{2^s-1} x_2^{2^{s+1}-1}, v_{s,2} = x_1^{2^{s+1}-1} x_2^{2^s-1}.$$

In particular, $v_{0,1} = x_2$, $v_{0,2} = x_1$. Suppose $\theta = a_1 v_1 + a_2 v_2 = a_1 x_2 + a_2 x_1 \in (QP_2)_1^{GL_2}$ with $a_1, a_2 \in \mathbb{F}_2$. Then $\rho_1(\theta) = a_1 v_2 + a_2 v_1 \equiv \theta$. So, we get $a_1 = a_2$. Since $\rho_2(\theta) \equiv a_1 v_1 + a_2(v_1 + v_2) \equiv \theta$, we obtain $a_1 = a_2 = 0$. Hence, $(QP_2)_1^{GL_2} = 0$ and $(QP_2)_n^{GL_2} = 0$.

Now, we consider the degree $n = 2^{s+t} + 2^s - 2$ with s, t non-negative integers, $t \geq 2$. Since $(\widetilde{Sq}_*)^s : (QP_2)_n \rightarrow (QP_2)_{2^t-1}$ is an isomorphism of GL_2 -modules, we need only to compute $(QP_2)_{2^t-1}^{GL_2}$. According to Peterson [25], $(QP_2)_{2^t-1}$ is the vector space of dimension 3 with a basis consisting of 3 classes represented by the following monomials:

$$u_{t,1} = x_1^{2^t-1}, u_{t,2} = x_2^{2^t-1}, u_{t,3} = x_1 x_2^{2^t-2}.$$

Suppose $\theta_t = a_1 u_{t,1} + a_2 u_{t,2} + a_3 u_{t,3}$ with $a_1, a_2, a_3 \in \mathbb{F}_2$ and $[\theta_t] \in (QP_2)_{2^t-1}^{GL_2}$. By a simple computation, we have $\rho_1(\theta_t) = a_1 u_{t,2} + a_2 u_{t,1} + a_3 u_{t,3} \equiv \theta_t$, hence $a_1 = a_2 = a$. Then, $\rho_2(\theta_t) \equiv a(u_{t,1} + u_{t,2}) + a u_{t,2} + a_3(u_{t,2} + u_{t,3}) \equiv \theta_t$. So, we get $a_3 = a$. Hence, $\theta_t = a p_{2,0,t}$ with $p_{2,0,t} = u_{t,1} + u_{t,2} + u_{t,3}$ and

$$(QP_2)_n^{GL_2} = \langle [\psi^s(p_{2,0,t})] \rangle.$$

Combining the above results, we obtain

Proposition 3.1.2 *Let n be a non-negative integer. We have*

$$(QP_2)_n^{GL_2} = \begin{cases} \langle [p_{2,s}] \rangle, & \text{if } n = 2^{s+1} - 2, s \geq 0 \\ \langle [p_{2,s,t}] \rangle, & \text{if } n = 2^{s+t} + 2^s - 2, s \geq 0, t \geq 2, \\ 0, & \text{otherwise,} \end{cases}$$

where $p_{2,s,t} = \psi^s(p_{2,0,t})$.

Recall that $(P_2)^* = \Gamma(a_1, a_2)$. For any $s, t \geq 0$, we set

$$q_{2,s,t} := a_1^{(2^s-1)} a_2^{(2^{s+t}-1)} \in P((P_2)_{2^{s+t}+2^s-2}^*).$$

Since $\langle q_{2,s,0}, p_{2,s} \rangle = 1$ and $\langle q_{2,s,t}, p_{2,s,t} \rangle = 1$ for every $s \geq 0, t \geq 2$, from Proposition 3.1.2, we get the following.

Proposition 3.1.3 For n a non-negative integer, we obtain

$$\mathbb{F}_2 \otimes_{GL_2} P((P_2)_n^*) = \begin{cases} \langle [q_{2,s,0}] \rangle, & \text{if } n = 2^{s+1} - 2, s \geq 0 \\ \langle [q_{2,s,t}] \rangle, & \text{if } n = 2^{s+t} + 2^s - 2, s \geq 0, t \geq 2, \\ 0, & \text{otherwise.} \end{cases}$$

It is easy to see that $\phi_2(q_{2,s,t}) = \lambda_{2^s-1} \lambda_{2^{s+t}-1}$ is a cycle in $\Lambda^{2,*}$. Applying Theorem 2.2, we get

$$Tr_2([q_{2,s,t}]) = [\phi_2(q_{2,s,t})] = [\lambda_{2^s-1} \lambda_{2^{s+t}-1}] = h_s h_{s+t}.$$

Since $h_s h_{s+1} = 0$, applying Theorem 2.1, we have

$$\text{Ext}_{\mathcal{A}}^{2,m}(\mathbb{F}_2, \mathbb{F}_2) = \begin{cases} \langle h_s^2 \rangle, & \text{if } m = 2^{s+1}, \text{ with } s \geq 0, \\ \langle h_s h_{s+t} \rangle, & \text{if } m = 2^{s+t} + 2^s, \text{ with } s \geq 0, t \geq 2, \\ 0, & \text{otherwise.} \end{cases}$$

Theorem 3.1.1 is completely proved.

3.2. Determination of Tr_3

In this subsection, we present the proof of the following.

Theorem 3.2.1 (Boardman [2]) *The third Singer algebraic transfer*

$$Tr_3 : \mathbb{F}_2 \otimes_{GL_3} P((P_3)^*) \longrightarrow \text{Ext}_{\mathcal{A}}^{3,*+3}(\mathbb{F}_2, \mathbb{F}_2)$$

is an isomorphism.

To prove this theorem, Boardman [2] computed the space $QP_3^{GL_3}$ by using a basis consisting of the all the classes represented by certain polynomials in P_3 . It is difficult to use his method for $k = 4$, where there are 315 polynomials instead of 21. We also compute this space, however we use the admissible monomial basis for QP_3 that is different from the one of Boardman in [2]. Our approach can be apply for $k = 4$ by using the admissible monomial basis for QP_4 which is given in [14, 15].

From a result of Wood [24], we need only to compute $QP_3^{GL_3}$ in the degree n with $\mu(n) \leq 3$.

3.2.1. The case $n = 2^{t+1} - 2$

According to Kameko [23], $(QP_3)_n$ is a vector space with a basis consisting of all the classes represented by the following monomials:

$$\begin{aligned} v_{t,1} &= x_2^{2^t-1} x_3^{2^t-1}, \quad v_{t,2} = x_1^{2^t-1} x_3^{2^t-1}, \quad v_{t,3} = x_1^{2^t-1} x_2^{2^t-1}, \quad \text{for } t \geq 1, \\ v_{t,4} &= x_1 x_2^{2^t-2} x_3^{2^t-1}, \quad v_{t,5} = x_1 x_2^{2^t-1} x_3^{2^t-2}, \quad v_{t,6} = x_1^{2^t-1} x_2 x_3^{2^t-2}, \quad \text{for } t \geq 2, \\ v_{t,7} &= x_1^3 x_2^{2^t-3} x_3^{2^t-2}, \quad \text{for } t \geq 3 \end{aligned}$$

Set $p_{3,t} = \sum_{i=1}^7 v_{t,i}$, with $t \geq 3$. By a direct computation, we have

Proposition 3.2.2 For any non-negative integer t , we have

$$(QP_3)_{2^{t+1}-2}^{GL_3} = \begin{cases} \langle 1 \rangle, & \text{if } t = 0, \\ 0, & \text{if } t = 1, 2, \\ \langle [p_{3,t}] \rangle, & \text{if } t \geq 3. \end{cases}$$

Recall that $(P_3)^* = \Gamma(a_1, a_2, a_3)$. We set

$$q_{3,t} = a_1^{(0)} a_2^{(2^t-1)} a_3^{(2^t-1)} \in P((P_3)_{2^{t+1}-2}^*).$$

Since $\langle p_{3,t}, q_{3,t} \rangle = 1$, we get

$$\mathbb{F}_2 \otimes_{GL_3} P((P_3)_{2^{t+1}-2}^*) = \begin{cases} \langle [1] \rangle, & \text{if } t = 0 \\ 0, & \text{if } t = 1, 2, \\ \langle [q_{3,t}] \rangle, & \text{if } t \geq 3. \end{cases}$$

It is easy to see that $\phi_3(q_{3,t}) = \lambda_0 \lambda_{2^t-1}^2$ is a cycle in $\Lambda^{3,*}$. By Theorem 2.2, we have

$$Tr_3([q_{3,t}]) = [\phi_3(q_{3,t})] = [\lambda_0 \lambda_{2^t-1}^2] = h_0 h_t^2.$$

According to Theorem 2.1, we have

$$\text{Ext}_{\mathcal{A}}^{3,2^{t+1}+1}(\mathbb{F}_2, \mathbb{F}_2) = \langle h_0 h_t^2 \rangle.$$

Since $h_0 h_1 = 0$ and $h_0 h_2^2 = 0$, from the above equalities we see that Theorem 3.2.1 is true in this case.

3.2.2. The case $n = 2^{t+u} + 2^u - 3$

If $u > 1$ then $\mu(n) = 3$, hence the iterated Kameko homomorphism

$$(\widetilde{Sq}_*^0)^{u-1} : (QP_3)_{2^{t+u}+2^u-3} \rightarrow (QP_3)_{2^{t+1}-1}$$

is also an isomorphism GL_3 -modules. Hence, we need only to compute $(QP_3)_{2^{t+1}-1}^{GL_3}$. According to Kameko [23], $(QP_3)_n$ is a vector space with a basis consisting of all the classes represented by the following monomials:

$$\begin{aligned} u_{t,1} &= x_3^{2^{t+1}-1}, \quad u_{t,2} = x_2^{2^{t+1}-1}, \quad u_{t,3} = x_1^{2^{t+1}-1}, \quad \text{for } t \geq 0, \\ u_{t,4} &= x_2 x_3^{2^{t+1}-2}, \quad u_{t,5} = x_1 x_3^{2^{t+1}-2}, \quad u_{t,6} = x_1 x_2^{2^{t+1}-2}, \quad \text{for } t \geq 1, \\ u_{1,7} &= x_1 x_2 x_3, \quad \text{for } t = 1, \\ u_{t,7} &= x_1 x_2^2 x_3^{2^{t+1}-4}, \quad u_{t,8} = x_1 x_2^{2^t-1} x_3^{2^t-1}, \\ u_{t,9} &= x_1^{2^t-1} x_2 x_3^{2^t-1}, \quad u_{t,10} = x_1^{2^t-1} x_2^{2^t-1} x_3, \quad \text{for } t \geq 2, \\ u_{t,11} &= x_1^3 x_2^{2^t-3} x_3^{2^t-1}, \quad u_{t,12} = x_1^3 x_2^{2^t-1} x_3^{2^t-3}, \quad u_{t,13} = x_1^{2^t-1} x_2^3 x_3^{2^t-3}, \quad \text{for } t \geq 3, \\ u_{t,14} &= x_1^7 x_2^{2^t-5} x_3^{2^t-3}, \quad \text{for } t \geq 4. \end{aligned}$$

Set $p_{3,t,1} = \sum_{i=1}^7 u_{t,i}$ for $t \geq 1$ and $\bar{p}_{3,t,1} = \sum_{j=7}^{14} u_{t,j}$ for $t \geq 4$. By a direct computation we have

Proposition 3.2.3 For any integers $t \geq 0$, $u > 0$, we have

$$(QP_3)_{2^{t+u}+2^u-3}^{GL_3} = \begin{cases} 0, & \text{if } t = 0, \\ \langle [p_{3,t,u}] \rangle, & \text{if } 1 \leq t \leq 3, \\ \langle [p_{3,t,u}], [\bar{p}_{3,t,u}] \rangle, & \text{if } t \geq 4, \end{cases}$$

where $p_{3,t,u} = \psi^{u-1}(p_{3,t,1})$, $\bar{p}_{3,t,u} = \psi^{u-1}(\bar{p}_{3,t,1})$.

We set

$$q_{3,t,u} = a_1^{(2^{u-1}-1)} a_2^{(2^{u-1}-1)} a_3^{(2^{t+u}-1)}, \quad \bar{q}_{3,t,u} = a_1^{(2^u-1)} a_2^{(2^{t+u-1}-1)} a_3^{(2^{t+u-1}-1)}.$$

It is easy to see that $q_{3,t,u}, \bar{q}_{3,t,u} \in P((P_3)_{2^{t+1}-2}^*)$ and

$$\begin{aligned} \langle p_{3,t,u}, q_{3,t,u} \rangle &= 1, \quad \langle p_{3,t,u}, \bar{q}_{3,t,u} \rangle = 0, \\ \langle \bar{p}_{3,t,u}, q_{3,t,u} \rangle &= 0, \quad \langle \bar{p}_{3,t,u}, \bar{q}_{3,t,u} \rangle = 1. \end{aligned}$$

So, we get

$$\mathbb{F}_2 \otimes_{GL_3} P((P_3)_{2^{t+u}+2^u-3}^*) = \begin{cases} 0, & \text{if } t = 0, \\ \langle [q_{3,t,u}] \rangle, & \text{if } 1 \leq t \leq 3, \\ \langle [q_{3,t,u}], [\bar{q}_{3,t,u}] \rangle, & \text{if } t \geq 4. \end{cases}$$

By applying Theorem 2.2, we have

$$\phi_3(q_{3,t,u}) = \lambda_{2^{u-1}-1}^2 \lambda_{2^{t+u}-1},$$

$$\phi_3(\bar{q}_{3,t,u}) = \lambda_{2^u-1}^2 \lambda_{2^{t+u-1}-1}^2$$

are the cycles in $\Lambda^{3,*}$. So, we obtain

$$\text{Tr}_3([q_{3,t,u}]) = [\phi_3(q_{3,t,u})] = [\lambda_{2^{u-1}-1}^2 \lambda_{2^{t+u}-1}] = h_{u-1}^2 h_{t+u},$$

$$\text{Tr}_3([\bar{q}_{3,t,u}]) = [\phi_3(\bar{q}_{3,t,u})] = [\lambda_{2^u-1}^2 \lambda_{2^{t+u-1}-1}^2] = h_u h_{t+u-1}^2.$$

According to Theorem 2.1, we have

$$\text{Ext}_{\mathcal{A}}^{3,2^{t+u}+2^u}(\mathbb{F}_2, \mathbb{F}_2) = \langle h_u h_{t+u-1}^2, h_{u-1}^2 h_{t+u} \rangle.$$

If $t = 0$ then $h_u h_{u-1}^2 = h_u^2 h_{u-1} = 0$. If $t = 1$ then $h_u h_{t+u-1}^2 = h_u^3 = h_{u-1}^2 h_{u+1} = h_{u-1}^2 h_{t+u}$. If $t = 2$ then $h_u h_{t+u-1}^2 = h_u h_{u+1}^2 = 0$. If $t = 3$ then $h_u h_{t+u-1}^2 = h_u h_{u+2}^2 = 0$. Hence, from the above equalities we can easily see that Theorem 3.2.1 is true in this case.

3.2.3. The case $n = 2^{s+u+1} + 2^{u+1} + 2^u - 3$

If $u > 0$ then $\mu(n) = 3$, hence the iterated Kameko homomorphism

$$(\widetilde{Sq}_*^0)^u : (QP_3)_{2^{s+u}+2^u-3} \rightarrow (QP_3)_{2^{s+1}}$$

is also an isomorphism of GL_3 -modules. Hence, we need only to compute $(QP_3)_{2^{s+1}}^{GL_3}$.

According to Kameko [23], $(QP_3)_{2^{s+1}}$ is a vector space with a basis consisting of all the classes represented by the following monomials:

$$\begin{aligned} v_{s,1} &= x_2 x_3^{2^{s+1}-1}, \quad v_{s,2} = x_2^{2^{s+1}-1} x_3, \quad v_{s,3} = x_1 x_3^{2^{s+1}-1}, \\ v_{s,4} &= x_1 x_2^{2^{s+1}-1}, \quad v_{s,5} = x_1^{2^{s+1}-1} x_3, \quad v_{s,6} = x_1^{2^{s+1}-1} x_2, \quad \text{for } s \geq 1, \\ v_{1,7} &= x_1 x_2 x_3^2, \quad v_{1,8} = x_1 x_2^2 x_3, \quad \text{for } s = 1, \\ v_{s,7} &= x_2^3 x_3^{2^{s+1}-3}, \quad v_{s,8} = x_1^3 x_3^{2^{s+1}-3}, \quad v_{s,9} = x_1^3 x_2^{2^{s+1}-3}, \\ v_{s,10} &= x_1 x_2 x_3^{2^{s+1}-2}, \quad v_{s,11} = x_1 x_2^{2^{s+1}-2} x_3, \quad v_{s,12} = x_1 x_2^2 x_3^{2^{s+1}-3}, \\ v_{s,13} &= x_1 x_2^3 x_3^{2^{s+1}-4}, \quad v_{s,14} = x_1^3 x_2 x_3^{2^{s+1}-4} \quad \text{for } s \geq 2 \\ v_{15} &= x_1^3 x_2^4 x_3, \quad \text{for } s = 2. \end{aligned}$$

Set $\bar{p}_0 = v_{2,10} + v_{2,11} + v_{2,14} + v_{2,15}$. By a direct computation, we have

Proposition 3.2.4 For any integers $s > 0, u \geq 0$ and $n = 2^{s+u+1} + 2^{u+1} + 2^u - 3$, we have

$$(QP_3)_n^{GL_3} = \begin{cases} \langle [\psi^u(\bar{p}_0)] \rangle, & \text{if } s = 2, \\ 0, & \text{if } s \neq 2. \end{cases}$$

We set

$$\begin{aligned} \bar{c}_u &= a_1^{(3 \cdot 2^u - 1)} a_2^{(4 \cdot 2^u - 1)} a_3^{(4 \cdot 2^u - 1)} + a_1^{(2 \cdot 2^u - 1)} a_2^{(5 \cdot 2^u - 1)} a_3^{(4 \cdot 2^u - 1)} \\ &\quad + a_1^{(2 \cdot 2^u - 1)} a_2^{(3 \cdot 2^u - 1)} a_3^{(6 \cdot 2^u - 1)} + a_1^{(2 \cdot 2^u - 1)} a_2^{(2 \cdot 2^u - 1)} a_3^{(7 \cdot 2^u - 1)} \end{aligned}$$

is an element in $(P_3)^* = \Gamma(a_1, a_2, a_3)$. By a direct computation, we can see that $\bar{c}_u \in P((P_3)_{2^{t+u}+2^u-3}^*)$ and $\langle \psi^u(\bar{p}_0), \bar{c}_u \rangle = 1$. So, we get

$$\mathbb{F}_2 \otimes_{GL_3} P((P_3)_n^*) = \begin{cases} \langle [\bar{c}_u] \rangle, & \text{if } s = 2, \\ 0, & \text{if } s \neq 2. \end{cases}$$

For $u = 0$, we have $\bar{c}_0 = a_1^{(2)} a_2^{(3)} a_3^{(3)} + a_1^{(1)} a_2^{(4)} a_3^{(3)} + a_1^{(1)} a_2^{(2)} a_3^{(5)} + a_1^{(1)} a_2^{(1)} a_3^{(6)}$.

A direct computation shows

$$\begin{aligned} \phi_3(a_1^{(2)} a_2^{(3)} a_3^{(3)}) &= \lambda_2 \lambda_3^2 + \lambda_1 \lambda_4 \lambda_3 + \lambda_1 \lambda_3 \lambda_4, \\ \phi_3(a_1^{(1)} a_2^{(4)} a_3^{(3)}) &= \lambda_1 \lambda_4 \lambda_3 + \lambda_1 \lambda_3 \lambda_4 + \lambda_1 \lambda_2 \lambda_5, \\ \phi_3(a_1^{(1)} a_2^{(2)} a_3^{(5)}) &= \lambda_1 \lambda_2 \lambda_5 + \lambda_1^2 \lambda_6, \\ \phi_3(a_1^{(1)} a_2^{(1)} a_3^{(6)}) &= \lambda_1^2 \lambda_6. \end{aligned}$$

Hence, we obtain $\phi_3(\bar{c}_0) = \lambda_2 \lambda_3^2$. By Theorem 2.2, we have $Tr_3([\bar{c}_0]) = [\lambda_2 \lambda_3^2] = c_0$.

Since $[\bar{c}_u] = (\widetilde{Sq}_*^0)^u([\bar{c}_0])$, we get

$$Tr_3([\bar{c}_u]) = Tr_3((\widetilde{Sq}^0)^u([\bar{c}_0])) = (Sq^0)^u Tr_3([\bar{c}_0]) = (Sq^0)^u(c_0) = c_u.$$

By Theorem 2.1, we have $h_u h_{u+1} = 0$. Hence,

$$\text{Ext}_{\mathcal{A}}^{3, 2^{s+u+1}+2^{u+1}+2^u}(\mathbb{F}_2, \mathbb{F}_2) = \begin{cases} \langle h_u h_{u+1} h_{u+3}, c_u \rangle = \langle c_u \rangle, & \text{if } s = 2, \\ \langle h_u h_{u+1} h_{s+u+1} \rangle = 0, & \text{if } s \neq 2. \end{cases}$$

Theorem 3.2.1 in this case follows from the above equalities.

3.2.4. The case of the generic degree

In this subsection, we consider the degree

$$n = 2^{s+t+u} + 2^{t+u} + 2^u - 3,$$

with s, t, u non-negative integers.

The subcases either $s = 0$ or $t = 0$ have been determined in Subsections 3.2.1 and 3.2.2. The case $s > 0$ and $t = 1$ has been determined in Subsection 3.2.3. So, we assume that $s > 0$ and $t > 1$.

The iterated homomorphism

$$(\widetilde{Sq}^0)^u : (QP_3)_{2^{s+t+u}+2^{t+u}+2^u-3} \rightarrow (QP_3)_{2^{s+t}+2^t-2}$$

is an isomorphism of GL_3 -modules. So, we need only to compute $(QP_3)_{2^{s+t}+2^t-2}^{GL_3}$.

The subcase $s = 1$. Then $n = 2^{t+1} + 2^t - 2$. According to Kameko [23], $(QP_3)_n$ is the vector space with a basis consisting of all the classes represented by the following monomials:

$$\begin{aligned} v_{t,1} &= x_2^{2^t-1} x_3^{2^{t+1}-1} & v_{t,2} &= x_2^{2^{t+1}-1} x_3^{2^t-1} & v_{t,3} &= x_1^{2^t-1} x_3^{2^{t+1}-1} \\ v_{t,4} &= x_1^{2^t-1} x_2^{2^{t+1}-1} & v_{t,5} &= x_1^{2^{t+1}-1} x_3^{2^t-1} & v_{t,6} &= x_1^{2^{t+1}-1} x_2^{2^t-1} \\ v_{t,7} &= x_1 x_2^{2^t-2} x_3^{2^{t+1}-1} & v_{t,8} &= x_1 x_2^{2^{t+1}-1} x_3^{2^t-2} & v_{t,9} &= x_1^{2^{t+1}-1} x_2 x_3^{2^t-2} \\ v_{t,10} &= x_1 x_2^{2^t-1} x_3^{2^{t+1}-2} & v_{t,11} &= x_1 x_2^{2^{t+1}-2} x_3^{2^t-1} & v_{t,12} &= x_1^{2^t-1} x_2 x_3^{2^{t+1}-2} \\ v_{t,13} &= x_1^3 x_2^{2^{t+1}-3} x_3^{2^t-2}, \\ v_{t,14} &= x_1^3 x_2^3 x_3^4 \text{ for } t = 2, \text{ and } v_{t,14} = x_1^3 x_2^{2^t-3} x_3^{2^{t+1}-2} \text{ for } t > 2. \end{aligned}$$

By a direct computation using the above basis, we obtain

Proposition 3.2.5 *For any integers $t > 1, u \geq 0$ and $n = 2^{t+u+1} + 2^{t+u} + 2^u - 3$, we have $(QP_3)_n^{GL_3} = 0$.*

By Theorem 2.1 $h_{t+u} h_{t+u+1} = 0$, so we have

$$\text{Ext}_{\mathcal{A}}^{3,2^{t+u+1}+2^{t+u}+2^u}(\mathbb{F}_2, \mathbb{F}_2) = \langle h_u h_{t+u} h_{t+u+1} \rangle = 0.$$

Hence, from the above equalities, we can see that

$$\text{Tr}_3 : \mathbb{F}_2 \otimes_{GL_3} P((P_3)_{2^{t+u+1}+2^{t+u}+2^u-3}^*) \longrightarrow \text{Ext}_{\mathcal{A}}^{3,2^{t+u+1}+2^{t+u}+2^u}(\mathbb{F}_2, \mathbb{F}_2)$$

is a trivial isomorphism.

Now, suppose that $s, t > 1$ and $n = 2^{s+t} + 2^t - 2$. From the results of Kameko [23], we see that $(QP_3)_n$ is the vector space of dimension 21 with a basis consisting of all the classes represented by the following monomials:

$$\begin{aligned} v_{s,t,1} &= x_2^{2^t-1} x_3^{2^{s+t}-1} & v_{s,t,2} &= x_2^{2^{s+t}-1} x_3^{2^t-1} \\ v_{s,t,3} &= x_1^{2^t-1} x_3^{2^{s+t}-1} & v_{s,t,4} &= x_1^{2^t-1} x_2^{2^{s+t}-1} \\ v_{s,t,5} &= x_1^{2^{s+t}-1} x_3^{2^t-1} & v_{s,t,6} &= x_1^{2^{s+t}-1} x_2^{2^t-1} \\ v_{s,t,7} &= x_2^{2^{t+1}-1} x_3^{2^{s+t}-2^t-1} & v_{s,t,8} &= x_1^{2^{t+1}-1} x_3^{2^{s+t}-2^t-1} \\ v_{s,t,9} &= x_1^{2^{t+1}-1} x_2^{2^{s+t}-2^t-1} & v_{s,t,10} &= x_1 x_2^{2^t-2} x_3^{2^{s+t}-1} \\ v_{s,t,11} &= x_1 x_2^{2^{s+t}-1} x_3^{2^t-2} & v_{s,t,12} &= x_1^{2^{s+t}-1} x_2 x_3^{2^t-2} \\ v_{s,t,13} &= x_1 x_2^{2^t-1} x_3^{2^{s+t}-2} & v_{s,t,14} &= x_1 x_2^{2^{s+t}-2} x_3^{2^t-1} \\ v_{s,t,15} &= x_1^{2^t-1} x_2 x_3^{2^{s+t}-2} & v_{s,t,16} &= x_1 x_2^{2^{t+1}-2} x_3^{2^{s+t}-2^t-1} \\ v_{s,t,17} &= x_1 x_2^{2^{t+1}-1} x_3^{2^{s+t}-2^t-2} & v_{s,t,18} &= x_1^{2^{t+1}-1} x_2 x_3^{2^{s+t}-2^t-2} \\ v_{s,t,19} &= x_1^3 x_2^{2^{s+t}-3} x_3^{2^t-2} & v_{s,t,20} &= x_1^3 x_2^{2^{t+1}-3} x_3^{2^{s+t}-2^t-2}, \\ v_{s,2,21} &= x_1^3 x_2^3 x_3^{2^{s+2}-4}, \text{ for } t = 2 \text{ and } v_{s,t,21} = x_1^3 x_2^{2^t-3} x_3^{2^{s+t}-2} \text{ for } t > 2. \end{aligned}$$

We set

$$p_{3,s,t,u} = \begin{cases} \sum_{1 \leq j \leq 21, j \neq 13, 15} \psi^u(v_{s,2,j}), & \text{if } t = 2, \\ \sum_{1 \leq j \leq 21} \psi^u(v_{s,t,j}), & \text{if } t > 2. \end{cases}$$

By a direct computation using this basis, we get

Proposition 3.2.6 *For any integers $s, t > 1, u \geq 0$ and $n = 2^{s+t+u} + 2^{t+u} + 2^u - 3$, we have $(QP_3)_n^{GL_3} = [p_{3,s,t,u}]$.*

By Theorem 2.1, we have

$$\text{Ext}_{\mathcal{A}}^{3,2^{s+t+u}+2^{t+u}+2^u}(\mathbb{F}_2, \mathbb{F}_2) = \langle h_u h_{t+u} h_{s+t+u} \rangle.$$

Note that $\psi^u(v_{s,t,1}) = x_1^{2^u-1} x_2^{2^{t+u}-1} x_3^{2^{s+t+u}-1}$. Consider the element

$$q_{3,s,t,u} = a_1^{(2^u-1)} a_2^{(2^{t+u}-1)} a_3^{(2^{s+t+u}-1)} \in \mathbb{F}_2 \otimes_{GL_3} P((P_3)_n^*).$$

Since $\langle p_{3,s,t,u}, q_{3,s,t,u} \rangle = 1$, from Proposition 3.2.6, we obtain

$$\mathbb{F}_2 \otimes_{GL_3} P((P_3)_n^*) = \langle [q_{3,s,t,u}] \rangle.$$

It is easy to see that $\phi_3(q_{3,s,t,u}) = \lambda_u \lambda_{t+u} \lambda_{s+t+u}$, hence using Theorem 2.2 we get

$$Tr_3([q_{3,s,t,u}]) = [\lambda_u \lambda_{t+u} \lambda_{s+t+u}] = h_u h_{t+u} h_{s+t+u}.$$

Theorem 3.2.1 is completely proved.

4. Determination of Tr_4 in some internal degrees

In this section, we explicitly determined Tr_4 in some internal degrees. Our main result is the following.

Theorem 4.1 *Let s be a positive integer and let n be one of the degrees $2^{s+1} - 1$, $2^{s+1} - 2$, $2^{s+1} - 3$. Then, the homomorphism*

$$Tr_4 : \mathbb{F}_2 \otimes_{GL_4} P((P_4)_n^*) \longrightarrow \text{Ext}_{\mathcal{A}}^{4,n+4}(\mathbb{F}_2, \mathbb{F}_2)$$

is an isomorphism.

We prove the theorem by computing the space $(QP_4)_n^{GL_4}$.

4.1. The case $n = 2^{s+1} - 3$

Proposition 4.1.1 (see [15, 26]) *Let $n = 2^{s+1} - 3$ with s a positive integer. Then, the dimension of the $\mathbb{F}_2$ -vector space $(QP_4)_n$ is determined by the following table:*

$n = 2^{s+1} - 3$	$s = 1$	$s = 2$	$s = 3$	$s \geq 4$
$\dim(QP_4)_n$	4	15	35	45

A basis for $(QP_4)_n$ is the set consisting of all the classes represented monomials $a_j = a_{s,j}$ which are determined as follows:

For $s = 1$, $a_{1,1} = x_4$, $a_{1,2} = x_3$, $a_{1,3} = x_2$, $a_{1,4} = x_1$.

For $s \geq 2$,

$$\begin{aligned} a_{s,1} &= x_2^{2^{s-1}-1} x_3^{2^{s-1}-1} x_4^{2^s-1} & a_{s,2} &= x_2^{2^{s-1}-1} x_3^{2^s-1} x_4^{2^{s-1}-1} \\ a_{s,3} &= x_2^{2^s-1} x_3^{2^{s-1}-1} x_4^{2^{s-1}-1} & a_{s,4} &= x_1^{2^{s-1}-1} x_3^{2^{s-1}-1} x_4^{2^s-1} \\ a_{s,5} &= x_1^{2^{s-1}-1} x_3^{2^s-1} x_4^{2^{s-1}-1} & a_{s,6} &= x_1^{2^{s-1}-1} x_2^{2^{s-1}-1} x_4^{2^s-1} \\ a_{s,7} &= x_1^{2^{s-1}-1} x_2^{2^s-1} x_3^{2^{s-1}-1} & a_{s,8} &= x_1^{2^{s-1}-1} x_2^{2^{s-1}-1} x_4^{2^s-1} \\ a_{s,9} &= x_1^{2^s-1} x_2^{2^{s-1}-1} x_3^{2^{s-1}-1} & a_{s,10} &= x_1^{2^s-1} x_3^{2^{s-1}-1} x_4^{2^{s-1}-1} \\ a_{s,11} &= x_1^{2^s-1} x_2^{2^{s-1}-1} x_4^{2^{s-1}-1} & a_{s,12} &= x_1^{2^s-1} x_2^{2^{s-1}-1} x_3^{2^{s-1}-1} \end{aligned}$$

For $s = 2$, $a_{2,13} = x_1 x_2 x_3 x_4^2$, $a_{2,14} = x_1 x_2 x_3^2 x_4$, $a_{2,15} = x_1 x_2^2 x_3 x_4$.

For $s \geq 3$,

$$\begin{aligned} a_{s,13} &= x_1 x_2^{2^{s-1}-2} x_3^{2^{s-1}-1} x_4^{2^s-1} & a_{s,14} &= x_1 x_2^{2^{s-1}-2} x_3^{2^s-1} x_4^{2^{s-1}-1} \\ a_{s,15} &= x_1 x_2^{2^{s-1}-1} x_3^{2^{s-1}-2} x_4^{2^s-1} & a_{s,16} &= x_1 x_2^{2^{s-1}-1} x_3^{2^s-1} x_4^{2^{s-1}-2} \\ a_{s,17} &= x_1 x_2^{2^s-1} x_3^{2^{s-1}-2} x_4^{2^{s-1}-1} & a_{s,18} &= x_1 x_2^{2^s-1} x_3^{2^{s-1}-1} x_4^{2^{s-1}-2} \\ a_{s,19} &= x_1^{2^{s-1}-1} x_2 x_3^{2^{s-1}-2} x_4^{2^s-1} & a_{s,20} &= x_1^{2^{s-1}-1} x_2 x_3^{2^s-1} x_4^{2^{s-1}-2} \\ a_{s,21} &= x_1^{2^{s-1}-1} x_2^{2^s-1} x_3 x_4^{2^{s-1}-2} & a_{s,22} &= x_1^{2^s-1} x_2 x_3^{2^{s-1}-2} x_4^{2^{s-1}-1} \\ a_{s,23} &= x_1^{2^s-1} x_2 x_3^{2^{s-1}-1} x_4^{2^{s-1}-2} & a_{s,24} &= x_1^{2^s-1} x_2^{2^{s-1}-1} x_3 x_4^{2^{s-1}-2} \\ a_{s,25} &= x_1 x_2^{2^{s-1}-1} x_3^{2^{s-1}-1} x_4^{2^s-2} & a_{s,26} &= x_1 x_2^{2^{s-1}-1} x_3^{2^s-2} x_4^{2^{s-1}-1} \\ a_{s,27} &= x_1 x_2^{2^s-2} x_3^{2^{s-1}-1} x_4^{2^{s-1}-1} & a_{s,28} &= x_1^{2^{s-1}-1} x_2 x_3^{2^{s-1}-1} x_4^{2^s-2} \\ a_{s,29} &= x_1^{2^{s-1}-1} x_2 x_3^{2^s-2} x_4^{2^{s-1}-1} & a_{s,30} &= x_1^{2^{s-1}-1} x_2^{2^{s-1}-1} x_3 x_4^{2^s-2} \end{aligned}$$

For $s = 3$,

$$\begin{aligned} a_{3,31} &= x_1^3 x_2^3 x_3^5 x_4^2 & a_{3,32} &= x_1^3 x_2^5 x_3^2 x_4^3 & a_{3,33} &= x_1^3 x_2^5 x_3^3 x_4^2 \\ a_{3,34} &= x_1^3 x_2^3 x_3^3 x_4^4 & a_{3,35} &= x_1^3 x_2^3 x_3^4 x_4^3 \end{aligned}$$

For $s \geq 4$,

$$\begin{aligned}
 a_{s,31} &= x_1^3 x_2^{2^{s-1}-3} x_3^{2^{s-1}-2} x_4^{2^s-1} & a_{s,32} &= x_1^3 x_2^{2^{s-1}-3} x_3^{2^s-1} x_4^{2^{s-1}-2} \\
 a_{s,33} &= x_1^3 x_2^{2^s-1} x_3^{2^{s-1}-3} x_4^{2^{s-1}-2} & a_{s,34} &= x_1^{2^s-1} x_2^3 x_3^{2^{s-1}-3} x_4^{2^{s-1}-2} \\
 a_{s,35} &= x_1^3 x_2^{2^{s-1}-3} x_3^{2^{s-1}-1} x_4^{2^s-2} & a_{s,36} &= x_1^3 x_2^{2^{s-1}-3} x_3^{2^s-2} x_4^{2^{s-1}-1} \\
 a_{s,37} &= x_1^3 x_2^{2^{s-1}-1} x_3^{2^{s-1}-3} x_4^{2^s-2} & a_{s,38} &= x_1^{2^{s-1}-1} x_2^3 x_3^{2^{s-1}-3} x_4^{2^s-2} \\
 a_{s,39} &= x_1^3 x_2^{2^{s-1}-1} x_3^{2^s-3} x_4^{2^{s-1}-2} & a_{s,40} &= x_1^3 x_2^{2^s-3} x_3^{2^{s-1}-2} x_4^{2^{s-1}-1} \\
 a_{s,41} &= x_1^3 x_2^{2^s-3} x_3^{2^{s-1}-1} x_4^{2^{s-1}-2} & a_{s,42} &= x_1^{2^{s-1}-1} x_2^3 x_3^{2^s-3} x_4^{2^{s-1}-2} \\
 a_{s,43} &= x_1^7 x_2^{2^s-5} x_3^{2^{s-1}-3} x_4^{2^{s-1}-2}
 \end{aligned}$$

For $s = 4$, $a_{4,44} = x_1^7 x_2^7 x_3^9 x_4^6$, $a_{4,45} = x_1^7 x_2^7 x_3^7 x_4^8$.

For $s \geq 5$, $a_{s,44} = x_1^7 x_2^{2^{s-1}-5} x_3^{2^s-3} x_4^{2^{s-1}-2}$, $a_{s,45} = x_1^7 x_2^{2^{s-1}-5} x_3^{2^{s-1}-3} x_4^{2^s-2}$.

Proposition 4.1.2 *Let s be a positive integer. Then, $(QP_4)_{2^{s+1}-3}^{GL_4} = 0$.*

For simplicity, we prove the proposition in detail for $s \geq 5$. The other cases can be proved by the similar computations.

For any monomials $z_1, z_2, \dots, z_m$ in P_k and for a subgroup $G \subset GL_k$, we denote $G(z_1, z_2, \dots, z_m)$ the G -submodule of QP_k generated by the set $\{[z_i] : 1 \leq i \leq m\}$. We have the following.

Lemma 4.1.3 i) *For any $s \geq 5$, there is a direct summand decomposition of the Σ_4 -modules:*

$$(QP_4)_{2^{s+1}-3} = \Sigma_4(a_{s,1}) \oplus \Sigma_4(a_{s,13}) \oplus \Sigma_4(a_{s,31}) \oplus \Sigma_4(a_{s,25}, a_{s,35}, a_{s,43}).$$

$$(ii) \quad \Sigma_4(a_{s,1})^{\Sigma_4} = \langle [p_{4,s,1}] \rangle, \text{ with } p_{4,s,1} = \sum_{j=1}^{12} a_{s,j}.$$

$$(iii) \quad \Sigma_4(a_{s,13})^{\Sigma_4} = \langle [p_{4,s,2}] \rangle, \text{ with } p_{4,s,2} = \sum_{j=13}^{24} a_{s,j}.$$

$$(iv) \quad \Sigma_4(a_{s,31})^{\Sigma_4} = \langle [p_{4,s,3}] \rangle, \text{ with } p_{4,s,3} = \sum_{j=31}^{34} a_{s,j}.$$

$$(v) \quad \Sigma_4(a_{s,25}, a_{s,35}, a_{s,43})^{\Sigma_4} = \langle [p_{4,s,4}] \rangle, \text{ with } p_{4,s,4} = \sum_{j=25}^{30} a_{s,j} + \sum_{j=39}^{43} a_{s,j} + a_{s,45}.$$

Proof. We obtain Part i) by a simple computation using Proposition 4.1.1. We prove Part v) in detail. The others can be proved by the similar computations. By a simple computation we see that the set $\{[a_{s,j}] : j = 25, \dots, 30, 35, \dots, 45\}$ is a basis for $\Sigma_4(a_{s,25}, a_{s,35}, a_{s,43})$. Suppose $[f] \in \Sigma_4(a_{s,25}, a_{s,35}, a_{s,43})^{\Sigma_4}$, then

$$f \equiv \sum_{j=25}^{30} \gamma_j a_{s,j} + \sum_{j=35}^{45} \gamma_j a_{s,j}$$

with $\gamma_j \in \mathbb{F}_2$. By a direct computation, we get

$$\begin{aligned}
 \rho_1(f) + f &\equiv (\gamma_{25} + \gamma_{28})(a_{s,25} + a_{s,28}) + (\gamma_{26} + \gamma_{29})(a_{s,26} + a_{s,29}) \\
 &\quad + (\gamma_{27} + \gamma_{41})a_{s,35} + (\gamma_{27} + \gamma_{40})a_{s,36} + (\gamma_{37} + \gamma_{38})(a_{s,37} + a_{s,38}) \\
 &\quad + (\gamma_{39} + \gamma_{42})(a_{s,39} + a_{s,42}) + (\gamma_{41} + \gamma_{43})a_{s,44} + (\gamma_{40} + \gamma_{43})a_{s,45} \equiv 0, \\
 \rho_2(f) + f &\equiv (\gamma_{26} + \gamma_{27})(a_{s,26} + a_{s,27}) + (\gamma_{28} + \gamma_{30})(a_{s,28} + a_{s,30}) \\
 &\quad + (\gamma_{35} + \gamma_{37})(a_{s,35} + a_{s,37}) + (\gamma_{29} + \gamma_{36} + \gamma_{40})(a_{s,36} + a_{s,40}) \\
 &\quad + (\gamma_{39} + \gamma_{41})(a_{s,39} + a_{s,41}) + (\gamma_{42} + \gamma_{43} + \gamma_{44})(a_{s,43} + a_{s,44}) \\
 &\quad + (\gamma_{29} + \gamma_{42})(a_{s,38} + a_{s,45}) \equiv 0, \\
 \rho_3(f) + f &\equiv (\gamma_{25} + \gamma_{26})(a_{s,25} + a_{s,26}) + (\gamma_{28} + \gamma_{29})(a_{s,28} + a_{s,29}) \\
 &\quad + (\gamma_{35} + \gamma_{36})(a_{s,35} + a_{s,36}) + (\gamma_{30} + \gamma_{37} + \gamma_{39})(a_{s,37} + a_{s,39}) \\
 &\quad + (\gamma_{30} + \gamma_{38} + \gamma_{42})(a_{s,38} + a_{s,42}) + (\gamma_{40} + \gamma_{41})(a_{s,40} + a_{s,41}) \\
 &\quad + (\gamma_{30} + \gamma_{44} + \gamma_{45})(a_{s,44} + a_{s,45}) \equiv 0.
 \end{aligned}$$

The above equalities imply $\gamma_j = 0$ for $j = 35, 36, 37, 38, 44$ and $\gamma_j = \gamma_{25}$ for $j \neq 35, 36, 37, 38, 44$. The lemma is proved. $\square$

Proof of Proposition 4.1.2. Let $f \in P_4$ such that $[f] \in (QP_4)_{2^{s+1}-3}^{GL_4}$. Since $\Sigma_4 \subset GL_4$, we have $[f] \in (QP_4)_{2^{s+1}-3}^{\Sigma_4}$. Then, $f \equiv \sum_{j=1}^4 \gamma_j p_{4,s,j}$ with $\gamma_j \in \mathbb{F}_2$. By a direct computation, we get

$$\begin{aligned} \rho_4(f) + f &\equiv (\gamma_1 + \gamma_4)a_{s,3} + \gamma_1 a_{s,9} + (\gamma_2 + \gamma_3)a_{s,15} \\ &\quad + \gamma_2 a_{s,21} + \text{other terms} \equiv 0. \end{aligned}$$

The last equality implies $\gamma_j = 0$ for $j = 1, 2, 3, 4$. The proposition follows. $\square$

From Theorem 2.1, we have $\text{Ext}_{\mathcal{A}}^{4,2^{s+1}+1}(\mathbb{F}_2, \mathbb{F}_2) = 0$. Hence, Theorem 4.1 holds for $n = 2^{s+1} - 3$.

4.2. The case $n = 2^{s+1} - 2$

Since Kameko's homomorphism in the degree $2^{s+1} - 2$,

$$(\widetilde{Sq}_*)^0_{2^{s+1}-2} : (QP_4)_{2^{s+1}-2} \rightarrow (QP_4)_{2^s-3}$$

is an epimorphism of GL_4 -modules, using Proposition 4.1.2, we have

$$(QP_4)_{2^{s+1}-2}^{GL_4} \subset (\text{Ker}(\widetilde{Sq}_*)^0_{2^{s+1}-2})^{GL_4}.$$

From [15, 26], we have the following.

Proposition 4.2.1 (see [15, 26]) *Let s be a positive integer. Then,*

$$\dim(\text{Ker}(\widetilde{Sq}_*)^0_{2^{s+1}-2}) = \begin{cases} 6, & \text{if } s = 1, \\ 20, & \text{if } s = 2, \\ 35 & \text{if } s \geq 3. \end{cases}$$

A basis for $(\text{Ker}(\widetilde{Sq}_*)^0_{2^{s+1}-2})$ is the set consisting of all the classes represented monomials $b_j = b_{s,j}$ which are determined as follows:

$$\begin{aligned} \text{For } s \geq 1, \\ b_{s,1} &= x_3^{2^s-1} x_4^{2^s-1} & b_{s,2} &= x_2^{2^s-1} x_4^{2^s-1} & b_{s,3} &= x_2^{2^s-1} x_3^{2^s-1} \\ b_{s,4} &= x_1^{2^s-1} x_4^{2^s-1} & b_{s,5} &= x_1^{2^s-1} x_3^{2^s-1} & b_{s,6} &= x_1^{2^s-1} x_2^{2^s-1} \end{aligned}$$

$$\begin{aligned} \text{For } s \geq 2, \\ b_{s,7} &= x_2 x_3^{2^s-2} x_4^{2^s-1} & b_{s,8} &= x_2 x_3^{2^s-1} x_4^{2^s-2} & b_{s,9} &= x_2^{2^s-1} x_3 x_4^{2^s-2} \\ b_{s,10} &= x_1 x_3^{2^s-2} x_4^{2^s-1} & b_{s,11} &= x_1 x_3^{2^s-1} x_4^{2^s-2} & b_{s,12} &= x_1 x_2^{2^s-2} x_4^{2^s-1} \\ b_{s,13} &= x_1 x_2^{2^s-2} x_3^{2^s-1} & b_{s,14} &= x_1 x_2^{2^s-1} x_4^{2^s-2} & b_{s,15} &= x_1 x_2^{2^s-1} x_3^{2^s-2} \\ b_{s,16} &= x_1^{2^s-1} x_3 x_4^{2^s-2} & b_{s,17} &= x_1^{2^s-1} x_2 x_4^{2^s-2} & b_{s,18} &= x_1^{2^s-1} x_2 x_3^{2^s-2} \end{aligned}$$

$$\text{For } s = 2, b_{2,19} = x_1 x_2 x_3^2 x_4^2, b_{2,20} = x_1 x_2^2 x_3 x_4^2.$$

$$\begin{aligned} \text{For } s \geq 3, \\ b_{s,19} &= x_2^3 x_3^{2^s-3} x_4^{2^s-2} & b_{s,20} &= x_1^3 x_3^{2^s-3} x_4^{2^s-2} & b_{s,21} &= x_1^3 x_2^{2^s-3} x_4^{2^s-2} \\ b_{s,22} &= x_1^3 x_2^{2^s-3} x_3^{2^s-2} & b_{s,23} &= x_1 x_2^2 x_3^{2^s-4} x_4^{2^s-1} & b_{s,24} &= x_1 x_2^2 x_3^{2^s-1} x_4^{2^s-4} \\ b_{s,25} &= x_1 x_2^{2^s-1} x_3^2 x_4^{2^s-4} & b_{s,26} &= x_1^{2^s-1} x_2 x_3^2 x_4^{2^s-4} & b_{s,27} &= x_1 x_2 x_3^{2^s-2} x_4^{2^s-2} \\ b_{s,28} &= x_1 x_2^{2^s-2} x_3 x_4^{2^s-2} & b_{s,29} &= x_1^3 x_2^5 x_3^{2^s-6} x_4^{2^s-4} & b_{s,30} &= x_1 x_2^2 x_3^{2^s-3} x_4^{2^s-2} \\ b_{s,31} &= x_1 x_2^3 x_3^{2^s-4} x_4^{2^s-2} & b_{s,32} &= x_1 x_2^3 x_3^{2^s-2} x_4^{2^s-4} & b_{s,33} &= x_1^3 x_2 x_3^{2^s-4} x_4^{2^s-2} \\ b_{s,34} &= x_1^3 x_2 x_3^{2^s-2} x_4^{2^s-4} \end{aligned}$$

$$\text{For } s = 3, b_{3,35} = x_1^3 x_2^3 x_3^4 x_4^4, \text{ and for } s \geq 4, b_{s,35} = x_1^3 x_2^{2^s-3} x_3^2 x_4^{2^s-4}.$$

We set

$$p_{4,s} = \begin{cases} x_1 x_2 x_3^6 x_4^6 + x_1^3 x_2^3 x_3^4 x_4^4, & \text{if } s = 3, \\ \sum_{j=1}^{35} b_{s,j} & \text{if } s \geq 4. \end{cases}$$

By a direct computation using Proposition 4.2.1, one gets the following.

Proposition 4.2.2 *Let s be a positive integer. Then,*

$$(\text{Ker}(\widetilde{Sq}_*)^0_{2^{s+1}-2})^{GL_4} = \begin{cases} 0, & \text{if } s \leq 2, \\ \langle [p_{4,s}] \rangle & \text{if } s \geq 3. \end{cases}$$

For simplicity, we will prove this proposition in detail for $s \geq 4$. The others can be proved by the similar computations. We have the following.

Lemma 4.2.3 i) For any $s \geq 4$, there is a direct summand decomposition of the Σ_4 -modules:

$$(\text{Ker}(\widetilde{Sq}_*)^0)_{2^{s+1}-2} = \Sigma_4(b_{s,1}) \oplus \Sigma_4(b_{s,7}) \oplus \Sigma_4(b_{s,19}) \oplus \Sigma_4(b_{s,23}) \oplus \Sigma_4(b_{s,29}, b_{s,30}).$$

$$(ii) \quad \Sigma_4(b_{s,1})^{\Sigma_4} = \langle [\bar{p}_{4,s,1}] \rangle, \text{ with } \bar{p}_{4,s,1} = \sum_{j=1}^6 b_{s,j}.$$

$$(iii) \quad \Sigma_4(b_{s,7})^{\Sigma_4} = \langle [\bar{p}_{4,s,2}] \rangle, \text{ with } \bar{p}_{4,s,2} = \sum_{j=7}^{18} b_{s,j}.$$

$$(iv) \quad \Sigma_4(b_{s,19})^{\Sigma_4} = \langle [\bar{p}_{4,s,3}] \rangle, \text{ with } \bar{p}_{4,s,3} = \sum_{j=19}^{22} b_{s,j}.$$

$$(v) \quad \Sigma_4(b_{s,23})^{\Sigma_4} = \langle [\bar{p}_{4,s,4}] \rangle, \text{ with } \bar{p}_{4,s,4} = \sum_{j=23}^{26} b_{s,j}.$$

$$(vi) \quad \Sigma_4(b_{s,29}, a_{s,30})^{\Sigma_4} = \langle [\bar{p}_{4,s,5}], [\bar{p}_{4,s,6}] \rangle, \text{ where}$$

$$\bar{p}_{4,s,5} = \sum_{j=27}^{29} b_{s,j}, \quad \bar{p}_{4,s,6} = \sum_{j=30}^{35} b_{s,j}.$$

Proof. From Proposition 4.2.1 we easily obtain Part i). Now, we prove Part vi) in detail. The others can be proved by the similar computations. By a direct computation we see that the set $\{[b_{s,j}] : j = 27 \leq j \leq 35\}$ is a basis for $\Sigma_4(b_{s,29}, b_{s,30})^{\Sigma_4}$. Suppose $[f] \in \Sigma_4(b_{s,29}, b_{s,30})^{\Sigma_4}$, then $f \equiv \sum_{j=27}^{35} \gamma_j b_{s,j}$ with $\gamma_j \in \mathbb{F}_2$. By a direct computation, we obtain

$$\begin{aligned} \rho_1(f) + f &\equiv (\gamma_{28} + \gamma_{29} + \gamma_{30} + \gamma_{35})b_{s,27} + (\gamma_{31} + \gamma_{33})(b_{s,31} + b_{s,33}) \\ &\quad + (\gamma_{32} + \gamma_{34})(b_{s,32} + b_{s,34}) \equiv 0, \\ \rho_2(f) + f &\equiv (\gamma_{27} + \gamma_{28} + \gamma_{32} + \gamma_{33})(b_{s,27} + b_{s,28}) \\ &\quad + (\gamma_{30} + \gamma_{31})(b_{s,30} + b_{s,31}) + (\gamma_{34} + \gamma_{35})(b_{s,34} + b_{s,35}) \equiv 0, \\ \rho_3(f) + f &\equiv (\gamma_{28} + \gamma_{29} + \gamma_{30} + \gamma_{35})b_{s,27} + (\gamma_{31} + \gamma_{32})(b_{s,31} + b_{s,32}) \\ &\quad + (\gamma_{33} + \gamma_{34})(b_{s,33} + b_{s,34}) \equiv 0. \end{aligned}$$

The above equalities imply $\gamma_j = \gamma_{27}$ for $j = 27, 28, 29$ and $\gamma_j = \gamma_{30}$ for $30 \leq j \leq 35$. The lemma is proved. $\square$

Remark 4.2.4 For $s = 3$, Parts i) to v) of Lemma 4.2.3 hold. We replace Part vi) with $\Sigma_4(b_{3,29}, a_{3,30})^{\Sigma_4} = [p_{4,3}]$.

Proof of Proposition 4.2.2. Let $f \in P_4$ such that $[f] \in \text{Ker}(\widetilde{Sq}_*)^{GL_4}_{2^{s+1}-2}$. Then, $[f] \in \text{Ker}(\widetilde{Sq}_*)^0_{2^{s+1}-2}$. Hence, $f \equiv \sum_{j=1}^6 \gamma_j \bar{p}_{4,s,j}$ with $\gamma_j \in \mathbb{F}_2$. By a direct computation, we have

$$\begin{aligned} \rho_4(f) + f &\equiv (\gamma_1 + \gamma_2)(b_{s,2} + b_{s,3}) + (\gamma_2 + \gamma_4)(b_{s,7} + b_{s,8}) + (\gamma_2 + \gamma_5)b_{s,9} \\ &\quad + (\gamma_2 + \gamma_3)(b_{s,14} + b_{s,15}) + (\gamma_3 + \gamma_6)b_{s,19} + (\gamma_4 + \gamma_6)b_{s,25} \\ &\quad + (\gamma_2 + \gamma_3 + \gamma_4 + \gamma_5)b_{s,27} + (\gamma_5 + \gamma_6)(b_{s,31} + b_{s,32}) \equiv 0. \end{aligned}$$

The last equality implies $\gamma_j = \gamma_1$ for $1 \leq j \leq 6$. The proposition follows. $\square$

From Theorem 2.1, we have

$$\text{Ext}_{\mathcal{A}}^{4,2^{s+1}+2}(\mathbb{F}_2, \mathbb{F}_2) = \begin{cases} 0, & \text{if } s \leq 2, \\ \langle d_0 \rangle & \text{if } s = 3, \\ \langle h_0^2 h_s^2 \rangle & \text{if } s \geq 4. \end{cases}$$

Denote $q_{4,s} \in P((P_4^*)_{2^{s+1}-2})$ by setting

$$\begin{aligned} q_{4,3} &= a_1^{(1)} a_2^{(1)} a_3^{(6)} a_4^{(6)} + a_1^{(1)} a_2^{(2)} a_3^{(5)} a_4^{(6)} + a_1^{(1)} a_2^{(3)} a_3^{(4)} a_4^{(6)} + a_1^{(1)} a_2^{(4)} a_3^{(3)} a_4^{(6)} + a_1^{(1)} a_2^{(5)} a_3^{(2)} a_4^{(6)} + a_1^{(1)} a_2^{(6)} a_3^{(1)} a_4^{(6)} \\ &\quad + a_1^{(2)} a_2^{(1)} a_3^{(6)} a_4^{(5)} + a_1^{(2)} a_2^{(2)} a_3^{(5)} a_4^{(5)} + a_1^{(2)} a_2^{(3)} a_3^{(4)} a_4^{(5)} + a_1^{(2)} a_2^{(4)} a_3^{(3)} a_4^{(5)} + a_1^{(2)} a_2^{(5)} a_3^{(2)} a_4^{(5)} + a_1^{(2)} a_2^{(6)} a_3^{(1)} a_4^{(5)} \\ &\quad + a_1^{(3)} a_2^{(1)} a_3^{(5)} a_4^{(5)} + a_1^{(3)} a_2^{(2)} a_3^{(6)} a_4^{(3)} + a_1^{(3)} a_2^{(3)} a_3^{(2)} a_4^{(6)} + a_1^{(3)} a_2^{(4)} a_3^{(1)} a_4^{(6)} + a_1^{(3)} a_2^{(5)} a_3^{(4)} a_4^{(3)} a_4^{(4)} a_4^{(3)} \\ &\quad + a_1^{(3)} a_2^{(6)} a_3^{(2)} a_4^{(3)} + a_1^{(4)} a_2^{(1)} a_3^{(6)} a_4^{(3)} + a_1^{(4)} a_2^{(2)} a_3^{(5)} a_4^{(3)} + a_1^{(4)} a_2^{(3)} a_3^{(4)} a_4^{(3)} + a_1^{(4)} a_2^{(4)} a_3^{(3)} a_4^{(3)} + a_1^{(4)} a_2^{(5)} a_3^{(2)} a_4^{(3)} \end{aligned}$$

$$\begin{aligned}
 &+ a_1^{(4)} a_2^{(6)} a_3^{(1)} a_4^{(3)} + a_1^{(5)} a_2^{(1)} a_3^{(3)} a_4^{(5)} + a_1^{(5)} a_2^{(2)} a_3^{(1)} a_4^{(6)} + a_1^{(5)} a_2^{(2)} a_3^{(2)} a_4^{(5)} + a_1^{(5)} a_2^{(2)} a_3^{(4)} a_4^{(3)} + a_1^{(5)} a_2^{(3)} a_3^{(1)} a_4^{(5)} \\
 &+ a_1^{(5)} a_2^{(3)} a_3^{(3)} a_4^{(3)} + a_1^{(5)} a_2^{(5)} a_3^{(1)} a_4^{(3)} + a_1^{(6)} a_2^{(1)} a_3^{(1)} a_4^{(6)} + a_1^{(6)} a_2^{(1)} a_3^{(2)} a_4^{(5)} + a_1^{(6)} a_2^{(1)} a_3^{(4)} a_4^{(3)} + a_1^{(6)} a_2^{(2)} a_3^{(3)} a_4^{(3)},
 \end{aligned}$$

and $q_{4,s} = a_1^{(0)} a_2^{(0)} a_3^{(2^s-1)} a_4^{(2^s-1)}$, for $s \geq 4$. Since $\langle [p_{4,s}], [q_{4,s}] \rangle = 1$ for any $s \geq 3$, we get

$$\mathbb{F}_2 \otimes_{GL_4} P((P_4)_{2^{s+1}-2}^*) = \begin{cases} 0, & \text{if } s \leq 2, \\ \langle [q_{4,s}] \rangle, & \text{if } s \geq 3. \end{cases}$$

By a direct computation, we obtain

$$\phi_4(q_{4,s}) = \begin{cases} \bar{d}_0 + \delta(\lambda_1 \lambda_9 \lambda_3^2 + \lambda_1 \lambda_3 \lambda_9 \lambda_3), & \text{if } s = 3, \\ \lambda_0^2 \lambda_{2^s-1}^2, & \text{if } s > 3. \end{cases}$$

From the above equalities and Theorem 2.2, we get

$$Tr_4([q_{4,s}]) = [\phi_4(q_{4,s})] = \begin{cases} [\bar{d}_0] = d_0, & \text{if } s = 3, \\ [\lambda_0^2 \lambda_{2^s-1}^2] = h_0^2 h_s^2, & \text{if } s > 3. \end{cases}$$

Theorem 4.1 holds for $n = 2^{s+1} - 2$.

4.3. The case $n = 2^{s+1} - 1$

First, we recall the following.

Proposition 4.3.1 (see [15, 26]) *Let $n = 2^{s+1} - 1$ with s a positive integer. Then, the dimension of the $\mathbb{F}_2$ -vector space $(QP_4)_n$ is determined by the following table:*

$n = 2^s - 1$	$s = 1$	$s = 2$	$s = 3$	$s = 4$	$s \geq 5$
$\dim(QP_4)_n$	14	35	75	89	85

A basis of $(QP_4)_n$ has been given in [15]. For $s \geq k - 2$, we set

$$\eta_{k,s} = \sum_{m=1}^{k-1} \sum_{1 \leq i_1 < \dots < i_m \leq k} x_{i_1} x_{i_2}^2 \dots x_{i_{m-1}}^{2^{m-2}} x_{i_m}^{2^{s+1}-2^{m-1}} \in (P_k)_{2^{s+1}-1}.$$

For $k = 4$, we denote

$$\bar{p}_{4,s} = \begin{cases} \eta_{4,s} + x_1 x_2^2 x_3^2 x_4^2, & \text{if } s = 2, \\ \eta_{4,s} + x_1 x_2^2 x_3^4 x_4^{2^{s+1}-8}, & \text{if } s \geq 3. \end{cases}$$

By a computation similar to the one in Proposition 4.2.1, one gets the following.

Proposition 4.3.2 *Let s be a positive integer. Then,*

$$(QP_4)_{2^{s+1}-1}^{GL_4} = \begin{cases} 0, & \text{if } s = 1, \\ \langle [\bar{p}_{4,s}] \rangle, & \text{if } s \geq 2. \end{cases}$$

From Theorem 2.1, we have

$$\text{Ext}_{\mathcal{A}}^{4, 2^{s+1}+3}(\mathbb{F}_2, \mathbb{F}_2) = \begin{cases} 0, & \text{if } s = 1, \\ \langle h_0^3 h_{s+1} \rangle, & \text{if } s \geq 2. \end{cases}$$

Denote $\bar{q}_{4,s} = a_1^{(0)} a_2^{(0)} a_3^{(2^s-1)} a_4^{(2^s-1)} \in P((P_4^*)_{2^{s+1}-1})$, for $s \geq 2$. It is easy to see that $\langle [\bar{p}_{4,s}], [\bar{q}_{4,s}] \rangle = 1$. Hence, we obtain

$$\mathbb{F}_2 \otimes_{GL_4} P((P_4)_{2^{s+1}-1}^*) = \begin{cases} 0, & \text{if } s = 1, \\ \langle [\bar{q}_{4,s}] \rangle, & \text{if } s \geq 2. \end{cases}$$

By a simple computation, we have $\phi_4(\bar{q}_{4,s}) = \lambda_0^3 \lambda_{2^s-1}$. Hence, using Theorem 2.2, one gets

$$Tr_4([\bar{q}_{4,s}]) = [\phi_4(\bar{q}_{4,s})] = [\lambda_0^3 \lambda_{2^s-1}] = h_0^3 h_{s+1}.$$

Theorem 4.1 is completely proved.

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Numerical analysis of local head loss coefficient at the inlet of a conduit connected to a free surface channel

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Abstract:

Numerical simulation have been carried out to observe and predict the mechanisms of stationary mixed flows in a free surface channel combined with a closed conduit. This study has been conducted with a wide range of discharge values, based on a free rectangular channel (4.5x0.98x0.50 m) at the upstream combined with a closed rectangular conduit (4.5 m length), located at the end of the channel. The height of the conduit is fixed at 100 mm and the conduit width is varied to form several other geometrical configurations. From the obtained numerical results, the local head losses at the transition location are computed and a relation between the local head loss coefficient at this transition and the water depth at the upstream free surface channel is proposed. It will be verified by experimental results in the next study.

Keywords: flow contraction, mixed flows, shallow water equations.

Classification number: 1.3

Introduction

In most cases, when one talks about the flows, two individual kinds of flow are usually mentioned, which are the free surface flows and the pressurised flows. Free surface flows are the flows where the top flow surface is subjected to atmospheric pressure, whether the channel section is opened or closed at the top [1]. Pressurised flows are under pressure and also referred to as conduit flows or pipe flows. In practice, the simultaneous occurrence of these flow kinds is observed in many hydraulic engineering applications. Additionally, some hydraulic structures are designed to combine free surface and pressurised sections (e.g. water intakes) [2, 3]. Such flows are named “mixed flows” and have been investigated in a lot of works from both numerical and experimental point of views.

The first studies of mixed flows regimes, conducted in the decades before and after - the World War 2, were hydraulic scale models that looked at the design of particular structures.

Recently, many authors have tried to establish generally applicable laws while studying particular structures or testing simulation models; and some scale models have been built [4]. However, these studies mainly focus on cases where the one-dimensional approximation is valid. For instance, see the application of a transient mixed-flow model in the design of a combined sewer storage-conveyance system [5] or a numerical study to simulate the flow conditions in a circulating water system of a thermal plant [6, 7] that was studied to define the characteristics of the transition from pressurised flow to free surface flow in a conduit, which provided some knowledge of this transition process. Li, et al. [8] conducted an investigation on the pressure transients in the sewer system; they conducted both mathematical and experimental modelling studies. Gomez, et al. [9] carried out a study to analyse the transition from free-surface to pressure flow at both ends of a pipeline. Vasconcelos, et al. [10] conducted a study about the numerical modelling of the transition between free surface and pressurised flow in storm sewers. Erpicum, et al. [2] carried out an experimental and numerical investigation of mixed flow in a gallery; Kerger [3] considered this flow with the air/water interaction on numerical simulation point of view.

On the other hand, 2D shallow flows, where the lateral velocity is not negligible with respect to the main direction one, are also common in hydraulic engineering. They have been extensively studied and modelled for years, for example, Dewals, et al. [11] analysed experimentally, numerically and theoretically the free surface flows in several shallow rectangular basins and Dufresne, et al. [12] carried out a numerical investigation on the flow patterns in rectangular shallow reservoirs. Such flows in mixed configurations, first mentioned in Nam, et al. [13], have not been fully studied thoroughly to date, neither numerically nor experimentally, especially for the flow patterns in transition regime from free surface (in a channel) to pressurised flow (in a conduit).

With the objective of contributing to the filling of this gap, a combined numerical/experimental study has been currently undertaken at the University of Liège (Belgium). The goals of

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this study are to assess the accuracy of an existing numerical model in representing 2D mixed flows configurations and to set up an analytical formulation to evaluate the local loss coefficient at the transition from a free surface channel to a rectangular conduit.

This paper presents the first results of the numerical simulation study, considering stationary mixed flow taking place in a free surface channel combined with a closed conduit aligned along one of the channel banks. This study has been used to define geometrical configurations and discharge ranges to be analysed experimentally as well as to choose the positions of measurement devices. In addition, numerical results provide a first data set to define the local head loss coefficient value at the transition position.

Test configurations

Geometry

The experimental study is based on the use of a 4.5 m long rectangular channel, 0.98 m wide and 0.50 m deep at the upstream, combined with a 4.5 m long rectangular cross section closed conduit aligned with side walls of the flume. The height of the conduit has been fixed to 100 mm because of discharge range considerations. The width of the conduit has been varied depending on the configurations. In this study, four geometrical configurations have been considered, namely model A-10, model B-10, model C-10 and model D-10, corresponding to a width of the conduit of L , $3L/4$, $2L/4$ and $L/4$, respectively. The conduit is located at the bottom of the channels along the right bank for all considered configurations. The dimensions and definition of these configurations are shown in Fig. 1.

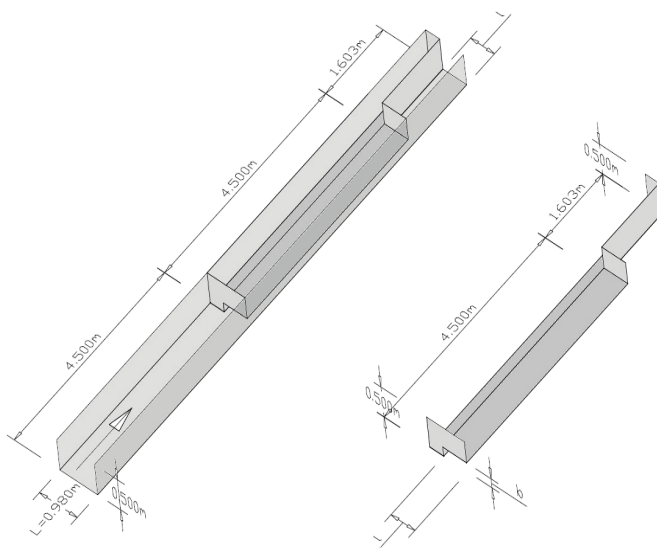


Fig. 1. Sketch of the geometrical configuration (L is the conduit width and b is the conduit height).

At the downstream, a 1.6 m long rectangular free surface channel reach has been added with a width equal to the width of the conduit in order to get a stationary downstream boundary condition and avoid a formation of a recirculation flow area, which had been discussed in Nam, et al. [13].

Hydraulic conditions

The steady discharges range was chosen depending on the geometric configuration in order to fit with the height of upstream channel walls. They are presented in the following Table 1. For the downstream water level, an example of a given discharge of $0.06 \text{ m}^3/\text{s}$ and configuration B-10 shows a linear relation between upstream water levels and downstream ones, as presented in detail in Fig. 2.

Table 1. Characteristic and considered discharges for each geometrical configuration.

Test configurations	L (m)	b (m)	Discharge (m^3/s)
A-10	$L=0.98$	0.10	0.020; 0.040; 0.050; 0.060; 0.070; 0.080; 0.090
B-10	$3L/4=0.735$	0.10	0.010; 0.020; 0.040; 0.060; 0.080; 0.090
C-10	$2L/4=0.49$	0.10	0.005; 0.010; 0.020; 0.040; 0.005; 0.060; 0.080
D-10	$L/4=0.245$	0.10	0.005; 0.010; 0.020; 0.025; 0.030; 0.035; 0.040

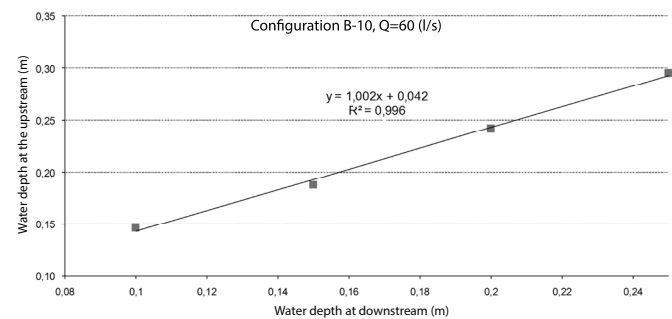


Fig. 2. Relation between upstream and downstream water depths, configuration B-10, $Q = 0.06 \text{ m}^3/\text{s}$.

Measurement cross sections

Specific cross sections have been selected to measure flow features, in order to compute the flow energy and to compare experimental and numerical results. They are located in Fig. 3. Sections 1 and 4 are far enough from the transition section to ensure uniform flow condition and thus, to help in computing the flow energy in the free surface channel and at the closed conduit, respectively. Sections 2, 3 and section 5, 6 are characteristic of the inlet and outlet flow of the conduit, respectively. In addition, the most outlet section of the model (the section at the end of the downstream free surface channel) is used to determine the downstream boundary condition, referred as the water depth, which is fixed at 0.15 (m), whatever be the discharge and geometrical configurations.

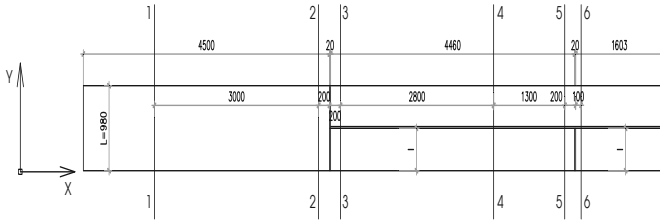


Fig. 3. Positions of the measurement cross sections - Plane view of the system.

Numerical simulations

Numerical model

The 2D multiblock flow solver WOLF2D, part of the modelling system WOLF, is based on the shallow water equations [14]. This set of equations is usually used to model two-dimensionnal unsteady open channel flows, i.e. natural flows where the vertical velocity component is small compared to both the horizontal components [15]. It is derived by depth-integrating the Navier Stoke equations. It counts for hydrostatic pressure distribution and uniform velocity components along the water depth.

Using unified pressure gradients, the shallow water equations' applicability is extended to pressurised flow. Considering the Preissmann slot model [16], pressurised flow can be calculated by the Saint-Venant equations by adding a conceptual slot on the top of a pipe. When the water depth is higher the maximum level of the cross-section pipe, it provides a free surface flow concept, for which the slot geometry affects on the gravity wave speed [3].

To deal with steady pressurised flows, the Saint Venant equations writes as in Eqs. 1-3. The Preissmann slot dimensions are the mesh size as in steady flow and the pressure is not related to the slot characteristics.

$$\frac{\partial h}{\partial t} + \frac{\partial ub}{\partial x} + \frac{\partial vb}{\partial y} = 0 \quad (1)$$

$$\frac{\partial}{\partial t}(bu) + \frac{\partial}{\partial x}\left(bu^2 + \frac{g(2h-b)b}{2}\right) + \frac{\partial}{\partial y}(buv) = -gh_b \frac{\partial z_b}{\partial x} + gh_r \frac{\partial z_r}{\partial x} + gh_j J_x \quad (2)$$

$$\frac{\partial}{\partial t}(bv) + \frac{\partial}{\partial y}\left(bv^2 + \frac{g(2h-b)b}{2}\right) + \frac{\partial}{\partial x}(buv) = -gh_b \frac{\partial z_b}{\partial y} + gh_r \frac{\partial z_r}{\partial y} + gh_j J_y \quad (3)$$

In equations 1-3, u is the velocity component along x axis, v is the velocity component along y axis, h is the water depth, b is the conduit heighth, z_b and z_r are the bottom and roof elevations, h_b , h_r , and h_j are equivalent pressure terms and J_x and J_y are the components along the axis of the energy slope. The bottom friction is conventionally modelled by the Manning formula [14]. To deal with both free surface and pressurised flows, b is computed as the minimum of the conduit elevation (infinity in case of free surface reach) and the water depth h (Fig. 4).

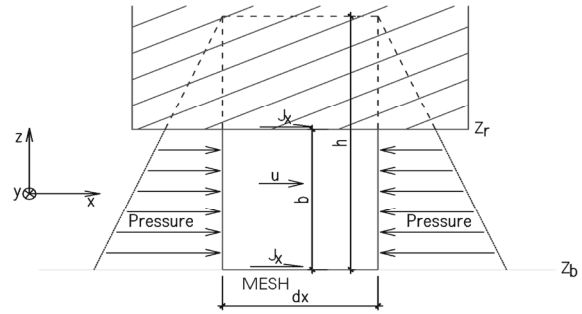


Fig. 4. Sketch of the mathematical model variables.

The conservative equations for the space discretisation was performed by tools of a finite volume scheme. This certifies a proper momentum and mass conservation, which is a requirement for handling reliably discontinuous solutions. Variable reconstruction at interfaces of cells was carried out by constant or linear extrapolation, leading to the case of a second-order spatial accuracy [15]. The flux treatment used an original flux-vector splitting technique [15]. The hydrodynamic fluxes were split and evaluated partly downstream and partly upstream according to the Von Neumann stability analysis requirements [17]. Explicit Runge-Kutta schemes were used for time integration.

Numerical computation features

Similar to many previous works of 2D shallow flows, in this study, a Cartesian grid was exploited, with a cell size of 0.01 m. Variable reconstruction at cells interfaces was performed linearly, in conjunction with slope limiting, leading to a second-order spatial accuracy [11].

Regarding the boundary conditions, the upstream boundary condition applied at the beginning of the inlet channel is the steady discharges into the model, which are presented in Table 1, and the downstream boundary condition applied at the outlet channel is generally an imposed water height of 0.15 (m) for all the considered configurations, whatever the discharge.

About the initial conditions, all the simulations were carried out starting from a channel with water at rest, having the required water depth $h=0.2$ (m), and in general, to ensure a convergence of the results.

Flow energy computation

Numerical simulations provide the value of water depth h (or pressure in the conduit) and the mean horizontal flow velocity components on each mesh of the computation domain. In each cross section, the mean flow energy E has been computed from this distributed result as follows:

$$E_i = \frac{\sum_{j=1}^N \left(h_j + \frac{v_j^2}{2g} \right)}{N} \quad (4)$$

where, i is the number of the cross sections ($i=1 \div 6$, see Fig. 2), N is the number of computation cells along a cross section and v_j is the velocity component of cell j , normal to the cross section.

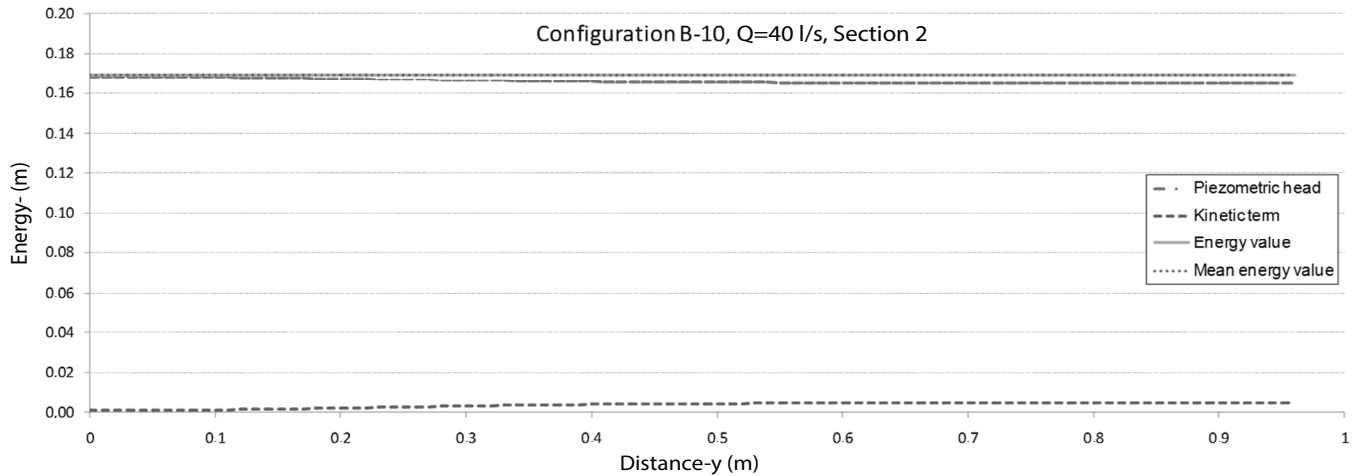


Fig. 5. Example of mean energy computation diagram of configuration B-10, Q= 40 l/s, and cross section 2.

Additionally, the mean energy computation is presented through a typical example of the geometrical configuration B-10, discharge value of 40 l/s at the cross section 2 on Fig. 5.

To evaluate the characteristics of flows at the transition position (at the conduit inlet), the local head loss due to the change of flow regimes and geometrical configurations has to be considered. From E_i values and assuming an uniform flow at the sections 1 and 4 on Fig. 2, the energy loss at this transition location (ΔE_T) is simply computed as:

$$\Delta E_T = \Delta E_{1-4} - \Delta E_{1-c} - \Delta E_{c-4} \quad (5)$$

where, ΔE_{1-4} is the total energy loss from section 1 to section 4. ΔE_{1-c} is the energy loss between section 1 and the section of the conduit inlet, ΔE_{c-4} is the energy loss between the section of the conduit inlet and section 4 (on Fig. 3). The friction resistances, which are computed according to the Manning's friction law with the uniform flow for both free surface channel and closed conduit reaches, are shown below in the following expressions:

$$\Delta E_{1-c/c-4} = J_{1-c/c-4} * l_{1-c/c-4} \quad (6)$$

$$J_{1-c/c-4} = \frac{(nv_{1-c/c-4})^2}{R_{1-c/c-4}^{4/3}} \quad (7)$$

$J_{1-c/c-4}$ are the energy slopes at the free surface channel and the conduit reaches; $v_{1-c/c-4}$ and $R_{1-c/c-4}$ are the uniform velocity and hydraulic radius at these portions, respectively; n is the Manning coefficient.

From ΔE_T values obtained in equation 5 and using the well-known formula for the local head loss computation, the head loss coefficient (k) at the transition location is computed following equation 8. It is important to correctly define the velocity (v). Particularly, all basic quantities are selected such that no problems occur on its determination. Frequently, v is the nominal velocity, for example, the mean value of the incoming or the outgoing velocities being investigated [18]. In this investigation, v -values are related to the upstream cross section of the transition, whatever be the discharge and geometrical configurations [13].

$$k = \frac{2g}{v^2} \Delta E_T \quad (8)$$

Results and discussion

Energy distribution

For a given discharge and geometrical configuration, the flow energy evolution along the system can be evaluated directly from the distribution of corresponding velocity and pressure (or water depth) values on selected cross sections. The energy distribution is featured by a profile of energy value along the channel and is represented in Figs. 6-7. Fig. 6 shows the results for configuration A-10, which has the maximum conduit width (l is equal L=0.98 m) while Fig. 7 shows the results of configuration D-10, which has the minimum conduit width (l is equal L/4=0.245 m) and smaller discharge values.

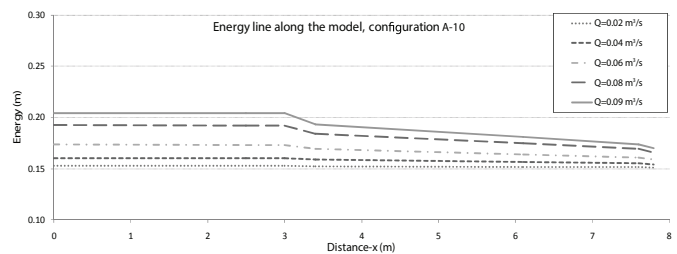


Fig. 6. Energy versus distance along the channel (sections 1-6 on Fig. 3), configuration A-10, Q=0.02-0.09 (m³/s).

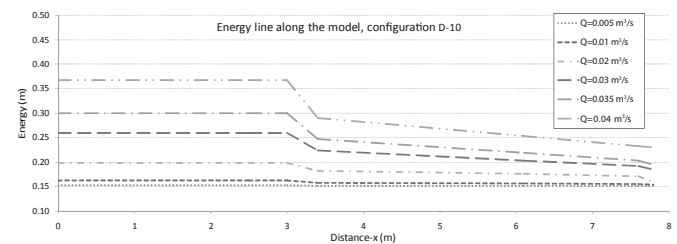


Fig. 7. Energy versus distance along the channel (sections 1-6 on Fig. 3), configuration D-10, Q=0.005-0.04 (m³/s).

These results show that, in general, the global head loss from upstream to downstream of the model is well reproduced. Additionally, it is easy to observe that the head losses are induced mainly at the conduit inlet and along the conduit while the head loss at the upstream free surface channel is much smaller. Moreover, the head loss is shown properly for the high discharge values ($Q > 0.03 \text{ m}^3/\text{s}$) and smaller conduit width; and not so clearly for smaller discharges ($Q < 0.02 \text{ m}^3/\text{s}$).

Local head loss and local head loss coefficient

Wherever the streamlines direct away from the axial direction of flow due to either a change in the wall geometry, a local head loss occurs [17]. Additionally, for the mixed flows, the local head loss takes into account the change of the flow regimes. The final results of these values are summarised and represented in Fig. 8 for all considered configurations. These results prove that the areas ratio is the most important parameter to induce head losses, a higher head loss corresponding with a smaller conduit width value, for example, the result of configuration D-10 in Fig. 8. This can be explained by a 2D flow effect and some recirculation areas at both the top and the left side wall of the conduit. In addition, it is clearly realised that the local head loss increased following the increase in the discharge values, and thus, the flow velocity inside the conduit for each configuration.

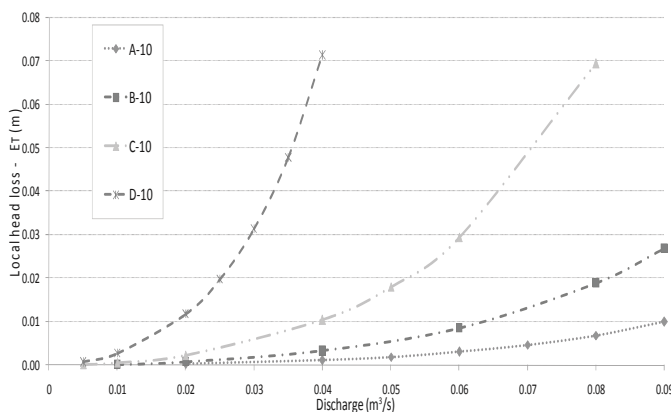


Fig. 8. Local head loss (at the transition location) versus the considered discharges for four configurations.

Regarding the local head loss coefficient (k), depending on the basic formula such as Gardel [19] and Idel'cik [20] to compute this k -value, it is only related with the referent cross sections (in case of flow contraction or expansion). In this study, from the obtained numerical results of k -values and the values of wetted areas at the cross sections 2 and 3 for whatever the

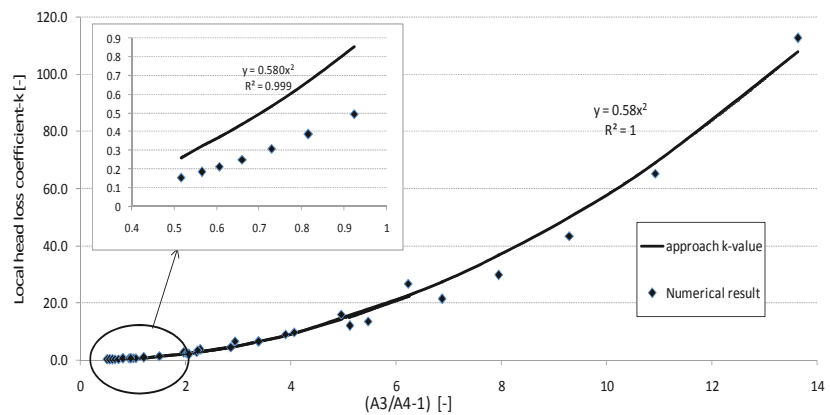


Fig. 9. Determination of the local head loss coefficient at the transition location, depending on the ratio between upstream and downstream cross section areas (at the free surface channel and the closed conduit, respectively).

discharge and all the configuration, a relation between k -value and such sections is proposed, and expressed as follows:

$$k = 0.58 \cdot (A_2/A_3 - 1)^2 \quad (9)$$

where, A_2 and A_3 are the wetted areas at the cross sections 2 and 3 (in the Fig. 3), respectively.

Figure 9 shows that the k -values are in extremely good accordance with equation 9 for all the ranges of the given discharge, except configuration A-10, which is considered to have 1D flow and small k -values.

Conclusions

Several numerical simulations have been carried out to observe the flow patterns of stationary mixed flows in a free surface channel combined with a rectangular conduit of variable width. Several configurations and a wide range of discharges have been carefully considered to simulate and determine the physical parameters, providing a large set of data to characterise the flow.

The numerical results provide a first data set to define the local head loss coefficient value at the transition position and help in defining the geometrical configurations and discharge ranges to be analysed experimentally as well as to choose the positions of measurement devices.

In the next steps, an experimental study will be carried out for the same geometrical configuration to verify the numerical results, especially for the proposed formula of the local head loss coefficient at the transition position, and a detailed analysis of both physical and numerical results will be performed in order to identify the possible causes of discrepancy. In addition, similar works will be conducted for other conduit geometries to enlarge the importance of 2D effects and thus,

the complexity of the flow.

Notations:

A_2 : wetted area of cross section 2

A_3 : wetted area of cross section 3

B : conduit height

G : gravity acceleration

H : water depth

h_b, h_p, h_j : equivalent pressure terms

i : number of the cross section

J_x : component along the x axis of energy slope

J_y : component along the y axis of energy slope

J_{1-c} : energy slope at free surface channel portion from section 1 to the conduit inlet section

J_{c-4} : energy slope at closed conduit reach from the conduit inlet section to section 4

k : local head loss coefficient

L : upstream channel width

L : conduit width

l_{1-c} : length of free surface channel from section 1 to the conduit inlet section

l_{c-4} : length of the conduit reach from the conduit inlet section to section 4
 N : number of computation cells along a cross section

N : manning coefficient

R_{1-c} : hydraulic radial of the upstream free surface channel

R_{c-4} : hydraulic radial of closed conduit portion

U : velocity component along x axis

V : velocity component along y axis

v_j : velocity component of cell j normal to the cross section

x, y : space coordinate terms z_b : elevation of conduit bottom

z_r : elevation of conduit roof

ΔE_T : energy loss at the transition

ΔE_{1-c} : energy loss from section 1 to the conduit inlet section

ΔE_{c-4} : energy loss from the conduit inlet section to section 4

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Arsenic contamination in groundwater in the Red river delta, Vietnam - a review

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Abstract:

Arsenic contamination in groundwater and its effect on human health has been a growing concern over recent decades. Some of the most severe incidents occurred in South and Southeast Asia, including the Red river delta, Vietnam. The highest concentration of arsenic found in the Red river delta was 810 µg/L, 16 times higher than the standard guidelines given by WHO for levels of arsenic concentration in groundwater (50 µg/L). However, the contamination levels were not uniform in the whole area. The arsenic levels might be affected by natural factors such as the characteristics of the aquifer, the chemical composition of groundwater and by human activities such as the exploitation of groundwater in the urban and industrial areas or irrigation in rural areas. Due to the complex mobilisation of arsenic in sediment and groundwater, questions remain about arsenic distribution, which are yet to be answered and are in need of further study.

Keywords: aquifers, arsenic contamination, arsenic mobilization, arsenic releasing mechanism, Fe oxy-hydroxide, groundwater, Red river delta.

Classification number: 2.2

Introduction

The Red river delta is one of the most densely populated regions in Vietnam, with a population of about 17 million people spread over an area of approximately 14,000 km². Over the last several decades, groundwater has become a common water source for domestic, manufacturing, breeding and cultivation purposes. However, due to the geochemical structure of the sediments in this delta, the groundwater in the aquifers here contains high arsenic content. Arsenic is a natural element in the sediment and mineral. The release of arsenic into groundwater only occurs under favourable conditions that lead to the contamination of groundwater. In Vietnam, the standard for arsenic concentration in groundwater is 50 µg/L and in drinking water it is 10 µg/L. Because of its high toxicity and adverse effects on human health in even small concentrations, a number of studies have been carried over the past twenty years to assess the arsenic contamination

level in groundwater in the Red river delta. The research group at the Research Centre for Environmental Technology and Sustainable Development, VNU University of Science is one of the first groups to study arsenic contamination in groundwater and has the most publications in this field in Vietnam. Approximately 20 publications related to arsenic contamination in groundwater in the Red river delta have been published in Vietnamese and international journals. We have implemented international collaboration projects for a long time, including Vietnam - German cooperation such as VIGERAS, a BMBF/DFG - MOST funded project on arsenic in the food chain, from 2008 till 2011. Recent studies have shown that a strong need exists for the development of methods to control arsenic in rice, that more comprehensive knowledge is needed about arsenic dynamics in the rhizosphere, especially about the behaviour of arsenic within the root plaque, to enhance knowledge of the mechanisms by which arsenic enters plants, that genetic predisposition of human beings and mental impact are not considered by the current threshold values, and this is a health challenge requiring greater attention [1].

Actual state of arsenic contamination in groundwater in the Red river delta, Vietnam

A detailed study on a large scale about the state of arsenic contamination in groundwater was carried out in 2011 by Winkel, et al. [2]. The results showed that about 7 million people in this delta have been using the groundwater contaminated by arsenic and other toxic elements such as manganese, selenium and barium. The authors analysed the chemical composition data from 512 groundwater samples, taken from the wells of private houses, to create the distribution maps for arsenic and other elements. The results showed that the arsenic concentration ranged from <0.1 to 810 µg/L, with 27% of the samples exceeding the value of 10 µg/L that is the WHO standard for arsenic level in drinking water. The wells with the highest concentration of arsenic were located along the two banks of the Red river up to a distance of approximately 20 km from the river. The Southwest area of the delta, which was the position of the ancient Red river, was also high in pollution (Fig. 1). Another finding from the results was that the distribution of arsenic varied from well to well, without any clear tendency.

Apart from the above study, there are some other researches that focused on specific areas on a smaller scale. For example, in 2001 the very first study on arsenic contamination in Vietnam was implemented by Berg, et al. [3]. The study site was Hanoi and its suburban districts. The range of arsenic in the samples was

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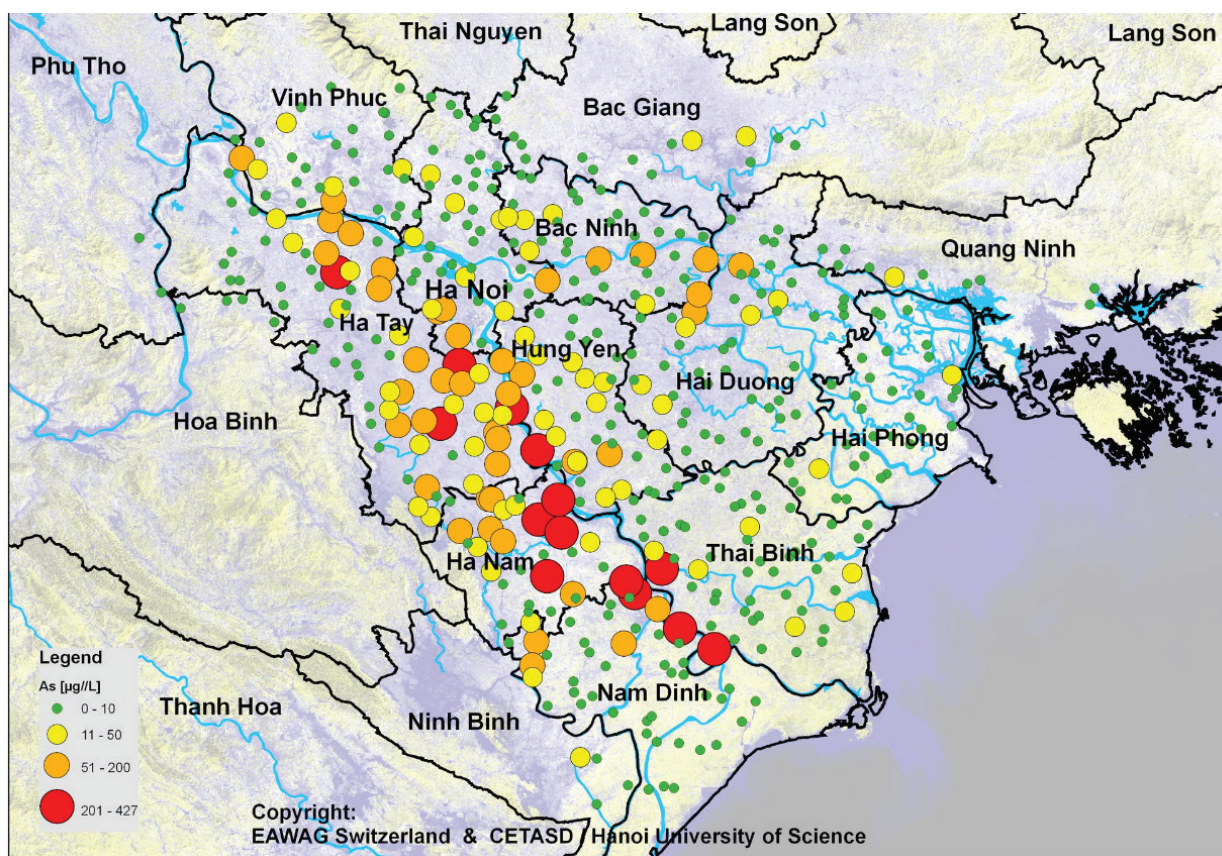


Fig. 1. Arsenic distribution in groundwater in the Red river delta, Vietnam.

from 1 to 3,050 $\mu\text{g/L}$, with an average of 159 $\mu\text{g/L}$. By analysing the untreated groundwater samples that were exploited from the deeper aquifer at 8 domestic water supply factories, they found that arsenic concentrations ranged from 240 to 320 $\mu\text{g/L}$ at 3 factories, and from 37-82 $\mu\text{g/L}$ at five other factories. After air bubbling and sand filters were applied at these factories to remove iron, the arsenic concentration decreased to 25-91 $\mu\text{g/L}$. However, 50% of the samples still contained high arsenic concentration, exceeding the Vietnamese standard at that time (50 $\mu\text{g/L}$).

Agusa, et al. (2006) studied the arsenic concentration in 25 groundwater samples in Gia Lam and Thanh Tri districts [4]. The variation range of arsenic here was from <0.1 to 330 $\mu\text{g/L}$, 40% higher than the WHO standard for drinking water (10 $\mu\text{g/L}$). In addition, 76% and 12% of the samples also exceeded the WHO standard for Mn and Ba, respectively.

Another study of Agusa, et al. (2014) expanded the study site to other areas in the Southwest of the Red river delta that showed signals of high contamination, such as Tu Liem, Dan Phuong, Hoai Duc (Hanoi) and Ly Nhan (Ha Nam) [5]. This study compared not only the contamination level in different areas, but also provided the distribution of arsenic concentration in a narrow area of about 1-2 km^2 . For instance, in Hoai Duc, Hanoi (formerly Ha Tay), the arsenic concentration in 33 samples ranged from <1-377 $\mu\text{g/L}$ with a mean value of 133 $\mu\text{g/L}$. 86% of the samples did not meet the standard for drinking water. 51% of the wells contained arsenic concentration higher than 300 $\mu\text{g/L}$. Compared to other parts of

the world, this was a very high contamination level, considered the cause of skin diseases occurring in Western India and Bangladesh. The contamination level was even higher in Ly Nhan (Ha Nam). The arsenic concentration in 15 groundwater samples was from 311-598 $\mu\text{g/L}$, averaging 420 $\mu\text{g/L}$. The contamination level in this area was similar for all the wells. If the inhabitants here use the groundwater directly for eating and drinking, there is an obvious risk of arsenic-related diseases. Fortunately, after filtering with sand filters, the mean arsenic concentration in groundwater in Ly Nhan reduced to 23 $\mu\text{g/L}$. Therefore, the risk of arsenic exposure through filtered drinking water greatly reduced. In contrast, the groundwater in Hoai Duc, even after the sand filters, still contained a high concentration of arsenic (averaged 74 $\mu\text{g/L}$). Some samples even reached an arsenic concentration of 309 $\mu\text{g/L}$. Arsenic filtering capacity of the sand filters depend on many factors such as iron, phosphate concentration in groundwater, the sand layer thickness, the temporal changing of sand layer during the period of use, etc. The wells in Dan Phuong contained arsenic concentration from <1-632 $\mu\text{g/L}$ ($n=13$), average 43 $\mu\text{g/L}$. In general, the distribution of arsenic in groundwater in the Red river delta was different from area to area. The reason for this difference is still an unanswered question which attracts international and Vietnamese scientists.

Quite different from the above study sites, in the Red river delta, there were areas that were free from arsenic contamination. In their study in 2014, Agusa, et al. found that the arsenic in

groundwater collected at Tu Liem was ($n=5$) $<1 \mu\text{g/L}$ [5]. The question here was whether arsenic was released into groundwater or not. Was it released into groundwater but then got transferred to other areas due to hydrologic conditions or was it re-absorbed in the sediment? These are hypotheses that are still being studied all over the world.

The arsenic contamination in groundwater in the Red river delta has been assessed systematically with high reliability. The results, which were published in international journals, show that the high arsenic contamination was concentrated in the Southwestern delta and along the Red river banks. The distribution can be quite different in a narrow area, with a non-contaminated area existing alongside a highly contaminated area. However, the finding results are applicable for the respective study sites only, and unsuitable for use in other contiguous areas. At present, arsenic contamination prediction are not capable, because we have not found the exact arsenic forming process and its transportation pathways in the aquifers. Determination of arsenic contamination needs to be done in detail and particularly for each well. However, this is unrealistic due to the limited funding compared to the large number of wells. A solution, which was used earlier, is using the arsenic determination toolkit to determine the arsenic concentrations in all the wells. Yet, the limitation in carrying out the experiment and quality controlling caused the unreliable of the results. Therefore, determination of the study areas and the arsenic contamination levels in groundwater in Vietnam are still in need of implementation.

Arsenic forming process in groundwater in the Red river delta, Vietnam

Studying the actual state of arsenic contamination is an important task in order to determine the range and the pollution levels. This information can be used for warning people living in the contaminated areas. The task therefore is to understand why arsenic is formed in groundwater, and whether the release of arsenic into groundwater is affected by human activities. These questions require the involvement of specialists from fields such as geochemistry, hydrology, water chemistry, soil bacteria, modelling, etc.

The geochemical process related to the arsenic forming and transportation model in an area on a bank of the Red river was studied by Postma, et al. (2007) [6]. The results showed that most the iron minerals here were in the form of goethite and partly hematite. Based on a hypothesis that arsenic exists mainly in iron minerals in sediment, a sediment extraction experiment was carried out by the research group to study the distribution of arsenic in iron minerals. The results showed that while most of the arsenic was linked with iron oxide, the amount of absorbed arsenic in the sediment surface was low. On the surface of iron oxide, As(III) only accounted for about 3% of the surface position; the remaining was carbonate and silicate. Part of the arsenic extracted from iron oxide was absorbed back into the mineral surface, leading to the decrease of arsenic concentration in groundwater.

Studying the groundwater chemical composition showed the reductive condition in the aquifers, which related to the degradation of organic compounds, the reduction of iron oxide and the formation of methane. The specific pressure of CO_2 in

groundwater increased due to the dissolution of carbonate in soil. Arsenic concentration showed an increasing trend according to depth and peaked at $550 \mu\text{g/L}$, mostly in the form of As(III). Arsenic concentration appeared to correlate with NH_4^+ , which indicated the relationship between the degradation of organic matter and arsenic release from the reduced iron oxide. From the analysis, one can also see that part of the iron (II) re-precipitated in the form of siderite (FeCO_3) that was less effective in absorbing arsenic. The extraction experiment with HCl and ascorbic acid (pH 3) showed that with river sediment, most of the iron and arsenic was reductively dissolved by ascorbic acid, while a very small amount of arsenic and iron was extracted by HCl. This indicated the link between arsenic and iron oxide. Moreover, the difference in extracted iron using ascorbic acid and HCl in river sediment indicated the reductive dissolution of Fe(III) caused by ascorbic acid. In spite of this, along with oxidised sediment, iron also was dissolved by ascorbic acid, but there was only a small amount of arsenic absorbed in the sediment. This proved that arsenic was not present in oxidised iron mineral in sediment [7].

In contrast, for sediment in the reductive aquifers, a large amount of Fe(II) and As was extracted using HCl. This might be because of the presence of the mineral that contained Fe(II) linked with origin-unknown. From the data of the ascorbic acid extraction, there were both As(V) and As(III) in river sediment, while the reductive sediment only contained As(III). This indicated that mineral analysis cannot be used to predict the activity of iron oxide related to arsenic release.

Studying the sediment in South and Southeast Hanoi, Berg, et al. (2008) realized that the arsenic content in sediment was in the range of $1.3\text{--}22 \mu\text{g/g}$ [8]. This was the common content of arsenic in natural sediment, and arsenic showed a strong relationship with iron content ($r^2>0.8$). In the peat area, the content of iron in sediment and water was higher than in other areas. The average mole ratio of Fe/As in water was 350 and in sediment it was 8,700. The high reductive iron in sediment might be the newly formed mineral and this mineral re-absorbed arsenic from groundwater into the sediment. For the water and sediment samples on the bank of the Red river, these ratios were 68 and 4,700, respectively. In this condition, the arsenic reabsorbing process hardly happened, and therefore the arsenic concentration in water was still remarkably high.

In another research in Southeast Hanoi, Eiche, et al. (2008) studied the difference in arsenic concentration at two sites that were approximately 700 m apart. The arsenic concentration at the low site (site L) was $<10 \mu\text{g/L}$, and at the high site (site H) was $600 \mu\text{g/L}$ [9]. Sediment extraction experiments were carried out to understand why arsenic was released at site H and not at site L. The results demonstrated that the mineralogy and geochemical properties of the sediments collected at these two sites were not significantly different. The major difference was in sediment colour. At the high arsenic concentration site, most of the arsenic was absorbed on the surface of grey sand that was a mixture of Fe(II)/Fe(III), whereas at the site with low arsenic concentration, arsenic was found to bond in strong links with brownish Fe(III) oxide. High iron concentration (14 mg/L) and low concentration of sulphur ($<0.3 \text{ mg/L}$) found at the polluted area indicated the reduction condition. NH_4^+ concentration was 10 mg/L , HCO_3^- concentration was 500 mg/L and dissolved P concentration was

6 mg/L. These figures indicated that there was Fe oxy-hydroxide reduction process by organisms. The precipitation processes to form siderite and vivianite due to oversaturation and the formation of amorphous Fe(II)/As(III) or iron sulphur might occur at site H. On the other hand, at site L, iron concentration was 1 mg/L and sulphur concentration was 3.8 mg/L. This conflicting phenomenon of the reductive/oxidised conditions at these two sites is yet to be explained.

The studies on the relationship between sediment mineralogy characteristics and the presence of arsenic in groundwater have not thrown up any clear answers. The common finding of most of the authors was that the reductive conditions occurred at the polluted sites, and at the unpolluted sides, the conditions were oxidised.

Arsenic mobilisation in the aquifers

Arsenic, which is released from sediment into groundwater, can be transported to other areas. While being transported, arsenic would take part in other chemical reactions, absorption and desorption processes. That is the reason why simple chemical reactions and tranquil correlation can hardly be used to explain the occurrence of arsenic. One research group has studied the mobilisation of arsenic in aquifers. Can arsenic be transported from a high concentration area to other areas which are free from arsenic?

Alexander van Geen, et al. (2013) initially acknowledged the alteration in hydrology flow and the redox properties of the aquifer due to water exploitation at one district in Southeast Hanoi [10]. The contour lines in figure 2 show that the groundwater level has fallen within the city. The decrease of groundwater level gradient stimulated the mobilisation of arsenic from the shallow aquifers on the riverside to the deeper aquifers. Arsenic infiltrated approximately 120 m from the polluted Holocene to the unpolluted Pleistocene. The results also indicated that arsenic in groundwater was absorbed into the sandy sediment; thereby the transportation rate decreased about 20 times compared to water transportation.

Expanding this research area, Mason O. Stahl, et al. found out that high intensity of groundwater pumping reversed the natural flow of groundwater [11]. In natural conditions, groundwater would pour into the rivers through the apertures along the banks of the rivers. However, in this case, the river water flowed back into the groundwater because of the lower groundwater level due to water pumping. Analysed results showed that the arsenic concentration in the newly alluvial shallow pore holes (<10 years) was remarkably high (about 1,000 µg/L). This amount of arsenic would move down to the deeper aquifers when the water level fell.

Recently, Postma, et al. (2010) used tritium-helium isotope to determine the age of groundwater along the banks of the Red river. The results showed that the age of the deep aquifer (about

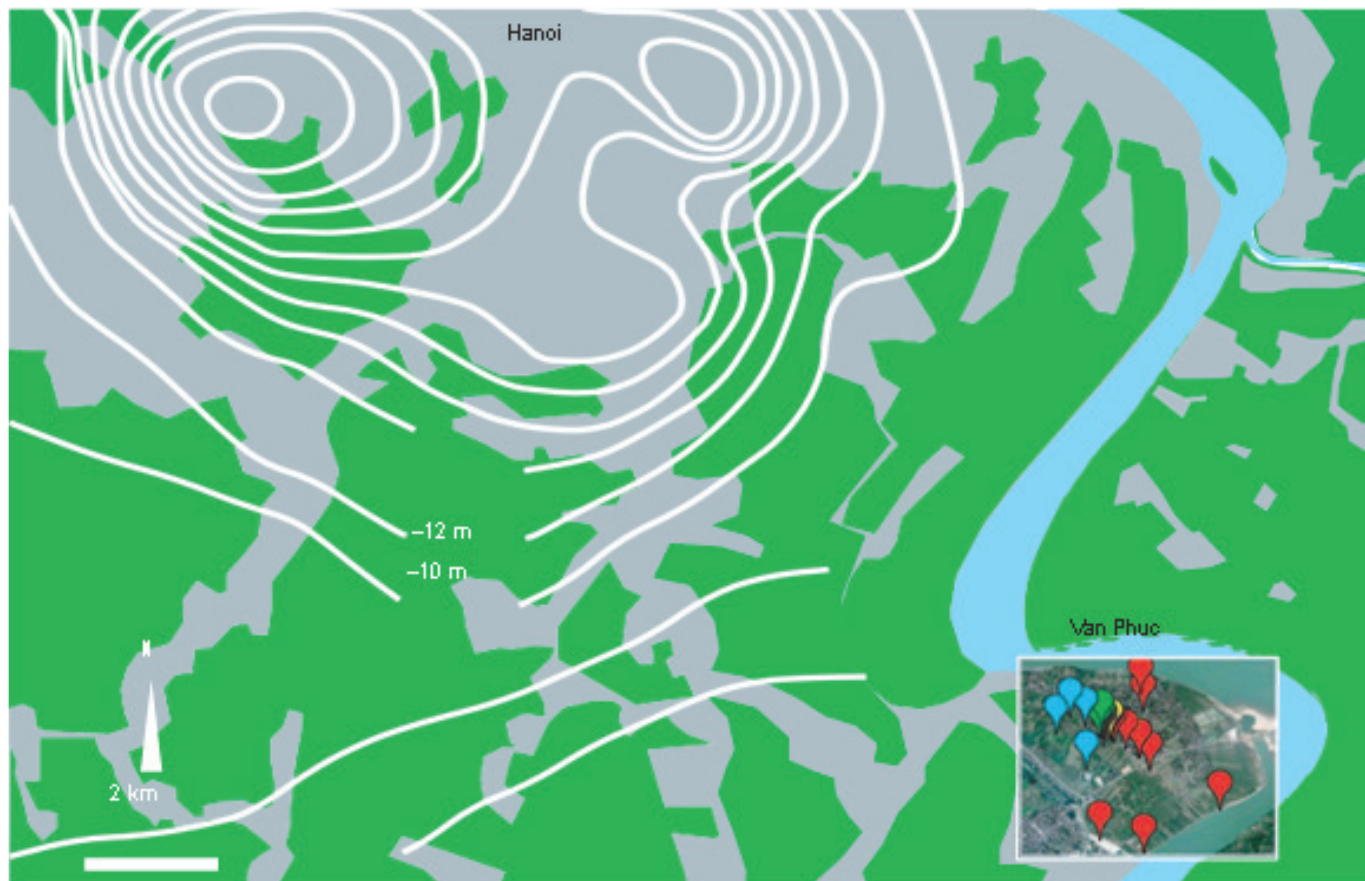


Fig. 2. Relationship between groundwater level and arsenic mobilisation in groundwater on the river banks of the Red river.

40 m deep) next to the river was approximately 1.3 ± 0.8 years [12]. This was equivalent to a vertical transportation rate of about 19 m/year. The conductivity and specific pressure of CO_2 indicated that the water in the sandy Holocene layers and gravelly Pleistocene layers was recharged by river water and this recharged water was also exploited. Dissolved oxygen in the recharged water was consumed in the oxidation of dissolved organic matter in water and sediment. If these processes continued to happen, the reduction of arsenic-bound iron oxides would occur and release arsenic into groundwater. Arsenic concentration in water was affected by the balance between arsenic being absorbed into sediment and desorption into groundwater.

Conclusions

The actual state of arsenic contamination in groundwater of the Red river delta has been established with the highest contaminated level of $810 \mu\text{g/L}$, 16 times higher than the WHO standard for arsenic concentration in groundwater. The South and Southwestern parts of the Red river were much more polluted than other areas. The contamination levels were not uniform in the whole area. The reason for this phenomenon was yet to be determined. In addition, groundwater in this area was polluted by other elements such as manganese, barium, iron and ammonium.

The release of arsenic from sediment into groundwater related to the dissolution redox processes of arsenic-bound iron oxy-hydroxide, demonstrated by the chemical composition of groundwater with a large amount of arsenic, reductive iron, ammonium, bicarbonate and methane. Arsenic released from sediment can be re-absorbed into newly forming minerals or transported to nearby areas.

Hydrological flows in the aquifers of the Red river delta may have changed a lot due to water exploitation in the urban and industrial areas or due to irrigation in rural areas. These changes have caused the penetration of arsenic from the polluted to the unpolluted aquifers. River water exploitation by banks filtration has also increased the risk of moving the reductive conditions from the riverside aquifers to older oxidised aquifers that have not so far been contaminated by arsenic.

Although the whole picture of arsenic contamination in groundwater still has unanswered questions, the above results are warnings about the arsenic pollution levels in groundwater and the effect of human activities on the valuable water resources in the Red river delta. We have recently instituted an international collaboration, namely integrated clean water technologies for rural regions of Vietnam, to face the challenges of arsenic groundwater contamination and decentralised sewage treatment. In the near future, we will continue this potential orientation in order to further improve the ground water quality and safe water supply based on detailed investigations about the biogeochemical aspects related to arsenic contamination and the corresponding health risk assessment in the Red river delta.

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Automated manufacturing of composites

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Abstract:

Long fibre reinforced polymer composite materials have found many applications in many industries, such as aerospace, automotive, marine, wind turbine, and sports. Techniques for the manufacturing of structures used in these industries have been mainly Hand Lay Up (HLU), and Liquid Composite Moulding. While there are a few automated methods of manufacturing, such as Filament Winding and Pultrusion, these techniques are restricted to make structures that consist of surfaces of revolution, or fibres that are aligned only along one direction. The conventional methods of manufacturing of composites are therefore very restricted, either in slow rate of production, or in the shapes of structures that can be made. The advent of Automated fibre Placement (AFP) machines and automated tape lay up machines have brought forward new capabilities where structures of different shapes may be manufactured at relatively higher speeds. This paper presents an overview of the applications of AFP for the processing of structures made from thermoset matrix and thermoplastic matrix composites. Advantages and disadvantages, along with issues associated with the use of this new technique in the processing of each type of material will be discussed.

Keywords: *Automated fibre Placement, automated tape lay up, automation, composite materials, composite structures, manufacturing, thermoplastic matrix composites, thermoset matrix composites.*

Classification number: 2.3

Introduction

Previous manufacturing methods

A common method for the manufacturing of composites is HLU. The stacks of the thermoset matrix composite materials deposited by HLU are cured either at room temperature (for the case of glass/polyester composites) or in an autoclave (for the case of carbon/epoxy composites). Other techniques, with some degree of automation, include Filament Winding, Pultrusion, Liquid Composite Moulding, and Compression Moulding. These techniques have been used to make important engineering structures. Their limitations include the shape of the article (cylindrical or spherical shape in the case of Filament Winding, fibres in only one direction in the case of Pultrusion, somewhat slower rate in the case of Liquid Composite Moulding, and small sized parts in the case of Compression Moulding). The increasing use of composites in larger structures (such as large airplane fuselage, large wind turbine blades) has given rise to the need for more automation. The two most commonly used machines for this automation are the automated tape laying (ATL) machine and the AFP. These two types of machines have many similarities in which they both can deposit composite material layers at high speed. They differ mainly in the width of the laid down material. ATL can deposit wider tapes [from 1/2 inch (12.7 mm) to 12 inches (304.8 mm) wide], while AFP delivers narrower tape [from 1/8 inch (3.18 mm) to 1/2 inch (12.7 mm)]. AFP can make up for the difference by using multi-tow courses. ATL is usually used for thermoset matrix composites, while AFP can be used for both thermoset matrix and thermoplastic matrix composites. In what follows, for the sake of brevity, AFP is described but many aspects of the description also apply to ATL.

Description of the AFP machine

For industrial applications, AFP machines can be very large. These machines can be used to make composite structures that are tens of meters long. They can deposit composite tows at the rate of hundreds of millimetres (or even metres) per second. Many companies in the aerospace industries have utilized these machines to make large composite structures over the past decades. A few examples are the fuselage of Boeing 787, and of the Airbus 380. The work done on AFP at the university

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level is relatively later than the activities in the industry. This is due to the high cost of the machine, the high demand for space to house the machine, and the high cost for its operation. However, due to the need to understand the mechanisms responsible for the performance of composite structures made using the technique, a few universities have invested in machines to study this technology, Concordia university included. Fig. 1 shows a photo of this machine at Concordia. The machine was manufactured by Automated Dynamics in New York (USA). It has 6 degrees of freedom. It can process both thermoset composites and thermoplastic composites. It uses a hot gas torch as the source of heating. Even though this machine is much smaller than the industrial type of machine, it has all the necessary features of a typical AFP machine. Fig. 2 shows a schematic of the device for tape deposition.

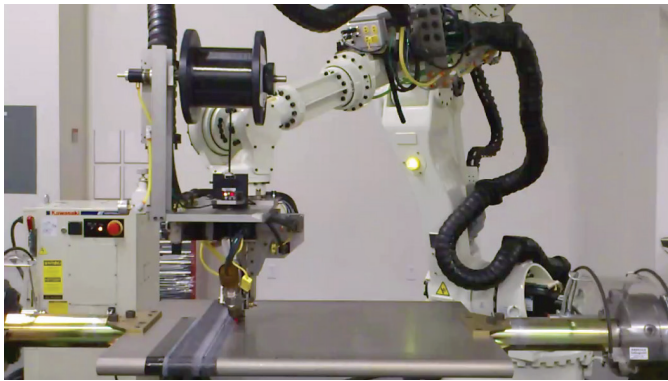


Fig. 1. Photo of an AFP machine.

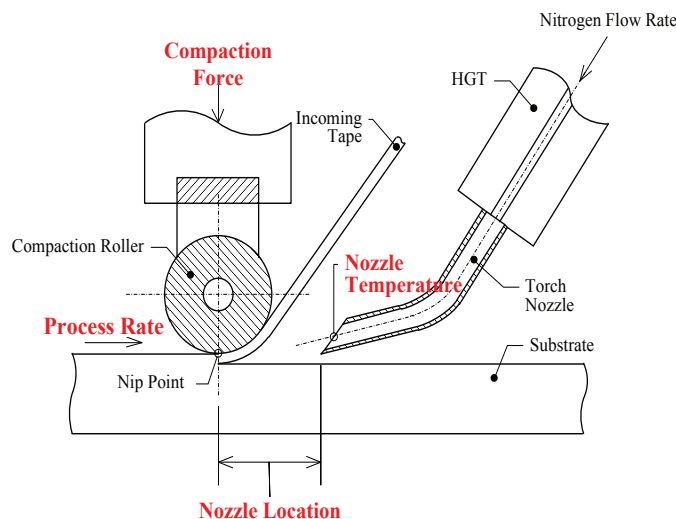


Fig. 2. Schematic of the tape deposition and devices.

Even though machines for automated manufacturing of composites are similar for both thermoset matrix and thermoplastic matrix composites, there are significant differences in the requirements for the intended purpose of the technology, the heating level, the need for subsequent

processes, and the defects that may occur in the part, etc. For thermoset matrix composites, the intention of the automation is restricted only to the fast rate of material deposition. On the other hand, the intention of doing automation for thermoplastic composites is to eliminate all aspects of the manual work. For some structures, it may not be possible to use other techniques to make the thermoplastic composite part, and automation is the only way. In what follows, the automated manufacturing of thermoset matrix composites, followed by that of thermoplastic composites, will be presented.

Automated manufacturing of thermoset matrix composites

Description

The process of manufacturing of thermoset matrix composites using the conventional method consists of the following stages:

1. Prepreg control.
2. Tool preparation.
3. Prepreg deposition.
4. Vacuum bagging.
5. Curing.
6. Nondestructive evaluation and testing.
7. Trimming and machining.
8. Assembly.

The automation of the process can come in for steps 3, 6, 7, and 8. For ATL and AFP processes, only step 3 (prepreg deposition) is automated.

The fibre placement process is shown schematically in Fig. 3. The fibre tape (or tows) is fed to the NIP point under a compression roller. Preheating (to enhance the tackiness of the tape) may or may not be used. The pressure applied by the roller may help to reduce the debulking efforts for the stack of layers. The main objective in using automated lay up is to increase the speed of material deposition. After the stack of prepreg layers has been laid, the subsequent steps (vacuum bagging, curing, etc.) need to be carried out as in a conventional process.

Step 6 mentions ‘Non destructive evaluation and testing’. This refers to the evaluation done on the final, solid piece of composites. In the case of automated material deposition, since many narrow strips are laid down, it is essential to check for the quality of the laid prepregs during the deposition period. Many defects such as tow misorientation, twisted tows, misalignment between neighbouring tows, laps, gaps, serrated edges due to cutting at the end of the courses, etc., need to be detected, and corrected if necessary at this stage. Leaving this detection to a later stage may make it impossible to detect the defects. As such, in addition to the Non destructive evaluation and testing in step 6, another step 3a (in situ defect detection) needs to be added for the automated process.

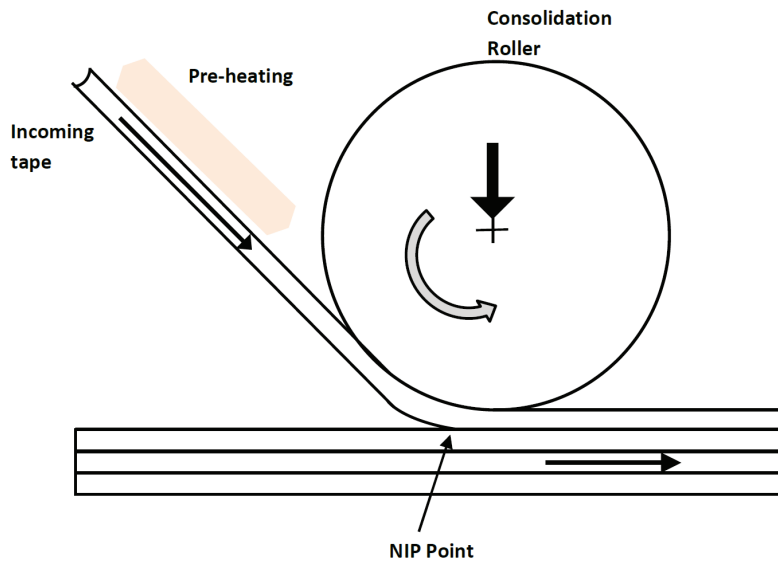


Fig. 3. Fibre placement process.

The process of automated manufacturing of composites

The automated machine usually consists of the following five main components:

A spindle axis to mount the mandrel: this spindle provides the rotation of the mandrel.

A mechanism to deliver the composite tows to the NIP point: composite tows can be single tow or multiple of tows. Simple machines can feed one tow at a time, or a course of up to 32 tows is possible. The tow width can vary from 1/8 inch (3.18 mm) up to 1/2 inch (12.7 mm). Composite tows are usually preregs of thermoset composites, such as glass/epoxy or carbon/epoxy. The tows normally come from creels, either mounted directly on the depositing head or from a chamber located in the vicinity of the machine. In the case of thermoset composites, to avoid some curing of the thermoset resin during storage before the AFP process, the tow chamber is usually refrigerated.

A mechanism to heat the tows: for thermoset composites, preheating of the prepreg may be done. Heating is used to slightly decrease the viscosity of the resin. This in turn serves to increase the tack of the tow(s) to facilitate bonding to the substrate.

A mechanism to apply pressure on the deposited tow for consolidation: it is necessary to apply pressure at the NIP point (Fig. 3) to consolidate the material.

For thermoset matrix composites, this pressure does not have to be very high. Normally, a load of about 40 lbs is sufficient. This consolidation load helps to eliminate the need for pressing used in HLU and possibly the need to do frequent debulking, which can save time. The AFP only does the deposition and consolidation of the stack of preregs, but it does not perform the curing procedure. The stack of preregs

needs to be bagged and cured after the AFP process. This procedure has the disadvantage that two processes are involved (deposition by AFP and bagging as well as curing afterwards) which is time consuming and costly. However, the advantage it has is that the defects that may be induced during the AFP process may be eliminated during the subsequent curing process.

A mechanism to move the NIP point forward: AFP is a continuous process. Once a strip of material is deposited, the machine advances the NIP point to the next material strip for continuous processing. It is desirable to have as fast a speed as possible from the production point of view. Since there is a secondary process of curing in either autoclave or oven, defects such as voids that occur during the deposition stage may be corrected during the secondary stage. As such, the speed of deposition can be high.

Advantages of AFP: there are many advantages in using the automated material deposition:

- Faster rate of material deposition - Reduced debulking time: with an increasing use of composite materials in many engineering structures, there is urgent need to increase the rate of production. The normal rate of material deposition by HLU is about 1 kg/hr. The rate of material deposition by AFP depends on the type of machine. A machine that deposits multiple tows has a higher rate of material deposition than a machine that deposits one tow at a time. The normal rate of material deposition of an AFP machine is about 10 kg/hr [1]. Besides the high rate of material deposition, the compaction applied during the AFP process helps reduce the time required for debulking as usually occurring during the HLU process.

- Less material wastage: since the process is one form of additive manufacturing, tows and layers of materials are deposited on design. As such, the material wastage is much less than in the case of HLU. Fig. 4 shows the situation where a sheet of preregs is cut at 45° to make 45° layers in a laminate ABCD, for HLU. The cut-off materials at the corners are a waste. There is a terminology in the aircraft industry called the Buy/Fly ratio, referring to how much material ends up flying from the amount that was bought. It can be seen from Fig. 4 that this ratio can be about 2. For parts with more complicated geometry, this ratio can go up to 3. This does not happen when narrow tows are placed at a certain desired orientation in the AFP process. Fig. 5 shows the configuration to make the laminate ABCD using AFP lay up tow-by-tow. It can be seen that there is a lot less waste of material. Composite materials are expensive. The use of AFP can reduce the material waste, which in turn results in cost saving and more environmentally friendly manufacturing.

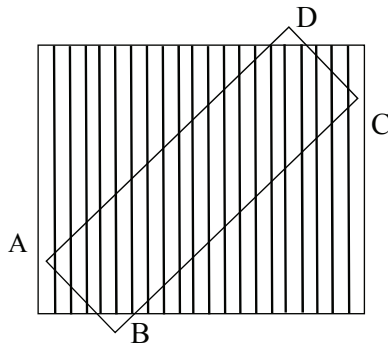


Fig. 4. Corner pieces in a sheet of preregs are cut off, resulting in material waste.

- More repeatability-Less variability: since AFP is done by machine, there is more repeatability and less variability in the quality of the part as compared to conventional process such as HLU, which depends on the skill of the workers at different periods of the work week. When numerous technicians are expected to interpret engineering drawings, while placing material in the same exact location and direction, the process falls short many times. Automation virtually eliminates this difficult feat. The responsibility for interpreting engineering flag notes and ambiguous drawings no longer lies in the hand of the technician. Instead, the engineer dictates and analyses pre-established machine paths before ever reaching the shop floor; and thus, eliminates potential waste of material and machine time [2].

- Less manual labour intensive: conventional composite manufacturing techniques, such as HLU, are labour intensive, whereas AFP is less labour intensive. The use of AFP evens out the difference in labour rates from one region to another.

- AFP is essential for large structures: to deposit composite materials on large structures, it is not practical to use HLU where people have to climb up on large frames. The use of automation allows the construction of large structures more easily.

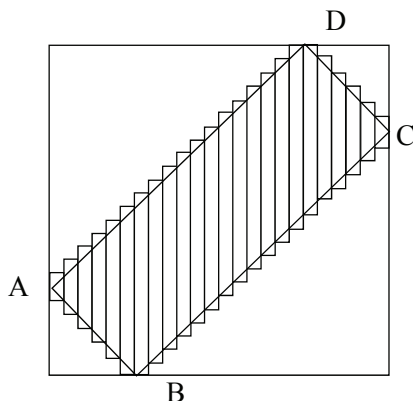


Fig. 5. Less waste of material when the tows are laid down using AFP.

- Ability to steer fibres: one unique characteristic of AFP, as compared to other techniques for the manufacturing of composites, is the ability to steer the fibres. As such, the fibre orientations can vary not only from one layer to another, but also from location to location within the same layer. It is then possible to orient the fibres in the direction where the load is high. This can result in more effective use of materials [3].

- Smoother transition between design as well as manufacturing and vice versa: since the path for AFP is designed and controlled by computers, the transition between design and manufacturing and vice versa is smoother as compared to conventional methods. Thanks to computer aided design, and analysis methods, such as finite element method, the design of composite structures has been well computerized. If a labour intensive technique such as HLU is used, the bottleneck for the process of product development lies with manufacturing. If automation for manufacturing can be done, then the transition between design and manufacturing can become seamless. This certainly can speed up the product development process.

Disadvantages of AFP

The disadvantages for automated composites manufacturing using either ATL or AFP are as follows:

New technology and cost of machine: AFP is a very new technique for manufacturing of composites. It has been used by major companies such as Boeing, Airbus, Bombardier and Bell Helicopter to make many aircraft components. From the university level, there has been limited amount of work done. As such, significant experience from industrial applications has been acquired; but the fundamental knowledge and understanding of the process is limited. Besides, the cost of the machine is very high, and not many universities or small companies can afford the machines.

Occurrence of laps and gaps: since narrow tows [between 1/8 inch (3.18 mm) to 1/2 inch (12.7 mm)] are used in the process, there may exist laps and gaps between the tows and courses. Situations where laps and gaps occur are summarised below:

Boundaries of areas where the border direction is at an angle with the fibre direction: when lay up is done to cover the surface of an area bounded by a border that is at an angle with the fibre direction (Fig. 6), either gaps or laps will exist. The figure shows the situation where strips of fibres need to be deposited to cover the area ABCDEFG. Vertical strips are to cover the area ABCD while inclined strips are to cover the area EFGA. In Fig. 6A, vertical strips in region ADE extend beyond the boundary AE and cause overlaps in the inclined strip on the side of AE. This is because the cutter in the AFP machine can only cut in a direction perpendicular to the strip direction. In Fig. 6B, the vertical strips in the region ADE are cut short of the boundary AE, giving rise to gaps.

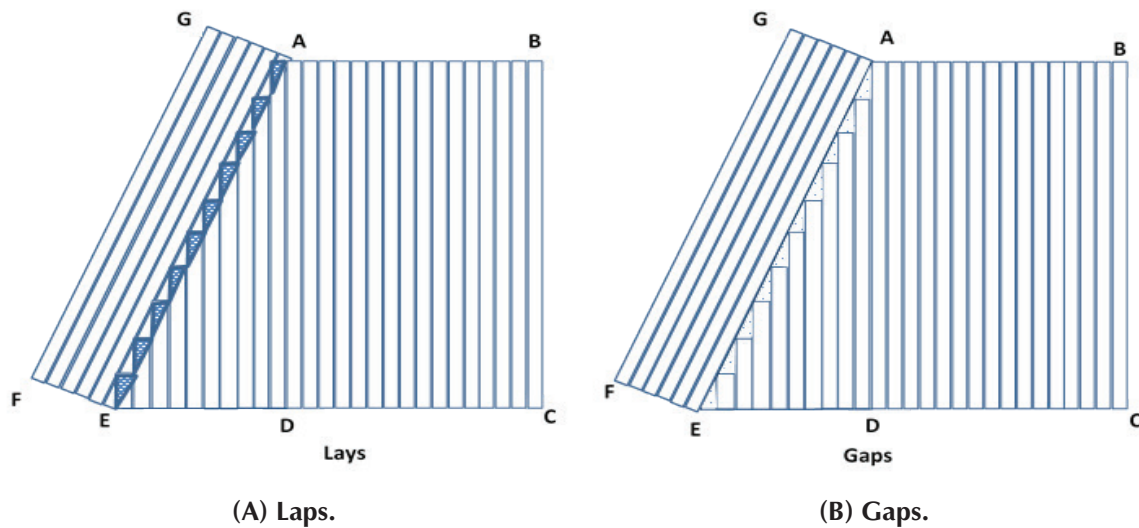


Fig. 6. Laying up over a non-rectangular area can produce laps or gaps.

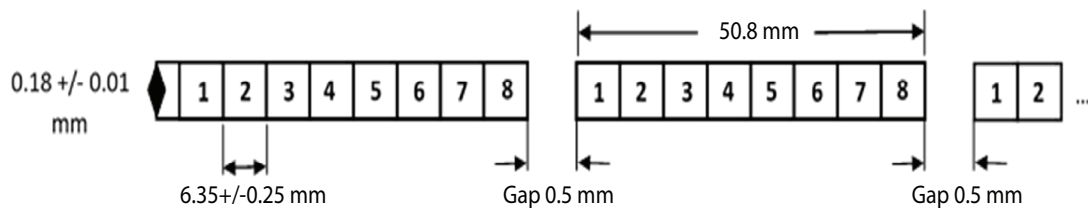


Fig. 7. Manufacturer recommended gap between courses [1].

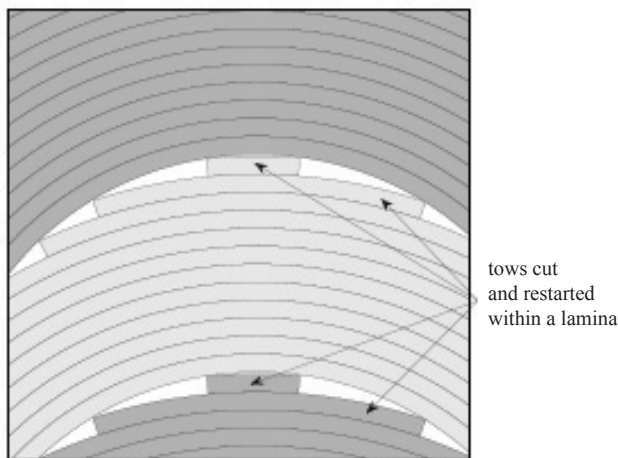


Fig. 8. Gaps created by fibre steering [4].

In a situation as in Fig. 6, where one cannot avoid either laps or gaps, gaps are preferred over laps. This is because laps give rise to stress concentrations. Gaps also give rise to stress concentration, but some resin flow during the process may fill up the gaps and reduce the stress concentration.

Aircraft manufacturers impose a gap of 0.5 mm between each series of n ribbons, with n depending on the placement head used. Fig. 7 illustrates this rule for tape laying head of $n = 8$ ribbons. This gap prevents the creation of an overlap, which

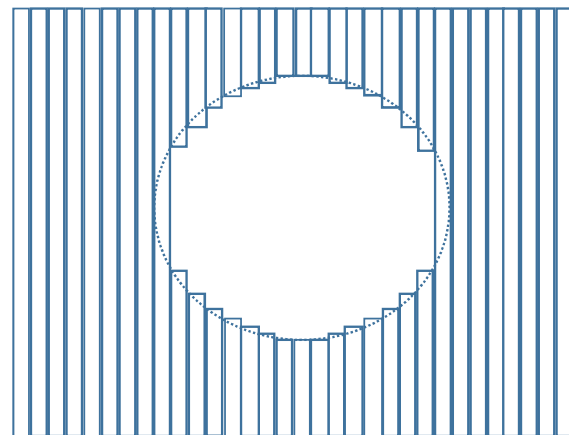


Fig. 9. Serrations at boundaries.

is generally forbidden by the aircraft manufacturers. The value of this gap is defined according to the machine tolerances. The placement of a caul plate on top of laminates containing gaps may also reduce the effect of the gaps [1].

Fibre steering: fibre steering creates curvatures. When regions of different curvatures meet, gaps can be created (Fig. 8).

Serrated edges at boundaries: during AFP laying up,

individual tows can be cut to fit the boundary of a curve. However, since the cut is always normal to the length direction of the tape, there are serrations at the curved boundaries (Fig. 9). As such, finishing work needs to be done.

Limitations and defects due to fibre steering: as mentioned above, AFP can provide fibre steering, which is advantageous. However, there are areas of limitations and issues:

- Limitation of radius for steering: The radius for steering depends on the limitation of the machine (how small a circle can the machine move around its perimeter). The other limitation is the width of the tow. During steering, the tow is sheared where the fibres on the outside of the steered circle have to move more than the fibres on the inside of the circle. When the fibres are constrained by the viscous matrix, there is strong resistance against shearing. If sufficient shear load is applied, buckling may occur. By using dry fibres (no matrix) [5], the resistance against shearing is less. The dry fibres can be laid up to make the preforms, and resin can be infused later as in the Liquid composite moulding process. There is also the idea of continuous shearing of fibres with simultaneous injection of resin to wet the fibres [6].

- Fold overs: if the steering radius is too small for the width of the tows, fold overs may occur (Fig. 10).



Fig. 10. Fold overs due to fibre steering (in the band with smaller radius).

Issues to be resolved

Considering both the advantages and disadvantages of using AFP for thermoset matrix composites, many major companies in the aerospace industry have used these processes to make important aerospace structures for the past several years. The remaining issues of concern are as follows:

High speed inspection of defects: even though the speed for material deposition is high, the speed for defect inspection is relatively slow. It is necessary to be able to detect the defects in situ such that correctional action can be taken before subsequent layers are placed. One recent technique is by taking thermal photographs of the material that is just deposited [7].

Design allowables for laminates containing defects: the existence of laps and gaps in placing tapes or tows using AFP cannot be avoided. As such, new design allowables for laminates containing these features need to be developed for design purposes. Some work has been done on static performance [8] and fatigue performance [9] of laminates containing gaps.

AFP for thermoplastic matrix composites

Traditional method of manufacturing - potential benefits

Traditional methods of manufacturing of thermoplastic composites (long fibre) have been some form of moulding, such as compression moulding, thermoforming (with membrane), or thermostamping (with match metal dies). These methods can provide good parts, but their limitations include the small size of the sample (limitation on the size of the mold); and these methods cannot be used to make structures of revolution, such as cylinders. The advent of the AFP machine enables the manufacturing of larger parts and parts with different shapes, such as curved panels, and parts with a surface of revolution, such as cylinders. Thermoplastic composites offer advantages over thermoset composites in the following aspects: No shelf life; the process can be done in one step, without the need for a secondary process such as curing in an autoclave or oven; thermoplastic composites have higher fracture resistance, as compared to thermoset matrix composites; and it is easier to recycle thermoplastic composites as compared to thermoset composites.

Particular characteristics of AFP for thermoplastic composites

The automated manufacturing of thermoplastic composites has many similarities with that for thermoset composites, in terms of kinematics of motion of the machine. However, there are many differences. Fig. 11 shows the schematic of AFP for thermoplastic composites.

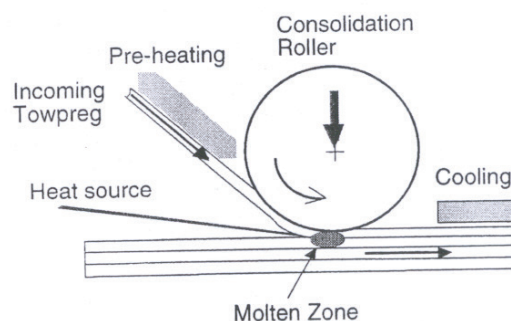


Fig. 11. AFP for thermoplastic composites.

Heating: for thermoplastic composites, intense heating needs to be done at the NIP area. Heating is usually done using a hot gas (nitrogen) torch, or a laser [10, 11]. For machines using the hot gas torch, the temperature at the nozzle

of the torch can go up to 950°C. This temperature can drop significantly at the NIP point. The hot gas is usually aimed at the roller (for the application of compression pressure), rather than directly on the thermoplastic tape. This means that the heating of the tape is done mostly by heat conduction from the roller, rather than by convection from the hot gas. This is to avoid excessive temperature of the tape and possible erosion of the material due to the flow of the hot gas. For machines using a laser, different types of lasers (near infrared diode laser, ytterbium fibre laser) with powers ranging from 2 to 20 kW are available. The advantage of laser heating over torch heating is that the laser heat is focussed on the composite rather than on the roller. This is because heating is done by the absorption of phonons by the fibres. The heated fibres then heat up the matrix material. As such, a soft roller such as a silicone rubber may be used (as compared to steel rollers used in a torch heating machine). However, the speed of movement of the machine has to be fast to avoid excessive heating. The fast speed of material deposition is desirable from the production point of view. On the other hand, too much speed also gives rise to void formation.

Deformation and transformation of the material during processing: the thermoplastic composite material undergoes significant transformation and deformation during processing. Fig. 12 shows the different stages that the material has to go through. Each of these different stages need to be well understood. For this, consider a volume of material to be followed in the whole process.

Stage A: stage A presents the position of a volume of material in a piece of tape that is being processed. Some preheating may be done on this material volume. The heat transfer equation can be written as follows:

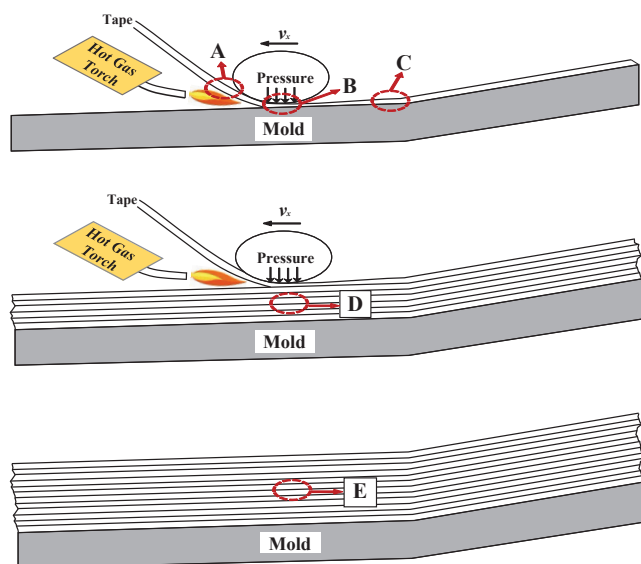


Fig. 12. Stages during the AFP process for thermoplastic composites.

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(K_{xx} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial T}{\partial z} \right) \quad (1)$$

Where ρ is the material density, c_p is the specific heat, K_{ij} are the coefficients of thermal conductivity, and T is the temperature of the material volume.

Stage B: three events occur at this stage.

First, intense heat is applied at this stage to melt the resin. For thermoplastic resin, such as PEEK (Polyetheretherketone), the melting point is about 390°C. The heat source used can be either a hot gas torch, a laser, or a heat lamp.

Secondly, sufficient amount of pressure needs to be applied to consolidate the new layer onto the substrate layer. Consolidation requires the flattening out of any waviness that existed inside the tow beforehand. Additionally, the surface of the incoming tow needs to get into intimate contact with the surface of the substrate. A degree of intimate contact D_{ic} is defined as the ratio of the surfaces not in contact over the overall surface of the tow. The degree of intimate contact varies from 0 (no intimate contact) to 1 (full intimate contact). To have full intimate contact, not only does the pressure need to be sufficient, but there should also be sufficient time for it to occur [10].

Thirdly, during the time of intimate contact, there should be sufficient time to allow for reputation of the molecules across the interface so that bonding takes place. The reputation motion of the molecules depends on the viscosity of the resin. Smaller viscosity would facilitate motion. To have good quality laminate, there should be good bonding.

Stage C: the intense heat source has gone past the volume of material. If a single roller is used, pressure is also released from this volume of material. The events that happen at this stage are as follows:

- Heat transfer: the volume of material is exposed to heat convection to the surrounding area. Equation (1) can be used again with a different boundary and initial conditions. The temperature of the material volume depends on the distance it is from the current NIP point.

- Crystallization: crystallization depends on the rate of cooling. The rate of cooling may depend on the distance of the material volume from the current NIP point. If there is significant variation in the rate of cooling along the distance, then the crystallization rate will also vary.

- Deconsolidation and formation of voids: if the temperature of the material volume is above the glass transition temperature, due to the release of pressure, the material may deconsolidate, and voids may form. This certainly depends on the speed of translation of the roller along the direction of the process. Slower speed will allow more time for the material volume to cool down, and hopefully the temperature may be below T_g

before the release of the pressure. However, this may run in an opposite direction to the desire of having a higher rate of production. One possible way to compensate for this is to add a second roller, as shown in Fig. 13.

- Solidification: if the material volume is far enough from the current NIP point, the material may cool past the T_g and solidification of the resin may take place.

- Relaxation: the time lapse from stage C to stage D depends on the speed of the process, or whether there is some interruption (pause). The material volume may undergo stress relaxation during this time.

Stage D: at this stage, the intense heat source returns to the same position as the material volume, except for the deposition of another material volume on top of the material volume under consideration. Events that happen at this stage are as follows:

- Heat transfer: equation (1) can be used again but with different boundary and initial conditions.

- Consolidation: due to the pressure applied on the upper material volume, the material volume under consideration may be under consolidation again. This influences the properties of the material volume.

The material volume may undergo stage D many times, depending on how many times the roller and heat source go over its position. For analysis, it is necessary to examine the state of the material volume as many times as necessary until its state becomes stabilised.

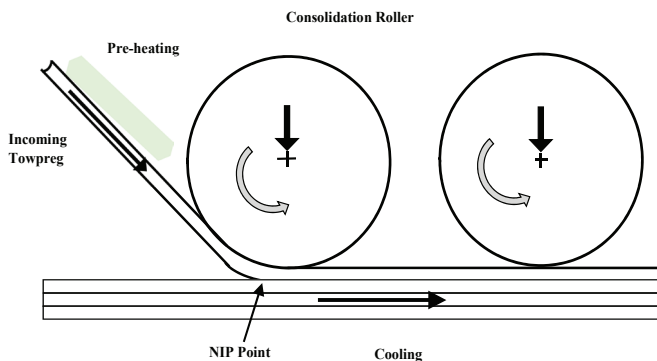


Fig. 13. Addition of a second roller to prevent deconsolidation.

Stage E: stage E represents the stabilised material state. The stresses that exist at stage E may be taken as the residual stresses in the piece of material produced by AFP.

Advantages and disadvantages

Post treatment: one of the main advantages in doing AFP for thermoplastic composites is the elimination of the post treatment of the composite structures after AFP. The secondary process in putting the composite structures in an autoclave, or oven (in case of vacuum bag only preregs) is time consuming

and costly. However, for this to be effective, the quality of the laminates made by AFP alone should be of sufficient quality. To achieve this, the speed of processing for thermoplastic composites needs to be very slow to allow enough time for autohesion. The time taken due to the slow speed is still much shorter than the time involved in going through a secondary process. In addition, the defects that may be created due to AFP material deposition for thermoplastic composites (such as laps, gaps) cannot be corrected in the secondary process, when it is intended that there is no secondary process.

Distortion of the part: there are significant temperature gradients in a composite part made of thermoplastic composites. The temperature gradient can be along three directions.

- There is a temperature gradient along the x direction (direction of movement of the NIP point), because the heat source moves along this direction. When the heat source is focussed at a certain location x_1 , the temperature at that location is high. At the next instant, the heat moves away to a location $x_2 = x_1 + \Delta x$, the temperature at x_1 decreases and becomes smaller than the temperature at x_2 , and so on.

- A similar situation occurs along the y direction. When a strip of material is laid along the x direction at a position y_1 , the temperature along the strip is higher than the temperature at other y locations.

- When many layers are placed one on top of the other, there is a temperature gradient along the z direction.

Due to these complex temperature gradients, a thermoplastic composite part tends to distort during processing, even for a unidirectional flat plate. Fig. 14 shows a distorted flat plate. In fact, the distortion occurs for structures with free edges. For structures without free edges, such as a cylindrical tube, the distortion does not occur. This is due to the constraint provided by the geometry.



Fig. 14. Distorted flat plate, made from unidirectional layers [12].

In-plane waviness: When the roller is made of hard material and particularly when the width of the roller is smaller than the width of the tow (which should be avoided), in-plane waviness of the fibres may occur (Fig. 15).



Fig. 15. In-plane waviness of fibres [13].

Ability to make unique structures: there are unique structures that can only be made using AFP, and that other techniques cannot. One example is thick curved thermoplastic composite tubes that can exhibit similar performance as thick aluminum tubes in terms of stiffness, strength, and elongation [14]. Fig. 16 shows such a tube. It is not possible to make thick thermoplastic composite tubes using other techniques of manufacturing.

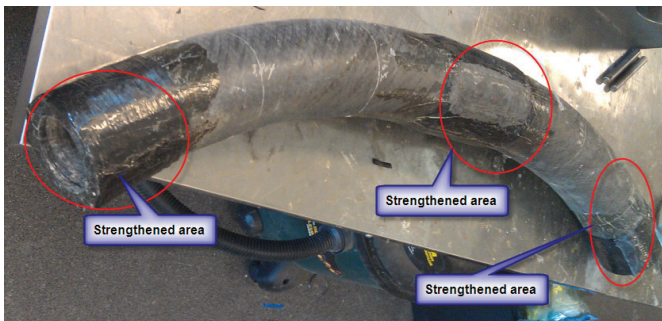


Fig. 16. A curved, thick thermoplastic composite tube made by AFP [15].

Issues of concern

There are more issues of concern for AFP processing of thermoplastic composites as compared to thermoset composites.

To produce laminates with quality similar to those made using compression moulding or autoclave: the conventional way to make structures out of thermoplastic composites is either compression moulding or autoclave. These techniques have their own advantages and disadvantages. For advantages, the quality of laminates made from these processes are usually good. For disadvantages, first the size of the sample is limited by the size of the press or the autoclave. Secondly, for compression moulding, it is sometimes difficult to assure

spatial uniformity of temperature and pressure. For autoclave processing, due to the high temperature required, sealing of the vacuum bag is difficult and expensive. For AFP, the main drawback is the duration of time that sub-laminates are under contact for autohesion is very short (in the order of a fraction of a second) as compared to minutes in compression or in autoclave. Another factor that contributes to the lack of bonding is the deconsolidation right after the NIP point. When the roller moves away from the material volume under consideration, the pressure on that material volume is released. If this happens before its temperature goes below the glass transition temperature T_g , deconsolidation will occur. The interlaminar strengths of samples made using AFP are usually less than those made using autoclave [16].

To produce laminate with a minimum amount of voids: voids occur due to the lack of consolidation (or de-consolidation). Also, if there are gaps that occur due to the misalignment of tows, for thermoset composites, these gaps may be filled with resin during the curing process in the secondary stage. However, for thermoplastic composites, since there is no secondary stage, these gaps will appear as voids. The application of a repass (running the process again with a similar temperature and pressure, but with no addition material deposited) may help reduce the void content [17].

To produce laminates with good surface finish: the use of hot gas at a high flow rate may produce rough surfaces. The roughness also occurs because these surfaces do not benefit from the close contact with a smooth mould. The use of a repass may improve the surface finish [17].

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Quality of life of children with idiopathic nephrotic syndrome according to clinical types

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Abstract:

Idiopathic nephrotic syndrome (INS) is a major manifestation of chronic idiopathic glomerulonephritis and a common disease in children. The cause and pathogenesis of the disease have not been clarified so far. The treatment is usually a long-term process, from a few months to several years, even decades, including the period of hospitalisation, outpatient treatment period and follow-up period after treatment. The INS patients are negatively affected by the disease and its treatment process. The aim of this study is to assess the health-related quality of life (QOL) of children with INS according to clinical types in Haiphong Children's Hospital. **Object:** Describe some factors related to the QOL of children with INS. **Subjects:** 71 patients diagnosed with INS, who are being monitored and treated at Haiphong Children's Hospital from 10/2015 to 05/2016. **Methods:** Prospective studies, descriptive cross-sectional. QOL of the patients is assessed by the PedsQL 4.0 scale; the higher score shows that the lower QOL. **Results:** The general QOL score of children with INS (21.24 ± 13.91) was higher than normal children (16.98 ± 10.20). Children with steroid-resistant INS have a higher score (31.62 ± 14.32) than children with steroid-dependent (20.57 ± 9.08) and responsive INS (14.58 ± 6.83). The QOL score of children with one of the symptoms Cushing's face, hirsutism or acne are significantly higher than children without the corresponding symptoms. Children who finished their treatment had a lower score (15.47 ± 7.42) than children being treated (21.33 ± 10.23). The average QOL score has a linear correlation with the duration of INS. **Conclusion:** The general QOL of children with INS substantially declined compared with that of healthy children. The QOL of children with steroid-dependent and resistant INS is lower than that of the children with steroid-responsive type. The QOL of children with one of the symptoms Cushing's face, hirsutism or acne is significantly lower than that of children without the corresponding symptoms. The QOL of children who completed treatment is higher than the group being treated. The longer the duration of treatment, the more the children's QOL declined.

Keywords: children, idiopathic nephrotic syndrome, quality of life.

Classification number: 3.2

Background

INS is a major manifestation of chronic idiopathic glomerulonephritis. The disease has a long duration, often recurs, needs long-term treatments and has many complications in itself and in the treatment processes [1, 2]. It negatively affects patients in terms of health, emotion and family economic condition, and hence, causes a negative impact on the QOL of the patients. So far, there are only a few studies on the QOL of children with chronic diseases in Vietnam, and there is no study on the QOL of children with INS in Haiphong [3]. Hence, how is the QOL of children with INS like? What are the factors relating to the QOL of children with INS? Those are the questions that need answers. Therefore, we conducted this study to: 1) Assess the health-related QOL of children with INS in Haiphong Children's Hospital, 2) Describe some of the factors related to the QOL of children with INS. Hopefully, the results will contribute to the treatment and improve the QOL of children with INS, which is a common disease in children in Vietnam.

Subjects and methods

Research subjects

71 patients with INS were monitored and treated at Haiphong Children's Hospital from 10/2015 to 05/2016.

The diagnostic criteria of INS according to ISKDC (International study of kidney diseases in children) are: edema, proteinuria ≥ 50 mg/kg/24 hours, serum protein decrease (≤ 56 g/l), serum albumin decrease (≤ 25 g/l) and serum cholesterol increase (≥ 5.5 mmol/l).

Classification of nephrotic syndrome according to responsiveness to steroid treatment:

- Steroid-responsive: after using continually, initial treatment is conducted with prednisone 2 mg/kg/day in 4 weeks. If the patient is in remission, it means negative or trace proteinuria.
- Steroid-dependent: the patients had 2 continuous relapse during the treatment or relapse occurred within 14 days after stopping medication.

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- Steroid-resistant: after using continually, initial treatment is conducted with prednisone 2 mg/kg/day in 4 weeks, the patients had no relief (positive proteinuria >50 mg/kg/day).

Patients with secondary nephrotic syndrome triggered after systemic lupus erythematosus, Henoch - Schonlein purpura, diabetes were excluded.

A control group data from the study of Nguyen Thi Thanh Mai, et al. [4] is used, which includes 74 healthy children in the same conditions of research group.

Research methodology

Study design: prospective studies, descriptive cross-sectional.

Each patient completed a designed medical record form, which includes information about age, gender, family circumstances, habitat geography, learning results, information about the disease such as duration, classification, treatment status and appearance symptoms. Besides, the QOL of patients are assessed by direct interviews using the scale PedsQL 4.0 of Pediatric Hospital and Health Center Sandiego, California. The PedsQL 4.0 scale is the result of research and development projects about the QOL assessment tools in the 15 years of the authors Varni, et al., that was published in 2002 [5]. This scale consists of 23 questions in four areas: health and physical activity, emotional, social friendships, learning at school and the given points based on the level of problems affecting children within 1 month before the evaluation: 0 point if it is never a problem, 1 point if it is almost never a problem, 2 points if it is sometimes a problem, 3 points if it is often a problem, 4 points if it is almost always a problem. The assessment of health problems and children's activities is out of a total points of 23, as explained above. The higher total score shows the higher difficulty levels, which means that the general QOL is lower.

Data is processed by the software SPSS 20.0.

The research was permitted and approved by the Council of Ethics in biomedical research of Haiphong University of Medicine and Pharmacy. The participation of the subjects in the study is voluntary. The information of the patients is confidential and only serve scientific research.

Results

General characteristics of the study subjects

The patients' age is from 6 to 18 years, and the average age is 11.2 ± 3.38 . 62% of them are primary school students. There are 57 males, 14 females, and the proportion of male to female is 4/1. 33.8% of the patients are from urban areas and the rest are from rural areas. The percentage of patients with onset INS is 23.9% and of recurrent type is 76.1%. The

percentage of patients with steroid-responsive INS is 74.6%, steroid-dependent and steroid-resistant types are both 12.7%. 78.9% patients are in treatment process and 21.1% of them have finished treatment.

QOL of children with INS (Tables 1, 2)

Table 1. Average QOL score of children with INS and healthy children.

Fields	Average PedsQL score of children with INS (n=71) ($\bar{X} \pm SD$)	Average PedsQL score of healthy children [4] (n=74) ($\bar{X} \pm SD$)	p
Physical health	7.55 $\pm$ 5.96	5.03 $\pm$ 3.91	<0.05
Emotion	5.72 $\pm$ 3.45	4.85 $\pm$ 3.12	<0.05
Social life	4.73 $\pm$ 2.81	2.55 $\pm$ 2.40	<0.05
Learning	6.24 $\pm$ 3.52	4.51 $\pm$ 3.01	<0.05
General QOL	21.24 $\pm$ 13.91	16.98 $\pm$ 10.20	<0.05

Comment:

- The highest score belongs to the physical field.
- The score of the children with INS is significantly higher than that of the healthy children, which means that the QOL of the patients is lower.

Table 2. The average QOL score of children with INS regarding disease classification and treatment status.

	n	Average PedsQL score ($\bar{X} \pm SD$)	p
Classify by development	Onset	17 14.85 $\pm$ 7.17	>0.05
	Recurrent	54 18.31 $\pm$ 8.93	
Classify by response to steroid treatment	Responsive	53 14.58 $\pm$ 6.83	<0.05
	Dependent	9 20.57 $\pm$ 9.08	
	Resistant	9 31.62 $\pm$ 14.32	
Continuing treatment	56	21.33 $\pm$ 10.23	<0.05
Finished treatment	15	15.47 $\pm$ 7.42	

Comment:

- The average QOL score of children with steroid-resistant nephrotic syndrome is the highest and the steroid-responsive group has the lowest score with a statistical difference.
- The children being treated have a higher average QOL score than the children who finished treatment with a statistical difference, which means that the QOL of children being treated is lower than the finished group.

Some factors related to the QOL of children with INS (Tables 3, 4; Fig. 1)

Table 3. The average QOL score and appearance characteristics.

Appearance characteristics		n	PedsQL score ($\bar{X} \pm SD$)	p
Cushing's face	Yes	38	21.37 $\pm$ 10.14	<0.05
	No	33	12.81 $\pm$ 5.46	
Hirsutism	Yes	39	22.13 $\pm$ 11.23	<0.01
	No	32	11.57 $\pm$ 6.58	
Acne	Yes	24	23.08 $\pm$ 10.19	<0.05
	No	47	13.93 $\pm$ 7.41	
Genital edema	Yes	30	18.03 $\pm$ 10.12	>0.05
	No	41	16.16 $\pm$ 9.56	

Comment: the PedsQL scores of children with one of the symptoms Cushing's face, hirsutism or acne are significantly higher, and the QOL is lower than that of children without the corresponding symptoms.

Table 4. The average QOL score in relation to types of INS and the learning outcomes of INS children.

Learning outcomes	Average PedsQL score ($\bar{X} \pm SD$)			p
	Steroid-responsive INS (n=53)	Steroid-dependent INS (n=9)	Steroid-resistant INS (n=9)	
Excellent (n=30)	11.90 $\pm$ 6.14	25.30 $\pm$ 7.07	None	<0.05
Good (n=33)	16.25 $\pm$ 8.90	22.33 $\pm$ 8.08	31.20 $\pm$ 10.05	<0.05
Medium (n=8)	17.20 $\pm$ 8.27	24.45 $\pm$ 9.90	43.40 $\pm$ 15.30	<0.05

Comment:

- There are no children with steroid-resistant INS who achieve excellent academic result. Among children with excellent academic result, the average PedsQL score in children with steroid-dependent INS is higher than that of the children with steroid-responsive INS with a statistical difference.

- Among children with good and medium results, the PedsQL score of children with steroid-resistant INS is the highest, followed by that of steroid-dependent INS group and then, steroid-responsive INS group with a statistical difference.

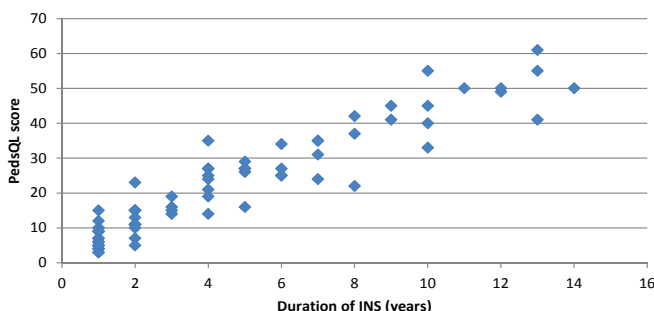


Fig. 1. Average PedsQL score and the disease duration.

Comment: the average QOL score has a linear correlation with the duration of INS, according to the equation $y = 1.9 + 4.7x$ (y is the PedsQL score, x is the duration of INS), with $r = 0.56$, $p < 0.05$.

Discussion

QOL of children with INS

- The average QOL score in the fields of children with INS increases. Compared with the children with nephrotic syndrome in the study of D.T.T. Binh [3] who were interviewed with the same scale of PedsQL, our team's scores did not differ significantly. Compared with a control group of 72 healthy children in the study of N.T.T. Mai, et al. [4] who also interviewed with the scale PedsQL, the QOL score is higher. Thereby, it can be seen that the groups of children with nephrotic syndrome in our study had significantly impaired QOL.

- Type of INS: we studied it in 2 ways by dividing the patients.

+ The first is based on the development of the disease; children with nephrotic syndrome who had recurrent episodes have higher QOL score than the children in the onset of illness. Relapses are common characteristics in patients with nephrotic syndrome; the relapse rate is high, which takes prolonged treatment time and the children's QOL is affected more. The causes of relapse may be infections (respiratory, digestive), allergies or children and families who do not comply with the treatment and arbitrarily change the dose or stop using medicine.

+ The second is based on the response to steroid treatment. The average QOL score of children suffering from steroid-resistant nephrotic syndrome is the highest (31.62 $\pm$ 14.32), followed by the steroid-dependent group (20.57 $\pm$ 9.08). These two groups of patients have an extremely high recurrence rate or are not treatable with steroids, and thus, the treatment will be more difficult and prolonged, which means that the QOL of these children are significantly reduced for the reasons mentioned above. Moreover, the QOL of children with steroid-responsive INS also declined, similar to a study by E.M. R  th, et al. [1].

- As for the treatment status, most patients in the study group were in the treatment process (78.9%). The rate of finished treatment is still low because the response to treatment with the drug is not an optimal or a recurrent disease. Every time, going for regular medical exams, despite discontinuation of therapy or treatment being continued, the children and family always have the psychological fear of relapse or worsening of the disease. The average QOL score in the group of children that finished treatment was significantly lower compared with the continuing treatment group. This is consistent to the study of D.T.T. Binh [3].

Some factors related to the QOL of children with nephrotic syndrome

- The QOL and the appearance symptoms: all appearance symptoms affect the QOL of children. The study results

showed that the average QOL score of children with one of the symptoms Cushing's face, hirsutism or acne was significantly higher than that of the children without the corresponding symptoms ($p < 0.05$). Specific research was conducted in the 2 fields of feelings and friendships-social relationship; children with acne have the most difficulty with highest emotion score and the highest social score. The symptoms often lead the children to lose confidence when communicating with friends, teachers and the people around them, making them not want to attend school regularly, afraid to play with friends or even not want to leave their home. According to researches by Soliday, et al. [6] and M. Metah, et al. [7] regarding the changes in the behaviour of children with nephrotic syndrome, the proportion of children having behavioural changes is 68%, which is higher than that of the healthy group with 21.6%.

- The average QOL score in relation to the types of INS and the learning outcomes of INS children.

D.T. Selewski, et al.'s study [8] shows that QOL score in the learning field increases, which means that the QOL related to learning is declined.

In our study, no children with steroid-resistant nephrotic syndrome achieve excellent school result. The average QOL score of children with steroid-resistant type is very high, in which children who achieve good and medium result are the highest, much higher than the other groups, with $p < 0.05$. The steroid-resistant type may not only cause children to treat persistently, use a variety of drugs but also make the children and their families depressed and worried that they will not be cured. With such influences, the children will not be able to concentrate in class learning, the impact on health and the disease appearance; additionally, the treatment greatly affects a child's learning. This shows that the need to find appropriate psychological measures help this group integrate life around, adjust psychosocial better.

- The QOL and the disease duration: the average disease duration of the research team was 4.69 ± 3.78 years and the children infected for 1 to 5 years accounted for the highest proportion (40.8%). According to our research, there is a linear correlation between the QOL and the duration of treatment: the longer duration of treatment, the more declined children's QOL. The affected children within one year are often in the onset or in the steroids-sensitive group, with no recurrence, and appeared with fewer side effects, not greatly affected by emotions, social and learning of children. Children must comply with the treatment, which many do not want to, and are even more anxious about the effectiveness of treatment, or whether the disease can worsen. A study of D.M. Youssef, et al. [9] shows that INS patients encounter significant problems with anxiety, depression and anger during treatment. Besides, many other factors mentioned in the study also reduced the QOL of children. Prolonged disease duration means that the children are affected much more by the QOL.

Conclusions

1. The QOL of children with INS according to clinical types:

- The general QOL of children with INS substantially

declines compared with that of the healthy children.

- The QOL of children with steroid-dependent and resistant nephrotic syndrome is lower than that of the children with steroid-responsive type.

2. Some factors related to the QOL of children with INS:

- The QOL of children with one of the symptoms Cushing's face, hirsutism or acne is significantly lower than that of the children without the corresponding symptoms.

- The QOL of children who finished treatment is higher than that of the treating group.

- There is a linear correlation between the QOL and the duration of treatment: the longer the duration of the treatment, the more the decline in the children's QOL.

Recommendation

- Continuing study to find new INS treatment methods that are more effective and have fewer complications.

- Training and guiding children's families to detect the recurrence of the disease early in order to have timely treatment and reduce complications.

- Finishing medication when the children meet the suitable criteria.

Competing interest

The authors declare that they have no competing interests.

Authors' contribution

Authors participated in study design, protocol development and performance, data analysis, interpretation of data and writing of the manuscript, carried out the clinical data collection and data analysis and read and approved the final manuscript.

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Methods for particle size reduction of liposomal amphotericin B

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Abstract:

Liposomal amphotericin B were prepared by thin film hydration technique. Particle size was reduced by ultrasonic device and high pressure homogeneous device. The size distribution was determined by dynamic light scattering by the Zetasizer ZS90 equipment. The morphology of amphotericin B liposomes was observed by Transmission electronic microscopy (TEM) with negative staining technique. The result shows that combining high-pressure homogenization and membrane extrusion provided monolayer liposomal amphotericin B with particle size less than 200 nm and homogeneously (PDI < 0.3).

Keywords: amphotericin B, liposomes, particle size.

Classification number: 3.3

Introduction

Liposome is a drug carrier with outstanding advantages of controlling the dissolution and of carrying drug to targeted organs [1]. There are many methods for the preparation of liposomes in which thin film hydration method is popularly used because of its advantages, such as: relatively simple pharmaceutical technique, uncomplicated implementation, applicable to all phospholipid, high efficiency in liposomes performance with other lipid-soluble drug substances, etc. However, one of the disadvantages of this method is that the received liposomes usually has big dimension, many layers and is heterogeneous (from about 50-1,000 nm) [1, 2]. As a result, in order to use liposome in the injection dosage form, it is necessary to make it smaller and more homogeneous in order to facilitate the sterile filter procedure and enhance the carrying of drugs to its target.

Liposomal amphotericin B were prepared using the thin film hydration method [3]. This study presents the results of the investigation of some methods' particle size reduction and homogenization of liposomal amphotericin B. This is an important and decisive step for the next study for the preparation of injection dosage form of liposomal amphotericin B.

Ingredients and methodology

Ingredients and equipment

- **Ingredients:** amphotericin B was purchased from Dr. Ehrenstorfer GmbH (Germany), phosphatidylcholin soybean hydrogenation (HSPC) and distearoyl phosphatidylglycerol (DSPG) were purchased from Lipoid (USA), cholesterol

(Chol) was purchased from Sigma Chemical Co. (St. Louis, Mo.), Polycarbonate membrane was purchased from Whatman (USA) and other chemicals which met the standards of USP, producers or pure chemistry.

- **Equipment:** Rovapor R-210 Rotary distillation system (Buchi, Germany), NS 29/32 2,000 ml globular jar, high-pressure membrane extruder EmulsiFlex-C5 (Avestin, Canada), Wisclean 40 kHz Ultrasonic bath (Korea), Ultrasonic probe UP200Ht (Hielscher, Germany), Zetasizer nano ZS90 analyzer size system (England), Transmission electronic microscopy (TEM) JEOL 1010 (Japan) and other standardised equipment, devices were used.

Methodologies

Liposome preparation: the liposomal amphotericin B were prepared by the thin film hydration method as previously described [3] with HSPC/DSPG/Chol at the molar ratio of 2.0/0.8/1.9. The amphotericin B/total phospholipid ratio was 9/100 (mol/mol), citrate-buffer [pH 5.0] was used as the hydration solution. The evaporation conditions were as follows: the solvent mixture was removed from liquid phase by rotated evaporator at 40°C and 150 rpm in the first 30 minutes, then continued at 50 rpm in the remaining time. The hydration conditions were as follows: the temperature was 50°C, the speed of rotation was 200 rpm.

Size reduced method:

+ Polycarbonate membrane extrusion method with mini-extruder device [1, 4].

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+ Ultrasonic methods with ultrasonic bath and ultrasonic probe [1].

+ High-pressure homogenization method in combination with membrane extrusion method [1].

Particle size distribution were determined by dynamic light scattering method with Zetasizer ZS90, morphology of particles by transition electronic microscope with negative staining technique [5-7].

Results and discussion

After being prepared by the thin film hydration method, liposomal amphotericin B's (original L-AmB) size ranged from 738 to 1,026 nm, the size distribution was 0.451-0.868. Those liposomal amphotericin B were used to investigate the effects of equipment and parameters in particle size reduced process in liposomal amphotericin B formulation.

Results from membrane extrusion method with mini-extruder device

Liposomal amphotericin B prepared in the previous step was extruded sequentially through 1,000-400-200 nm polycarbonate membrane with a manual mini-extruder device. Each of the samples were extruded 29 times at 60°C. Extruded liposome had low PDI (from 0.111-0.227), indicating homogeneous particle distribution. However, the particle size was still large (> 200 nm), the volume after each extrusion was only 1-10 ml, so it was not applicable to the mass scale.

Results from ultrasonic methods

Using ultrasonic probe: 200 ml original L-AmB was homogenized by UP200Ht ultrasonic probe (200 w, 26 kHz). After 1, 2, 3,... and 10 minutes, 1 ml of the sample was withdrawn and particle size distribution properties were characterised. The results were presented in Table 1.

Table 1. The particle size and particle distribution of liposomal amphotericin B samples using ultrasonic probe (n = 3).

Time (minute)	Particle size (d.nm)	PDI
Origin	566.0 ± 11.5	0.607 ± 0.019
1	256.7 ± 5.3	0.453 ± 0.031
2	202.9 ± 4.3	0.411 ± 0.031
3	175.4 ± 4.5	0.303 ± 0.008
4	148.1 ± 0.1	0.255 ± 0.008
5	146.6 ± 1.3	0.212 ± 0.025
6	139.1 ± 0.1	0.220 ± 0.028
7	139.4 ± 0.1	0.227 ± 0.001
8	140.6 ± 0.4	0.248 ± 0.004
9	141.3 ± 4.7	0.253 ± 0.001
10	145.9 ± 1.0	0.272 ± 0.007

As illustrated in Table 1, with ultrasonic probe method, after 4 minutes the samples with a particle size of under 200 nm were distributed relatively homogeneously (PDI < 0.3). The limitation of this method is that the samples usually have impurities (caused by releasing titan metal from probe) and are not appropriate for scale up.

Use ultrasonic bath: 200 ml of liposomal amphotericin B was put into a glass beaker and scanned in Wiseclean (40 kHz, 22 litres in capacity, containing 6 litres of water) ultrasonic bath for 20 minutes with an interrupting procedure: scanned for 30 seconds and stopped for 30 seconds (sample A1), scanned for 1 minute and stopped for 1 minute (sample A2), scanned for 2 minute and stopped for 2 minute (sample A3) (using iced water during the procedure to avoid heating of liposome suspension). After the homogenization process, the sample was taken to measure the particle size and particle distribution. The results are presented in Table 2.

Table 2. The particle size and particle distribution of liposomal amphotericin B samples using ultrasonic bath (n = 3).

Sample	Particle size (d.nm)	PDI
A1	522.13 ± 26.05	0.727 ± 0.075
A2	507.97 ± 33.62	0.713 ± 0.104
A3	662.30 ± 59.01	0.542 ± 0.051

As shown in Table 2, after 20 minutes, the samples had a particle size of above 500 nm, heterogeneous distribution (PDI > 0.5). The results indicated that ultrasonic bath was not an effective method to reduce particle size. These results were consistent with other studies [8-10] showing that reducing process was more effective when liposome was poured direct into the bath, with higher ultrasonic frequency (at least 80 kHz) and it should be adjusted during the operation.

Results from high-pressure homogenization method in combination with membrane extrusion method

Prepared liposomal amphotericin B was passed through Emulsiflex-C5 equipment alone or conjoined with extruder holder (placed 400 nm polycarbonate membrane) under a pressure at 5,000 psi (350 bar). The number of compressed cycles was investigated to determine suitable parameters.

The effect of the homogenization cycle: the results are presented in Table 3.

Table 3. The particle size and particle distribution of liposomal amphotericin B samples according to homogenization cycle.

Homogenization cycle	Particle size (d.nm)	PDI
0	882.6	0.508
1	174.0	0.408
2	149.2	0.364
3	141.9	0.376
4	135.1	0.382
5	130.5	0.371
6	121.1	0.376
7	112.5	0.306
8	110.0	0.294

Table 4. The particle size and particle distribution of liposomal amphotericin B samples according to the membrane extrusion times.

Times of extrusion	Particle size (d.nm)	PDI
0	149.2	0.364
1	134.3	0.337
2	134.9	0.281
3	131.8	0.274
4	131.6	0.275

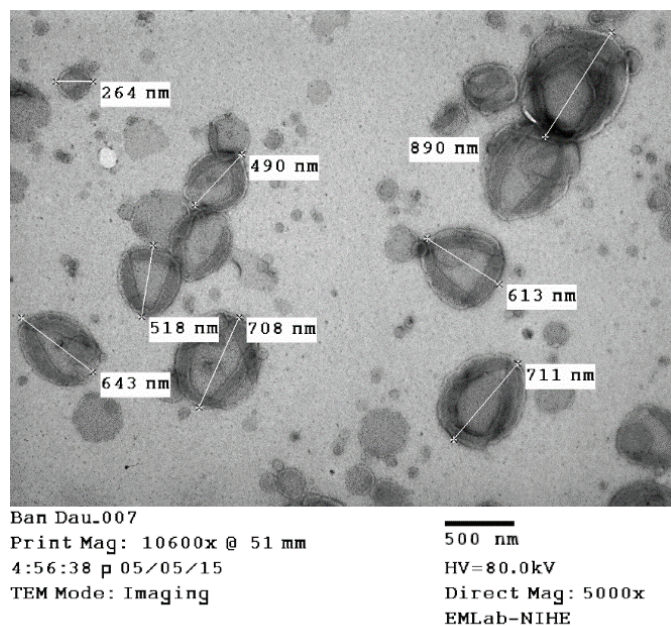
The results in Table 3 show that after the first cycle, the particle size was reduced to less than 200 nm. However, the particle distribution was still heterogeneous (PDI > 0.4). From the second cycle onwards, particle size gradually decreased and the PDI remained at about 0.3. Therefore, there was a requirement to combine with membrane extrusion method for getting more homogeneous system.

The effect of the membrane extrusion times: after passing through Emulsiflex-c5 equipment for 2 cycles as conducted above, samples were extruded through 400 nm polycarbonat membrane under a pressure of 500 psi. The results are presented in Table 4.

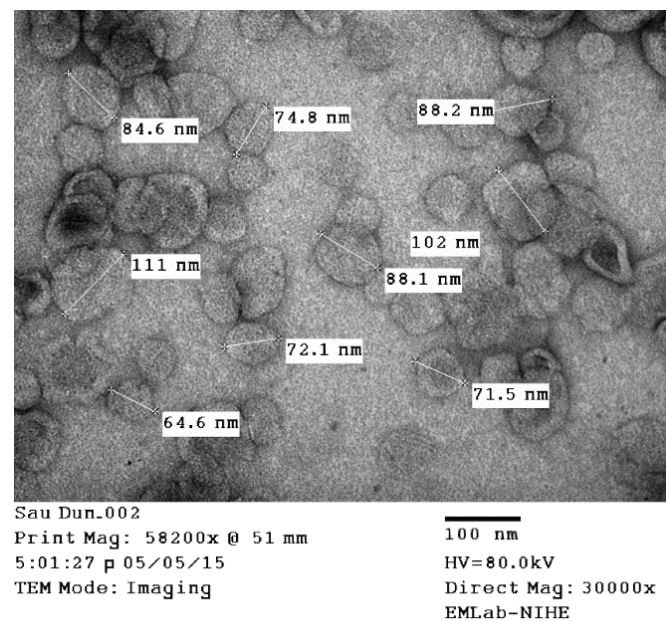
The TEM figures of samples taken after high-pressure homogenization method in combination with membrane extrusion are presented in Fig. 1.

It is illustrated in Table 4 and Fig. 1 that in the second cycle, after extruded through 400 nm membranes, the samples have a more homogeneous distribution with PDI < 0.3. There was not a significant difference in particle size and particle-size distribution between the second and the next cycles. Liposomes still had spherical shape and almost all of them had one layer, small particle size and relatively homogenous distribution.

The operation principle of the high-pressure homogenization method is the same as that of the polycarbonate membrane extrusion method with a gradually reduced pore size. Normally, high-pressure homogenization usually requires a number of cycles in order to obtain small and homogeneous liposome. However, the process of peeling the layers of liposome took



(A) Origin.



(B) After particle reduction.

Fig. 1. Original sample (A) and after particle reduction using high-pressure homogenization method in combination with membrane extrusion (B).

place under high-pressure and multi-cycle homogenization can break liposome resulting in loss of product. In addition, the temperature of the device may increase the effect on the stability of the liposome. In order to reduce the number of homogenization cycle (2 times), the combination of high-pressure homogenization and membrane extrusion method (using high-pressure membrane extruder EmulsiFlex-C5) selected in this study showed relatively optimal results and could be applied in practice.

Conclusions

The investigation into some methods used to reduce liposomal amphotericin B particle size was done; specifically, Membrane extrusion method using mini-extruder device resulted in highly homogeneous distribution ($PDI < 0.2$) but the particle size of liposomal amphotericin B was still larger than 200 nm. Ultrasonic method using ultrasonic probe after 4 minutes, resulted in small liposomal amphotericin B particle size (< 200 nm) and homogenous distribution ($PDI < 0.2$). Ultrasonic method using ultrasonic bath was used and all the investigated conditions resulted in large liposomal amphotericin B particle size (> 500 nm) and heterogeneous distribution ($PDI > 0.5$). The combined method of high-pressure homogenization method and membrane extrusion method under pressure of 5,000 psi and with 2 homogenization cycles, 2 times of extrusion through 400 nm polycarbonate membrane resulted in spherical liposomal amphotericin B, mostly with 1 layer, small particle size (< 200 nm) and relatively homogeneous distribution ($PDI < 0.3$).

These results will be the fundament for further studies on preparation of injection dosage form of liposomal amphotericin B.

ACKNOWLEDGEMENTS

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Use of *ITS* DNA barcode for identification of Jewels of Opar (*Talinum paniculatum*) collected in Thanh Hoa, Vietnam

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Abstract:

Jewels of Opar (*Talinum paniculatum*) is a herbaceous plant known for its highly medicinal value. This medicinal plant is listed in the Red List of Vietnam's medicinal plants and in the handbook of Vietnam's medicinal plants, both documents warranting its necessity for protection. Jewels of Opar contains bioactive substances such as phytosterols, saponins, flavonoids, tannins, steroids, and many other inorganic substances. Jewels of Opar plants collected in Thanh Hoa, Vietnam, are tree-like herbs, their green trunks grows straight up and then branch out. The shapes of the leaves vary; they are generally oval or ovate-oblong in shape, with wavy veins. The flowers of this tree have five reddish purple wings, two sepals, more than ten stamens, and a spherical ovary. Both the fruits and their seeds are small and black. Tuberous roots are cylindrical with many small roots, and the tubers themselves are sweet and spicy. *Internal transcribed spacer (ITS)* region isolated from *T. paniculatum* plants in Thanh Hoa, Vietnam is 643 bp in length. Based on the nucleotide sequences of the *ITS* region and using the basic local alignment search tool (BLAST) in the National Center for Biotechnology Information (NCBI), the Jewels of Opar samples collected in Thanh Hoa, Vietnam were determined to belong to *T. paniculatum* species, *Talinum* genus, Portulacaceae.

Keywords: DNA barcode, *ITS* marker, Jewels of Opar, medicinal plants, *Talinum paniculatum*.

Classification numbers: 3.3, 3.4

Introduction

Jewels of Opar (*T. paniculatum* Gaertn or *T. crassifolium* Willd or *T. patens* L.) is a species in the *Talinum* genus of the Portulacaceae. A herbaceous plant, it is well known for its medicinal value. Jewels of Opar is one of the medicinal plants included in the Red List of Vietnam medicinal plants and in the handbook of Vietnam's medicinal plants as a species that should be protected at the vulnerable level (VU A1A, c, d) [1]. Jewels of Opar contains substances such as phytosterols, saponins, flavonoids, tannins, steroids and several other inorganic substances. These substances have anti-viral effects and are very effective on Herpes' disease and skin infections. Besides, they can also be used as a supporting medicine for Parkinson's disease and heart disease and for lowering blood cholesterol... [2].

Currently, the identification of medicinal plants has been mainly based on morphological analysis. However, this method often encounters obstacles when the raw plant material has been completely or partially processed. According to Hebert, et al. (2003), the DNA barcode is one of the methods used as a method to identify the species. Some DNA regions within the nucleus genome and the chloroplast genome have been used in the identification of plant species [3]. The nucleus rADN genes are a multi-gene system coding for rRNA sequences that are both conservative and diverse when it comes to distinguishing close species. In the nucleus of the cell, rADN are arranged as random units, including DNA encoding 18S, 5.8S, 28S ribosomal RNA and alternating between non-encoding sequences *ITS1* and *ITS2* (internal transcribed spacers) located on either side of the 5.8S gene segment [4-6]. The coding sequences of three rADN genes, 18S, 5.8S, 28S, are more conservative than the sequences of *ITS1* and *ITS2*. Currently, the *ITS* region of the nuclear genome is considered to be one of the most useful tools for identifying and evaluating plant phylogeny [7]. In this work, the researchers present the results of using the *ITS* DNA barcode to identify the Jewels of Opar samples collected from Quan Hoa district and Bim Son town of the Thanh Hoa province of Vietnam.

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Material and methods

The Jewels of Opar (*T. paniculatum*) samples collected from Quan Hoa district and Bim Son town (Thanh Hoa province) were used for morphological and DNA barcode analysis.

The identification of *T. paniculatum* plants was done according to the method suggested by Nguyen Tien Ban (2013) [8] and Pham Hoang Ho (1999) [9]. The total DNA was isolated from young leaves based on the method proposed by Shaghai, et al. (1984) [10]. The amplification of *ITS* region by PCR with primer pair *ITS-F/ITS-R* was synthesized according to Kress, et al. (2005) [11]. The expected size of the amplified DNA fragment is 665 bp in length.

The *ITS* primer sequences: *ITS-F*: 5' ACGAATTCATGGTCCGGTGAAGTGTTTCG 3'; *ITS-R*: 5' TAGAATTCCTCCGGTTCGCTCGCCGTTACT 3'.

The thermal cycle of PCR occurs after the initial 94°C denaturation step over a duration of 4 minutes. The reaction was carried out followed over 40 cycles at 94°C for 30 seconds, 58°C for 60 seconds (annealing), 72°C for 60 seconds, and a final extension 72°C for 10 minutes. The PCR products were detected by electrophoresis on 1.0% agarose gel. Later, QIAquick Gel Extraction Kit was used to purify the PCR products.

The nucleotide sequence of the *ITS* region was determined by the ABI PRISM® 3100 sequencing Avant Genetic Analyzer using the BigDye® Terminator v3.1 Cycle Sequencing Kit. The *ITS* nucleotide sequence was analyzed using BLAST, BioEdit, and DNASTar software.

Results and discussion

Morphological characteristics of Jewels of Opar (*T. paniculatum*) plants

Figure 1 presents the morphological characteristics of Jewels of Opar. Jewels of Opar is a tree-like herb that grows straight up to about 30-50 cm in height. The trunk is green, smooth, and branching at the bottom. The leaves of Jewels of Opar are staggered; they are generally oval, ovate-oblong, or egg back shaped. They are thick, glossy, and wavy vein, without hairs. The flowers of the plants have five reddish purple wings, two sepals, more than ten stamens, and a spherical ovary. The fruits are small, and the ripe fruit is ash gray in color. The seeds are very small, slightly flat, and black. The tuberous roots are cylindrical, with many small dark brown roots. The shape of the tuber resembles a humanoid. The tubers are about 3-6 cm long and pinkish white. On drying out, the tubers turn black in color. Both the roots and the tubers are sweet and spicy.

The seeds of Jewels of Opar collected from Quan Hoa district and Bim Son town (Thanh Hoa) were cultivated and analyzed on the basis of the morphological characteristics of roots, tubers, stems, leaves, flowers, fruits, and seeds (Fig. 1).

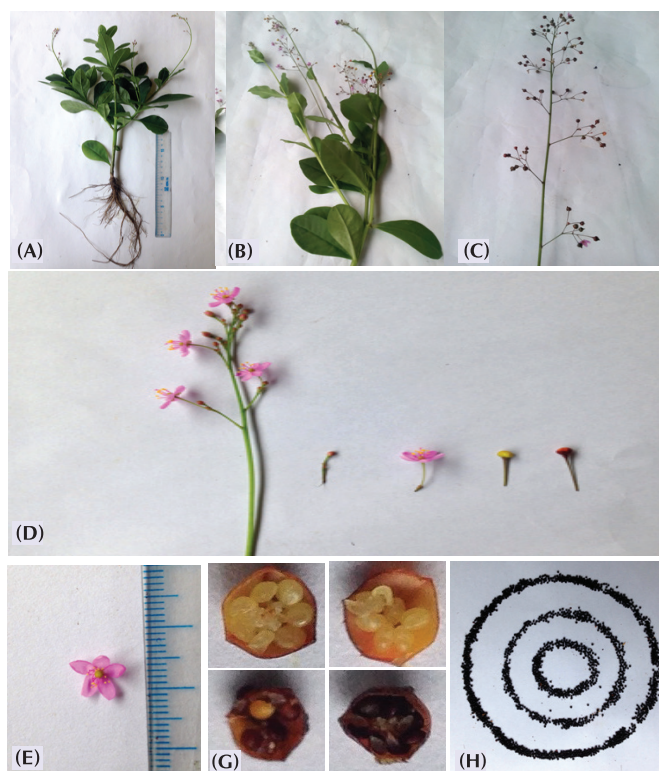


Fig. 1. Morphology of Jewels of Opar (*T. paniculatum*). (A): Jewels of Opar plant; (B): branches bearing flowers; (C): branches bearing fruit; (D, E): buds and flowers; (G): sliced fruit; (H): seeds.

An analysis of the growth and development of Jewels of Opar from seedling to flowering stage show that the seeds started to germinate after 6-7 days of their cultivation and the first leaves appeared after about 15 days. After 50 days, the roots of Jewels of Opar began to bulge and produce tubers. From the 65th day onwards, Jewels of Opar went on to produce flowers and fruits (Fig. 2).

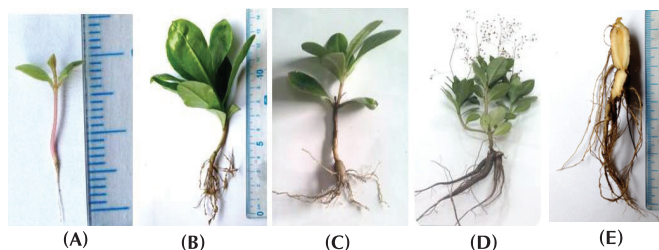


Fig. 2. The growth and development of Jewels of Opar. (A): 15-day-old seedling; (B): 40-day-old plant; (C): the roots began to bulge and produce tubers after 50 days; (D): the plant started to flower and produce fruits after 65 days; (E): tubers of 113-day-old Jewels of Opar.

According to Do Tat Loi, Jewels of Opar is a wild, herbaceous plant. The plants are cultivated in many places because of the medicinal value they carry [12]. Jewels of Opar are distributed across many localities such as Ha Giang, Tuyen

Quang, Hoa Binh, Lang Son, Cao Bang, Hai Phong, Thanh Hoa, and Nghe An... [9, 12]. Jewels of Opar can be planted by using the seed or the root. They are fast-growing trees, they can be harvested after a year, and the perennial Jewels of Opar will have larger tubers. Thus, it can be determined through the analytical results of the morphological characteristics and monitoring of growth and development of Jewels of Opar that the samples collected from Bim Son and Quan Hoa (Thanh Hoa) belong to the species *T. paniculatum*. Based on morphological characteristics, Pham Hoang Ho (1999) [9] and Do Tat Loi (2004) [12] classified Jewels of Opar as a type of ginsengs called Dong Duong ginseng. Its scientific name is *T. paniculatum*, belonging to *Talinum* genus, the Portulacaceae, Caryophyllales, and Magnoliopsida. However, if the plant is in its growing stage without flowers, it is easy to confuse it with the same species of *T. fruticosum*. In addition, the classification of Jewels of Opar encounters obstacles if the plants have been completely or partially processed. As a result, it is necessary to use an extra method and criterion for the classification. The DNA barcoding method with the *ITS* region can be used to accurately identify the Jewels of Opar samples without confusion with other herbs.

Characteristics of the *ITS* region isolated from Jewels of Opar plants

The total DNA was extracted from the leaves of Jewels of Opar and used to perform PCR with *ITS-F/ITS-R* primer pairs. PCR products were separated by electrophoresis on agarose gel with 1 kb DNA marker. The results showed that the PCR products of all samples obtained a DNA band of about 0.65 kb in size, which was similar to the predicted size of the *ITS* region (Fig. 3).

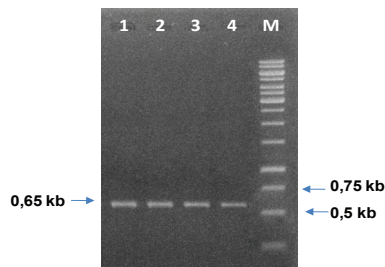


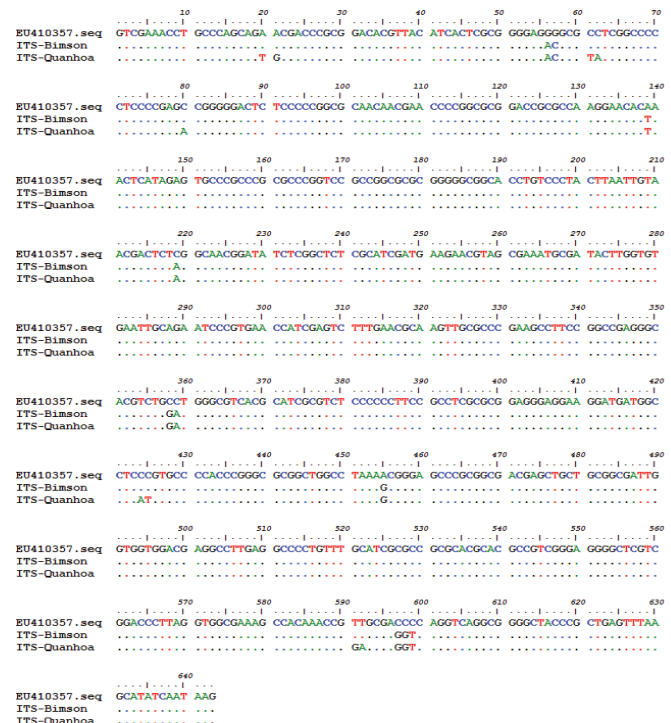
Fig. 3. PCR analysis of *ITS* region from genome of Jewels of Opar (M: DNA marker 1 kb; 1, 2: PCR products of two Jewels of Opar samples collected from Quan Hoa, Thanh Hoa; 3, 4: PCR products of two Jewels of Opar samples collected from Bim Son, Thanh Hoa).

The PCR products of *ITS* region were purified and then were sequenced. The results of the sequencing indicated an *ITS* segment of 643 bp in size. Using the BLAST tool in NCBI, the *ITS* sequences isolated from Jewels of Opar in Thanh Hoa province of Vietnam were 97-98% homologous to the three *ITS* sequences of *T. paniculatum* in GenBank, which had an accession number JF508608 [13], EU410357 [14], and L78094 [15]. The plant shares a 93% similarity with the *ITS* sequence of the *T. fruticosum*, *Talinum* genus with an accession number KJ380908 [16] in GenBank (Fig. 4).

Alignments Download GetBlast Graphics Distance tree of results					
Description	Max score	Total score	Query cover	E value	Ident Accession
<i>Talinum paniculatum</i> genomic DNA sequence contains 18S rRNA gene, ITS1, 5.8S rRNA gene, ITS2, 28S rRNA gene, isolate Quanhoa	1188	1188	100%	0.0	100% L785350.1
<i>Talinum paniculatum</i> genomic DNA sequence contains 18S rRNA gene, ITS1, 5.8S rRNA gene, ITS2, 28S rRNA gene, isolate Bimson	1138	1138	100%	0.0	99% L785351.1
<i>Talinum paniculatum</i> 18S ribosomal RNA gene, partial sequence; internal transcribed spacer 1, 5.8S ribosomal RNA gene, and internal	1083	1083	100%	0.0	97% EU410357.1
<i>Talinum paniculatum</i> 18S ribosomal RNA gene, partial sequence; internal transcribed spacer 1, 5.8S ribosomal RNA gene and internal	1013	1013	91%	0.0	98% L78094.1
<i>Talinum paniculatum</i> voucher Ccampo & Morales 1458 (RS4) 18S ribosomal RNA gene, partial sequence; internal transcribed spacer 1,	985	985	91%	0.0	97% JF508608.1
<i>Talinum fruticosum</i> voucher LCH42 18S ribosomal RNA gene, partial sequence; internal transcribed spacer 1, 5.8S ribosomal RNA gene	802	802	86%	0.0	93% KJ380908.1

Fig. 4. Analytical results of similarities between *ITS* sequences of Jewels of Opar samples from Bim Son and Quan Hoa (Thanh Hoa, Vietnam) compared with four *ITS* sequences in GenBank by BLAST tool.

As can be seen in Fig. 5, the comparative analysis of two *ITS* nucleotide sequences isolated from the Jewels of Opar samples collected from Bim Son and Quan Hoa (Thanh Hoa, Vietnam) and the *ITS* sequence with an accession number EU410357 in GenBank showed that there were 19 different nucleotide positions. If the *ITS* sequence with an accession number EU410357 in GenBank is used as the reference gene region, the mutation may be an explanation for the changes in the two *ITS* sequences isolated from the Jewels of Opar samples (Thanh Hoa, Vietnam), specifically T or G substituted for A; A or C substituted for G; G or T or A substituted for C; G or A substituted for T.



Thus, it can be concluded that the *ITS* region isolated from the Jewels of Opar samples from Bim Son and Quan Hoa (Thanh Hoa, Vietnam) is the *ITS* region of *T. paniculatum* species. The *ITS* sequences have been published in GenBank with the accession numbers LT853590.1 and LT853591.1. Fig. 6 shows the diagram of an *ITS* region isolated from *T. paniculatum* plants in Thanh Hoa, Vietnam.



Fig. 6. An *ITS* region of *T. paniculatum* in Thanh Hoa, Vietnam.

Genetic relationship among the species of the *Talinum* genus

An analysis of the genetic relationship between the species of *Talinum* genus was based on the nucleotide sequences of the *ITS* region in GenBank [17]. DNASTar software was used to establish a phylogenetic tree of the genetic relationship among *T. paniculatum* samples (Fig. 7).

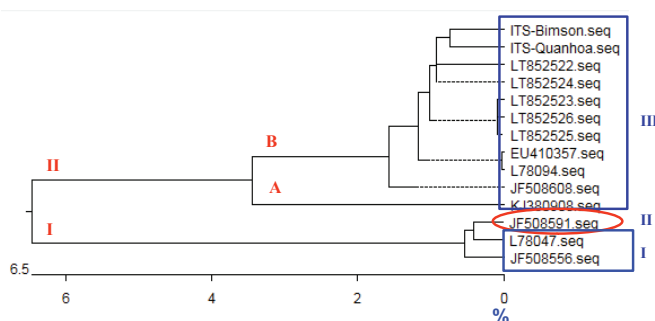


Fig. 7. Phylogenetic tree based on nucleotide sequences of *ITS* region.

Figure 7 shows the genetic relationship between two Jewels of Opar samples collected from Thanh Hoa, Vietnam and the *ITS* sequences of *T. paniculatum* species of the *Talinum* genus that have the following accession numbers: LT852522, LT852523, LT852524, LT852525, LT852526, EU410357, L78094, JF508608, and KJ380908, and the following sequences of Portulacaceae: L78047 (*Portulaca oleracea*), JF508591 (*Portulaca rotundifolia*), JF508556 (*Portulaca intraterranea*). In the diagram, all samples are classified into two large groups, wherein group I contains three *ITS* sequences (JF508591 L78047, JF508556) and group II consists of eleven *ITS* sequences of both genus *Talinum* and *Rotundifolia* of the family Portulacaceae. The genetic distance between the two genus *Talinum* and *Rotundifolia* is 6.5%. Branch II has two sub-branches - A and B. Sub-branch A has an *ITS* sequence with an accession number KJ380908 of *T. fruticosum*, and sub-branch B comprises of ten *ITS* sequences of the same species *T. paniculatum*. The UPGMA method was used to determine the genetic distance between *T. paniculatum* and *Talinum fruticosum*, which was calculated to about 3.5%.

Conclusions

Jewels of Opar (*T. paniculatum*) plants collected from Quan Hoa district and Bim Son town (Thanh Hoa, Vietnam) are tree-

like herbs. The trunk of Jewels of Opar is green and it grows straight up before branching out. The leaves are generally oval or ovate-oblong in shape, with wavy veins. The flower has five reddish purple wings, two sepals, more than ten stamens, and a spherical ovary. The fruits and seeds are both small and black. The tuberous roots are cylindrical with many small roots, while the tubers are sweet and spicy. The *ITS* region isolated from *T. paniculatum* plants in Thanh Hoa, Vietnam is 643 bp in length. Based on the nucleotide sequence analysis of *ITS* region, the Jewels of Opar samples collected from Bim Son and Quan Hoa (Thanh Hoa, Vietnam) were concluded to belong to *T. paniculatum* species, *Talinum* genus, Portulacaceae.

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Use of benthic diatom indices for assessing ecological status of the Sai Gon river, Vietnam

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Abstract:

In the present study, the Biological diatom index (BDI) and the Trophic diatom index (TDI) were calculated for the assessment the ecological status and the water quality of the Sai Gon river in comparison with the physico-chemical variables. In addition, a multivariate method was used to elucidate the main environmental variables driving the diatom community. A total of 87 diatom species were identified and used to calculate the diatom indices. The results of the biological data indicate that ecological status of upstream has a fine water quality; however, the downstream of the river was moderately polluted, and in some cases, of poor status. Canonical correspondence analysis (CCA) permutation tests demonstrated that diatom community was divided into two groups that corresponded to rural and urban characteristics. The BDI and TDI indices showed sensitivity to environmental stressors and served as potential application for bio-monitoring and water quality assessment of surface water in tropical region.

Keywords: *benthic diatoms, bio-indicator, Biological diatom index, Sai Gon river, Trophic diatom index.*

Classification number: 3.4

Introduction

The use of benthic diatoms for assessment of water quality in lentic systems has recently been applied in many countries. Due to their diversity and wide distribution in various habitats, diatoms are among the most common groups that are being used to monitor ecological status of rivers [1, 2]. Many diatom indices have been developed and applied for the classification water quality. As a multi-metric approach, the TDI originally developed by Kelly and Whitton (1995) [3], and the BDI developed by Lenoir and Coste (1996) [4], were commonly used in monitoring aquatic conditions. The TDI and BDI indices have been applied in several countries for assessing

water quality. Nevertheless, there was no study for assessing the ecological condition in Vietnam using these indices.

Water quality monitoring programs in Vietnam have been mainly based on water physico-chemical parameters [5]. However, the use of aquatic community composition in water quality assessment has several advantages compared to the physical and chemical variables. For example, aquatic communities can reflect the interactions between abiotic quality and the integrity of biotic factors. Therefore, they can accurately indicate water quality [2]. In addition, each group of aquatic communities can reflect the changes of water environment in different ways [6]. Aquatic communities such as phytoplankton, diatom, macroinvertebrates, zooplankton and fish have been used to assess the effects of pollutants on water quality. Currently, benthic diatom and benthic macroinvertebrates are the most widely used bioindicators in lentic water. The indices of Biological monitoring working party (BMWP^{VIETNAM}) and Average Tolerance Score per Taxa (ATSPT) calculated from benthic macroinvertebrate community have been developed and applied for the classification of the Vietnamese water quality [7, 8]. However, the use of freshwater benthic diatoms, especially in Vietnam, is in its infancy and is limited. Due to living on non-mobile substrates, diatom are more sensitive to pollution than other mobile organisms such as fishes, zooplankton and macroinvertebrates [6].

The Sai Gon river is important to Ho Chi Minh city, as it is the main water supply as well as the host of the Sai Gon port [9]. Over the past years, the industrial cluster and the urban population have grown considerably. This fast development has caused water pollution and *water quality degradation* of the river. In this study, the two diatom-based indices (the TDI and the BDI) were first applied for assessing the ecological status of the Sai Gon river.

Materials and methods

Study area

The Sai Gon river is located in Southern Vietnam, originating from Phum Daung in Southeastern Cambodia. The river flows south and southeast downstream along the western boundary of Binh Duong before entering the territory of Ho

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Chi Minh city and empties into the Dong Nai river at Nha Be, which, in turn, empties into the East Sea after flowing some 20 kilometres. The total length, catchment area and average flow rate of the Sai Gon river are 280 km, 4,750 km² and 85 m³/s, respectively [10].

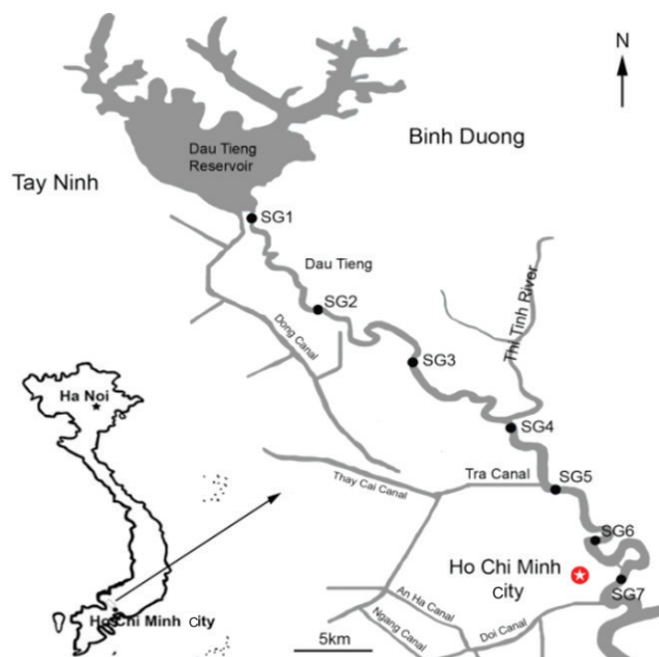


Fig. 1. Map of the Sai Gon river showing the seven study sites.

Environmental variables

The water samples were collected in dry and wet seasons at seven sampling stations coded SG1 to SG7, including rural upstream sites (SG1 to SG3; SG1: near Dau Tieng dam, SG2: Dau Tieng town, and SG3: Ben Suc bridge) and urban downstream sites (SG4 to SG7; SG4: close to the confluence of the Sai Gon and Thi Tinh rivers, SG5: Phu Long bridge, SG6: Binh Phuoc bridge, and SG7: Sai Gon bridge) of the Sai Gon river (Fig. 1). Water temperature, electrical conductivity, turbidity (TB), pH and dissolved oxygen concentration (DO) were measured on sites by using the Portable multi-meter (Hach 156, USA). The following variables total suspended solid (TSS), biochemical oxygen demand after 5 days (BOD₅), chemical oxygen demand (COD), total organic nitrogen (TN) and total phosphorus (TP) were measured according to APHA (2005) [11].

To measure the Total suspended solids (TSS), about 300-500 mL of water samples were filtered into a pre-weighed glass-fibre filter (Whatman GF/C, England) and dried completely at 95±5°C. Then, the TSS concentration was estimated gravimetrically. The total dissolved solid (TDS) was calculated from the conductivity concentration by multiplying with a factor of 0.6.

Diatom collection identification

Benthic diatoms were collected on hard substrates according to the method described by Chen, et al. (2016) [6], by brushing five substrates (stone, brick, wood, bamboo or five areas on the hard surfaces in urban area) over a surface area of 10 cm². Diatom samples were kept in 100 mL plastic vials and fixed with Lugol solution. In the laboratory, the diatom valves were cleaned with concentrated nitric acid, and then washed several times with distilled water according to the method described by Gray and Vis (2013) [12]. An aliquot of 1 mL sample was settled and counted on the Sedgewick rafter counting chamber. Diatom valves were examined under an inverted microscope (Olympus CK40-F200, Olympus, Tokyo, Japan) at 400× magnification. At least 500 diatom valves were counted for each sample; rare species were counted several times on some slides. Taxonomic identification and classification were based on the systems of Krammer and Lange-Bertalot (1986, 1988, 1991a, 1991b) [13-16]; Metzeltin and Lange-Bertalot (1998, 2002) [17, 18]; Krammer (2000) [19]; Rumrich, et al. (2000) [20]; and Wehr, et al. (2003) [21].

Calculating diatom metrics

Diatoms composition and abundance were used to calculate the BDI and TDI indices. The TDI index was first developed by Kelly and Whitton (1995) [3] and later revised by Kelly, et al. (2001) [22]. This index was calculated by using species composition and abundance of each diatom species. Each diatom species was given a sensitivity value from 1 to 5, where 1 indicates species that favour very low nutrients and 5 very high nutrients, and an indicator value from 1 to 3, where 3 means a species is a good indicator of nutrient sensitivity and 1 means that it is a poor indicator [3, 22]. Values were originally determined for each diatom species/genus based on the orthophosphate concentrations, where taxa are most abundant. The TDI is calculated as:

$$TDI = (WMS \times 25) - 25$$

where, the Weighted mean sensitivity (WMS) value is calculated as:

$$WMS = \frac{\sum_{j=1}^n a_j v_j i_j}{\sum_{j=1}^n a_j v_j}$$

where: a_j is abundance or density of valves of species j , v_j is indicator value (ranging from 1-3) and i_j is pollution sensitivity (ranging from 1-5) of species j . The generated TDI values vary from 0 (indicating very low nutrient concentrations) to 100 (indicating very high nutrient concentrations) [22].

The BDI index was calculated by using the Calculate BDI with Excel program. The ecological status and the water quality were classified based on the BDI values according to the method described by Lenoir and Coste (1996) [4], as shown in Table 1.

Table 1. Trophic status and water quality class based on BDI index.

BDI value	Quality class	Trophic status
>17	High quality	Oligotrophic
15-17	Fine quality	Oligo - mesotrophic
12-15	Moderate quality	Mesotrophic
9-12	Low quality	Meso - eutrophic
<9	Poor quality	Eutrophic

In addition, diatom indices, including species richness (S), Shannon-Weiner index (H), species evenness (J) and Simpson's diversity index (D), which are commonly used in water quality bioassessment [23], were used to characterise the diatom community structure and the environmental status at each site. These metrics were calculated by using the PRIMER V.5 analytical software.

Statistical analysis

One-way analysis of variance (ANOVA) was applied to examine the significance of the differences between the upstream and downstream sites. The analysis was completed by using Tukey's HSD test significant difference. The Pearson correlation analysis was used to determine the correlation between the diatom metrics and the environmental variables. All statistical analysis was done by using SPSS v.16.0 (IBM Corp., Armonk, NY, USA). Canonical Correspondence Analysis (CCA) was analysed by using the program CANOCO 4.5 for Windows to elucidate the main environmental variables' driving force in the diatom community and diatom metrics. All variables were log-transformed to normalise their distributions before analysis.

Results

Environmental variables

The physico-chemical variables measured in the field at each site were summarised in Table 2. The water of the Sai Gon river is slightly acidic. The pH value decreased at downstream and ranged from 5.5 to 6.3. DO values were low (less than 5 mg/L) and decreased at downstream sites. TDS, TSS, BOD₅ and COD increased gradually while moving towards the downstream of the river. Electrical conductivity is one of the environmental variable that changed significantly from 110 to 1,496 µS/cm between upstream and downstream sites. Additionally, nutrient pollutants increased at downstream with TN values ranging from 1.3 to 2.1 mg/L and TP values ranging from 0.1 to 0.5 mg/L. Based on the TN and TP values, the water quality of the Sai Gon river is now considered eutrophic to hypertrophic, according to the classification described by Forsberg and Ryding (1980) [24] (hypertrophic: total phosphate > 100 µg/L, total nitrogen > 1,500 µg/L; eutrophic: total phosphate, 25-100 µg/L; total nitrogen, 600-1,500 µg/L). Moreover, it was noted that the maximum values of nutrient pollutants were reported to three sites at urban downstream (SG5 to SG7). ANOVA results showed that there was no significant change in the water temperature, TB, pH, DO, BOD₅ and COD (ANOVA, p<0.05), while significant differences in TSS, TN and TP between dry and wet seasons (data not show) were observed.

Diatom composition and abundance

In total, 83 species of benthic diatom, corresponding to 19 genera, were identified in the Sai Gon river. The most abundant genera were *Navicula*, *Nitzschia*, *Eunotia* and *Coscinodiscus* with 13, 11, 6 and 6 species, respectively (Fig. 2A). The diatom composition and distribution were different between in rural and urbanised regions. On the spatial scale, the species named *Achnanthes minutissimum*, *Cymbella affinis* and *Eunotia robusta* were the consistently dominant species at rural sites (SG1 to SG3). However, tolerant species belonging to *Navicula* and *Nitzschia* were predominated at urban sites (SG4 to SG7).

Table 2. The mean ± SD (n=6) of physico-chemical variables measured at each site during the study period.

Site	SG1	SG2	SG3	SG4	SG5	SG6	SG7
pH	6.5±0.2	6.7±0.2	6.4±0.2	6.2±0.1	6.0±0.2	6.3±0.3	6.2±0.4
DO (mg/L)	4.7±0.3	4.6±0.4	4.4±0.5	3.3±0.7	3.5±0.8	3.2±0.3	3.3±0.4
Temperature (°C)	29.3±1.0	29.1±0.7	29.5±0.6	29.4±0.2	29.0±0.5	29.4±0.6	29.7±0.3
TDS (mg/L)	59.2±33.0	70.6±30.7	64.2±29.3	80.0±33.5	171.9±16.3	162.7±11.6	195.0±8.7
TSS (mg/L)	40.4±20.3	59.8±7.5	66.8±3.1	71.9±6.5	114.0±31.4	99.3±19.7	87.7±7.1
TB	38.2±3.9	49.5±5.3	52.8±0.8	85.5±19.9	70.6±4.1	79.0±18.9	71.3±4.0
Conductivity (mS/cm)	110±27	366±61	524±48	831±64	1200±99	1496±97	1438±155
BOD ₅ (mg/L)	4.1±1.0	4.3±0.3	5.1±0.6	5.0±0.2	6.1±0.2	5.7±0.9	5.6±0.2
COD (mg/L)	5.4±0.7	5.7±0.7	6.0±0.5	5.7±0.4	6.9±0.5	6.8±0.9	6.8±0.8
TN (mg/L)	1.3±0.4	1.4±0.1	1.4±0.1	1.8±0.1	2.0±0.2	1.8±0.3	2.1±0.1
TP (mg/L)	0.1±0.03	0.3±0.06	0.2±0.02	0.3±0.05	0.4±0.03	0.5±0.08	0.4±0.05

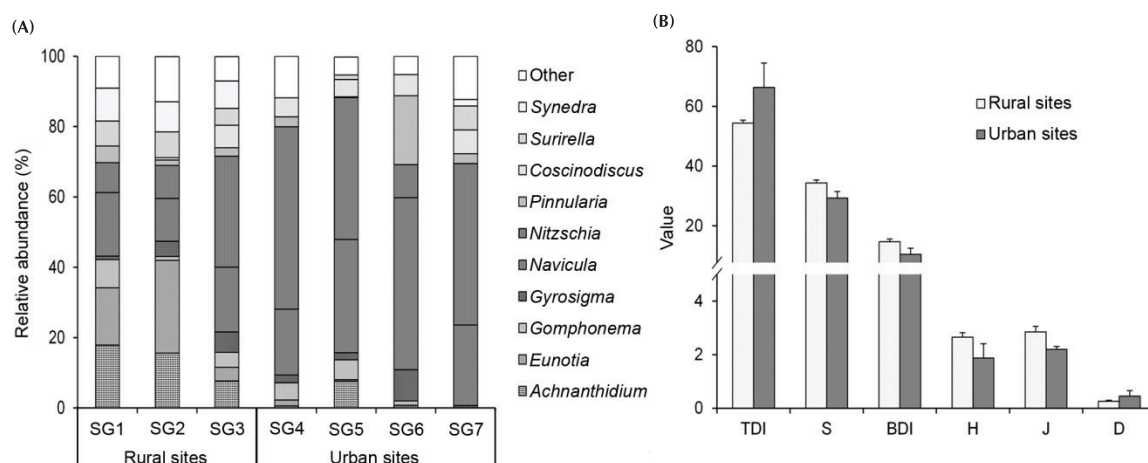


Fig. 2. (A) Composition of the 10 most dominant genera and (B) the diatom metrics of the Sai Gon river.

Table 3. Results of TDI and BDI indices with correspondent judgment and class of quality.

Site	BDI	TDI	Trophic status*		Quality class	Water quality
			A	B		
SG1	16.0	53.9	Oligo-mesotrophic	Eutrophic	Fine quality	A ₁
SG2	14.2	57.4	Mesotrophic	Eutrophic	Moderate quality	A ₁
SG3	13.5	51.8	Mesotrophic	Eutrophic	Moderate quality	A ₁
SG4	12.7	58.6	Mesotrophic	Hypertrophic	Moderate quality	A ₁
SG5	11.8	59.8	Meso-eutrophic	Hypertrophic	Low quality	A ₁
SG6	8.5	73.2	Eutrophic	Hypertrophic	Poor quality	A ₁
SG7	8.7	73.6	Eutrophic	Hypertrophic	Poor quality	A ₁

*Trophic status (A) based on the classification systems of Lenoir and Coste (1996) [4] and (B) based on the eutrophic classification systems of Forsberg and Ryding (1980) [24].

Diatom indices and ecological status assessment

The BDI and TDI indices were clearly different between urban sites and rural sites ($p < 0.05$), and they ranged from 10.4 to 14.6, and from 53.4 to 66.3, respectively (Fig. 2B). These diatom-based indices indicated a similar pattern of seasonal variation. The BDI decreased while the TDI values increased at downstream. Other diatom indices including species richness index (S), Shannon diversity (H), species evenness (J) and Simpson diversity (D) also showed that there were significant differences between urban sites and rural sites ($p < 0.05$). The lower course sites registered the lowest score of all indices, but had the highest value of relative abundance of dominant taxa and tolerance TDI score (Fig. 2B). The high TDI but lower BDI score in the urban sites indicated a higher impact from urbanisation downstream of the river.

The values of the TDI and BDI indices calculated for each site, with correspondent judgement and class of quality, is presented in Table 3. The water quality in the Sai Gon river varied between moderate to poor status, corresponding from

Oligo-mesotrophic to Hypertrophic (strongly polluted at downstream urban sites), based on the classification systems of Lenoir and Coste (1996) [4], Kelly, et al. (2001) [22] and Forsberg and Ryding (1980) [24]. However, based on BOD₅, COD and total nitrogen according to QCVN 08:2008 (the Vietnamese national technical regulations for surface water quality), water quality was classified into A₁ class, which could be used for drinking.

Canonical correspondence analysis

The environmental variables, diatom indices of abundance, species richness, TDI, BDI and H indices were used in the CCA analysis. The results for CCA exhibited 94.4% variability of the total axis with 91% for Axis-1 and 3.4% for Axis-2 of the total variance. The diatom abundance and TDI had a significant correlation with TP, TN, EC, TB, TDS, TSS, COD and BOD₅. Whereas species richness, BDI and H indices showed negative correlation with the above parameters, but correlative with DO (Fig. 3).

Of the 83 diatom taxa identified in this investigation, 31 taxa, with relative abundance $\geq 10\%$, were included in data analysis using CCA. In total, 97.8% of the variation between selected species and environmental variables were explained by the first two axes of CCA. The CCA was divided into two groups with difference species indicators. Group 1 was those species who were preferred in rural areas with higher DO and oligo-mesotrophic conditions. The other group included species tolerant to high urbanisation. Those species had positive correlation with TP, TN, TB, EC, TDS, TSS, COD and BOD_5 (Fig. 3).

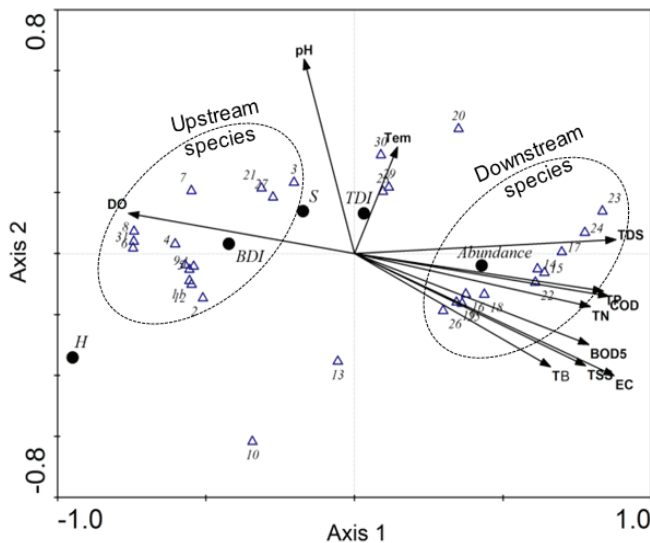


Fig. 3. Canonical correspondence analysis for environmental variables with biological indices and diatom community. Taxa codes correspond to those in Appendix 1.

Discussion

The Sai Gon river water quality was slightly acidic. This can be explained by surface run-off, which brought acidity from acid sulphate soils in the downstream area of the river basin. DO values were low in the Sai Gon river and rapidly decreased at downstream sites. The results were in agreement with Le, et al. (2016) [25], that the DO concentrations decreasing at downstream may be due to the consumption by heterotrophic bacteria and nitrifiers for the degradation of biodegradable organic matter. Water pollution from the Sai Gon river's tributaries adversely affected the raw water quality of the Sai Gon river, which resulted in increasing BOD_5 , COD, TSS and TDS at downstream sites. EC is a parameter related to salinity or chloride content [25]. The result of increasing EC at downstream of the river may be due to the seawater intrusion. According to previous studies, water quality of the Sai Gon river polluted mainly organic matter, heavy metal, e-EDCs and

microorganisms [25, 26]. Particularly, bacteria, heavy metal of Fe, Cd, Mn and e-EDCs had higher potential risk and may have an effect on human health as well as on safe water supply [9, 10, 26]. Results of this study showed that water quality of the Sai Gon river was also contaminated with nutrient concentration, particularly, nitrogen and phosphorus. This may be associated with stormwater runoff, increase in urban development and discharge of waste water due to human activities.

The Sai Gon river is affected simultaneously by multiple anthropogenic pressures, including heavy metal, organic pollution resulting on eutrophication and degradation of water quality [25]. Additionally, aquatic life is unique and reflects on these impacts. In this study, the use of more integrative diatom metrics together with the physico-chemical variables gain more reliable tools for water quality classification. Diatom indices are shown to be one of the most effective tools for monitoring the trophic status of the river [27]. In case of the Sai Gon river, the water quality varied between fine to poor status. According to these results, it was possible to conclude that only the upper part of this river currently supports conditions for the drinking water supplies. Generally, the downstream sites of the Sai Gon river had lower water quality than the upper stream sites. This common trend may be caused by an increase in human pressure and pollutants on the surrounding lands as water flows down [10].

Compared to water quality assessment solely based on physico-chemical variables, the diatom indices clearly added more information. Decrease in environmental quality on the Sai Gon river was indicated by the BDI and TDI indices, more so than by the physico-chemical variables. Diatom indices are potential tool to elucidate the possible impact of human activity differences on the river ecosystem with the degree of pollution. The BDI and TDI indices, developed in temperate region, is the most widely used diatom-based index for water quality monitoring tools [2]. However, they have never been applied in Vietnam waters. The TDI could reflect nutrient enrichment, mainly phosphorus. It permits rapid assessment of the overall condition of the complicated ecology of streams and rivers and be easily understood by non-technical managers [28]. The BDI is an index routinely used in France for ecological status assessment. It uses a list of key species that show different pollution sensitivities. Therefore, the BDI reflected the pollution sensitivity, or 'ecological profile' of each diatom species in the river [29]. This study suggested that the BDI and TDI indices would be able to distinguish sites of various degrees of pollution and therefore, they may be adequately applied in Vietnam and other regions for surface water monitoring purpose. These results well agree with the previous study that benthic diatom assemblages could be used to assess human impacts on streams across a rural to urban gradient [30].

Appendix 1. List of 31 most abundant diatom species from the Sai Gon river, Vietnam. The code number of diatom species was used in CCA analysis.

Code	Species	Upstream sites	Downstream sites
1	<i>Achnanthes brevipes</i>	+	
2	<i>Achnanthidium minutissimum</i>	+	
3	<i>Cyclotella striata</i>	+	+
4	<i>Cymbella affinis</i>	+	+
5	<i>Cymbella lanceolata</i>	+	+
6	<i>Cymbella sgracilis</i>	+	+
7	<i>Cymbella turgida</i>	+	
8	<i>Eunotia gracilis</i>	+	+
9	<i>Eunotia intermedia</i>		+
10	<i>Eunotia pectinalis</i>	+	
11	<i>Eunotia robusta</i>	+	+
12	<i>Fragilaria sp.</i>	+	+
13	<i>Gomphonema gracile</i>	+	+
14	<i>Melosira granulata</i>		+
15	<i>Melosira varians</i>		+
16	<i>Nacicula placentula</i>	+	+
17	<i>Nacicula salinarum</i>	+	+
18	<i>Navicula antonii</i>		+
19	<i>Navicula cryptocephala</i>	+	+
20	<i>Navicula cryptotenella</i>		+
21	<i>Navicula elegans</i>	+	
22	<i>Nitzschia angustatula</i>	+	+
23	<i>Nitzschia fonticola</i>	+	+
24	<i>Nitzschia palea</i>		+
25	<i>Nitzschia recta</i>	+	+
26	<i>Nitzschia umbonata</i>	+	
27	<i>Pinnularia major</i>	+	+
28	<i>Surirella capronii</i>	+	+
29	<i>Surirella elegans</i>	+	
30	<i>Surirella linearis</i>	+	+
31	<i>Synedra acus</i>	+	

Conclusions

In this study, the diatom metrics of BDI and TDI were applied to assess the water quality and the ecological status of the Sai Gon river. Results indicated that the benthic diatom community reflected the water quality and ecological status more accurately than the routine investigation of physico-chemical variables. Additionally, it differentiated the water quality and the ecological conditions in the Sai Gon river, Vietnam. Therefore, it is necessary to use diatoms together with the physico-chemical variables in the water quality monitoring program.

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Formation and chemistry of the groundwater resource in the Mekong river delta, South Vietnam

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Abstract:

The origin and chemistry of the groundwater in the middle Pleistocene (qp,³), lower Pleistocene (qp,₁), upper Pliocene (n₂²), lower Pliocene (n₂¹), and the Miocene (n₁³) in the Mekong river delta (MKRD) were investigated by using isotopic and geochemical techniques. The origin of the groundwater was evaluated based on the composition of the water stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) in the local precipitation, in water from the rivers system, and in the groundwater samples. The hydraulic interaction between the surface water and the groundwater as well as between the aquifers was assessed by a statistical treatment for the mean and standard deviation of the $\delta^{18}\text{O}$ signature and based on the ^{14}C -ages of the water samples taken from different aquifers. The salinization of groundwater in the deep aquifers was investigated using the $\delta^{18}\text{O}$ signature combined with the geochemical composition of the water samples. It was revealed that the groundwater in the deep aquifers in the MKRD could be divided into two groups. The first group is fresh and represents the regional precipitation with the long traveling time ranging from older than 100 years to older than 40 ka BP (kilo years Before Present). The second group is the regional precipitation that is recharged from the remote areas mixed with the seawater. Statistical treatment with the mean $\delta^{18}\text{O}$ using the Mann-Whitney test showed that the water from the Mekong river system did not or very weakly recharged the deep aquifers. The groundwater in the deep aquifers in that region was likely to be connate, so that fresh groundwater resource in the region seemed to be limited. The chemistry of the groundwater in the study region is controlled by the incongruent dissolution of the Mg-calcite as well as sulfate and iron oxy-hydroxide reductions by organic matters presented in the aquifer sediment. The groundwater in the deep aquifers in the MKRD from some locations was saline, but the salinity in most aquifers was thought to result from the migration of saline water entrapped in the marine sediment pores to the fresh water in the aquifers. Meanwhile, in other locations, the salinity was suggested to result from the salt intrusion due to the over-abstraction rate, as it was evident from the $\delta^{18}\text{O}$ vs. $[\text{Cl}^-]$ relationship, or due to the up conning of saline water from the deeper aquifers to the upper ones. Particular measures must be developed for the better management of groundwater in the MKRD to ensure a sustainable resource of freshwater being supplied to the local population in future.

Keywords: groundwater ^{14}C -age, Mekong river delta, saline pore water migration, salt intrusion, Vietnam, water stable isotopic composition.

Classification number: 4.2

Introduction

Water is a vital natural resource for every nation. The life on Earth is possible only due to the existence of water on it. Although Vietnam is located in a tropical region, however, during the last decades, it has severely suffered from water shortage. During the dry season (from November till April), most of the reservoirs in the central part of the country were dried-up. Therefore, the farmers had to take their cattle far away from their villages for water. In the MKRD, the salt intrusion was observed very deep in the inland through the river system. The drinking water for the population in the MKRD is mostly abstracted from the groundwater sources. The demand for

clean water has steadily increased, leading to the abstraction yield of groundwater in the region to be higher year by year. At present, the rate of groundwater abstraction from the MKRD is around $2.10^6 \text{ m}^3 \text{ a day}$ [1].

There were two contrary hypotheses of groundwater resource formation in the MKRD. Based on the results of a study conducted during the 1980s, Nguyen Kim Cuong and his co-workers concluded that the artesian groundwater in the MKRD is of the paleo-type, having been closely buried since the Delta was formed, and that this water has no recharge [2]. However, Vu Van Nghi and Wesling [3] hypothesized that the origin of the groundwater in the MKRD was due to the

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local precipitation, and that groundwater in the region was continuously recharged from the surface sources at a very slow rate. Louvat and Ho Huu Dung [4] had conducted a study on the groundwater in the MKRD using water stable isotopes and dating the water by the radiocarbon method to determine the possible recharge areas for the aquifers in the region. Results of the study led them to the conclusion that the groundwater in the study area is recharged from areas at an altitude of around 170 m above the mean sea level. The recharge areas could be on the northeast highland, i.e. the Tay Nguyen plateau and/or the Cambodian territory [4].

The aim of this study is to investigate in detail the origin and salinization of water from the most important aquifers in the MKRD, based on the isotopic and chemical composition of different types of water, namely, local precipitation, river water, and groundwater. The use of the water stable isotopic content in conjunction with the water ionic content might help in the identification of processes, such as evaporation and salinization/desalination or mixing that affect the water bodies [5]. However, the use of radioactive isotopes of the minerals dissolved in water, e.g. ^{14}C in the total dissolved inorganic carbon (TDIC) could offer an idea about the movement direction of groundwater as well as the interaction between the aquifers in the study region [6].

Study area

The study was conducted in the MKRD and Fig. 1 depicts a map of the study region. The total area of the delta is around 54,250 km², in which around 31,650,000 habitants have settled, among whom, almost 65% are farmers [7].



Fig. 1. A map of the MKRD that comprises the Long An, Tien Giang, Dong Thap, Vinh Long, Ben Tre, Tra Vinh, Soc Trang, Hau Giang, Can Tho, An Giang, Kien Giang, Bac Lieu, and Ca Mau.

Geology of the region

The MKRD is one of the five geologic structural blocks that created the terrestrial Vietnam, namely, the northeast and northwest blocks in the northern part, Truong Son and Kon Tum blocks in the central part, and the Nam Bo block in the southernmost part. The Nam Bo block was covered with a very thick (> 6,000 m) sequence of Cenozoic formations that have de-formed and become basins for sedimentation [8, 9]. The Neogene and Upper Paleogene are the main deposits found in the Nam Bo geologic block that belong to the deltaic and marine sediment [8].

Hydrology of the region

The hydrologic regime of the MKRD is dominated by the Mekong river system that consists of the Tien (Mekong) river and the Hau (Bassac) river. These rivers systems are the chief contributors of freshwater to the region for irrigation. Annually, the Mekong river system discharges a total of about 500 billion cubic meters of freshwater through the Mekong river delta [10].

Complicating the natural stream system of the Mekong delta is a closely integrated man-made network of approximately 4,000 km of canals and inland waterways. These are subject to the tidal incursions of brackish water from Bien Dong, which might extend far inland during the dry season (February to April) on the Mekong river system.

Hydrogeology of the region

To date, eight aquifers in the MKRD have been identified as shown in Fig. 2 and Fig. 3 along transect northeast toward southwest, NE-SW (Binh Phuoc - Ca Mau) and transect west toward east, W-E (Dong Thap - Tra Vinh), respectively [11, 12]. The aquifers found are Holocene (qh), upper, middle, and lower Pleistocene symbolized, respectively, as qp₃, qp₂³, and qp₁, upper Pliocene (n₂²), lower Pliocene (n₁¹), Neogene (n₁³), and bedrock (Mtz). From those aquifers, fresh water can be found only from the qp₂³ and qp₁, n₂², n₁², n₁³, Mtz, and occasionally in the qp₃ aquifers, but the Holocene aquifers contain either brackish or saline water that is not suitable for drinking purposes.

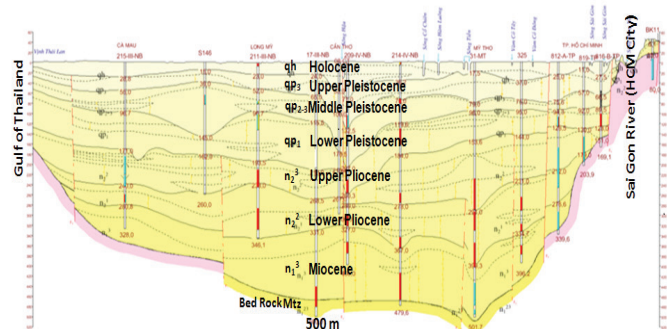


Fig. 2. The eight aquifers separated by the N-Q geologic structure along the transect NE-SW (Binh Phuoc - Ca Mau) in the MKRD [11, 12].

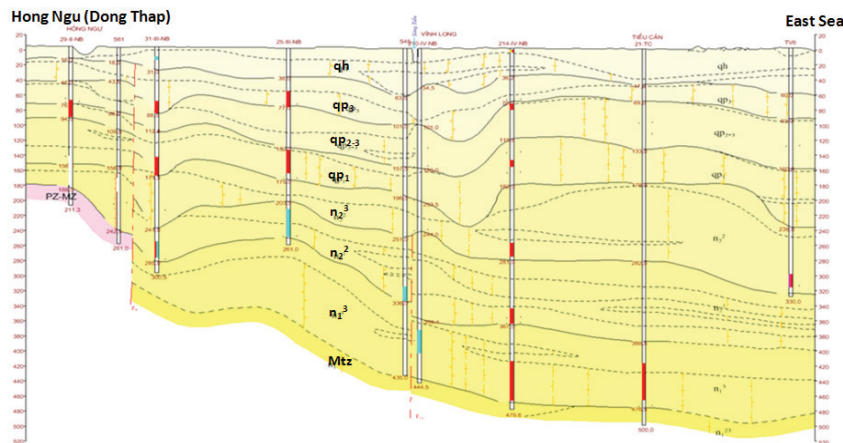


Fig. 3. The eight aquifers separated by the N-Q geologic structure along the transect W-E (Dong Thap - Tra Vinh) in the MKRD [11, 12].

The Holocene aquifers (qh) cover most of the plain with a thickness of up to 55 meters in the central part. The thickness of the upper Pleistocene aquifer (qp₃) is up to 33 m, from 50-55 m to 81 m on the land surface, following the middle Pleistocene (qp₂³) of a thickness up to 141 m. Between the Holocene and the Pleistocene aquifers, there are aquitards of various thicknesses. All the Pleistocene aquifers are confined.

The upper and lower Pliocene aquifers (n₂², n₂¹) are confined, and their thickness is up to 100-145 and 90-120 m, respectively, in between the Tien and the Hau rivers, and in the Ca Mau peninsula. The fractured basement aquifer (Mtz) is confined and the groundwater is only tapped by a few boreholes in the Kien Giang province [12].

Sampling sites and sampling procedure

Groundwater was sampled from five aquifers as follows: qp₂³, qp₁, n₂², n₂¹, and n₁³. The samples were taken along two transects corresponding to the NE toward SW and W toward S as shown in Fig. 4 and Fig. 5.

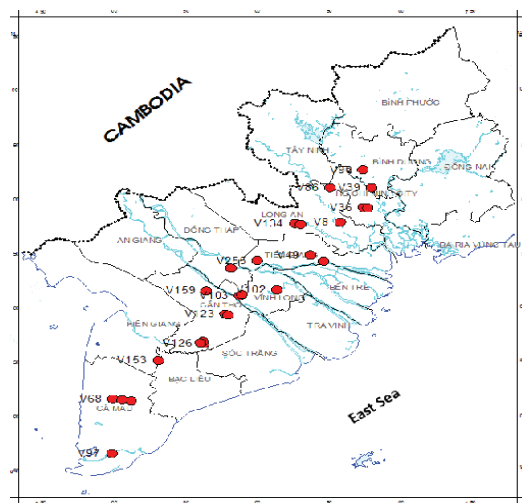


Fig. 4. Sampling locations along the transect NE toward SW (Binh Phuoc - Ca Mau).

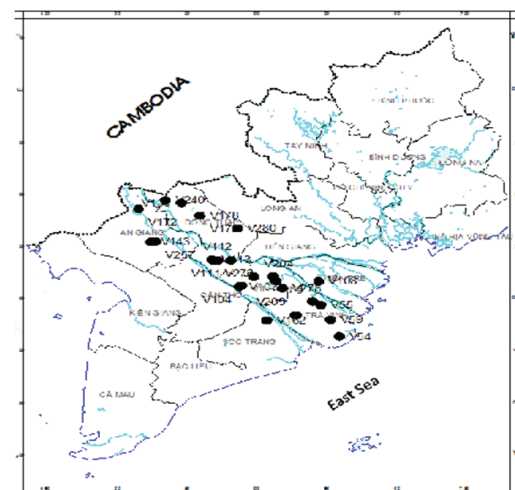


Fig. 5. Sampling locations along the transect W toward E (Dong Thap - Tra Vinh).

To take groundwater samples, a sampling procedure recommended by the IAEA was implemented [13]. Briefly, it was as follows:

First, the stagnant water in the wells was completely flushed out by pumping out till the pH and the temperature of the water were unchanged. Alkalinity, including concentrations of bicarbonate ($[\text{HCO}_3^-]$), carbonate ($[\text{CO}_3^{2-}]$), and free carbon dioxide ($[\text{CO}_2]$), in the groundwater samples was then determined by titration using a HCl 0.1N solution. The content of total dissolved inorganic carbon (TDIC) in the samples was calculated by summing up the concentrations of $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, and $[\text{CO}_2]$ [14].

The TDIC in the groundwater used to determine the content of carbon-13 and carbon-14 needed for the radiocarbon dating was precipitated in the form of BaCO_3 at pH = 10 by using a saturated BaCl_2 solution, following a procedure described in [13].

Rain water was collected monthly using a device constructed following an IAEA recommendation [15]. The device was installed on the roof of the premises of the Center for Nuclear Techniques in Ho Chi Minh (HCM) city. The surface water was sampled at a depth of 0.5 m from the surface and around 1 m from the bank of the Tien and Hau rivers.

For chemical analyses, around 100 ml of groundwater samples were first filtered through 0.45 mm mesh filters to remove the suspended matters and then they were split into two parts. One part was acidified with 2-3 drops of HNO_3 (65%, PA grade, Merck, Germany) to make pH of the samples 1-2. These samples were subjected to analysis for cations, whereas the other part was kept without acidification for anion analysis.

For the tritium determination, one liter of water was sampled into a HDPE bottle with a tight cap to avoid isotopic

exchange with the atmospheric moisture. The samples were transferred to the laboratory in Hanoi for further treatment and measurement for tritium activity.

Sample treatment and analytical procedure

The ionic content of the water samples was quantified by ion chromatography using a DIONEX 600 from the Institute for Nuclear Science and Technology (INST in Hanoi). Stable isotopes (^2H , ^{18}O , and ^{13}C) were analyzed at the INST with an Isotope Ratio Mass-Spectrometer (IR MS, MicroMass, JV, UK), equipped with an Elemental Analyzer (Eurovector, Italy). To determine the deuterium composition, the samples were pyrolyzed on a Ni catalyst at $1,050^\circ\text{C}$ to form hydrogen, followed by the purification on a chromatographic column before entering the ion source of the IS MS. The water oxygen was first converted into CO_2 gas by decomposing the water samples on glassy carbon at $1,250^\circ\text{C}$. The formed CO_2 was subjected to a chromatographic purification before entering the ion source of the IR MS.

Upon the arrival at the laboratory, the barium carbonates were carefully washed off with hot deionized water to remove the alkaline excesses and then dried under a vacuum. The dried carbonate samples with an amount of around 100 mg were then wrapped in tin capsules and subjected to decomposition at $1,250^\circ\text{C}$ with a CuO_2 catalyst in the Elemental Analyzer. The formed CO_2 was then allowed to pass through a chromatographic column to remove any contamination before entering the ion source of the IR MS to determine the carbon-13 content. The water stable isotopic composition and carbon-13 content in TDIC were expressed in the delta notation (δ) as follows:

$$\delta^2\text{H} = \left(\frac{R_{^2\text{H, sample}}}{R_{^2\text{H, std}}} - 1 \right) \cdot 1000 \quad (1)$$

$$\delta^{18}\text{O} = \left(\frac{R_{^{18}\text{O, sample}}}{R_{^{18}\text{O, std}}} - 1 \right) \cdot 1000 \quad (2)$$

$$\delta^{13}\text{C} = \left(\frac{R_{^{13}\text{C, sample}}}{R_{^{13}\text{C, std}}} - 1 \right) \cdot 1000 \quad (3)$$

where: $R_{^2\text{H, sample}}$, $R_{^2\text{H, std}}$, $R_{^{18}\text{O, sample}}$, $R_{^{18}\text{O, std}}$, $R_{^{13}\text{C, sample}}$, and $R_{^{13}\text{C, std}}$

are the isotopic ratios of $^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$, and $^{13}\text{C}/^{12}\text{C}$ samples and standards, respectively. The value of the delta notation is expressed in per mil (‰). The standard used in the analyses of the water stable isotopes is the Vienna Standard of Mean Ocean Water (VSMOW), but that for ^{13}C in TDIC is the Vienna Pee Dee Belemnite (VPDB) [16].

The precision of $\delta^2\text{H}$ was $\pm 2\%$, and that of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ was $\pm 0.2\%$. A quality assurance and quality control program was applied for the ionic content determination by analyzing the standard solutions supplied by the IC supplier (DIONEX). The standard deviation of the analytical results was more than $\pm 3\%$ from the certified value for a respective constituent.

For the tritium dating, the water samples were first subjected to distillation to remove the minerals dissolved until the electric conductivity was less than $10 \mu\text{S cm}^{-1}$. Around 500 ml of the distilled water samples were then subjected to the electrolytic enrichment for tritium at 4°C till around 10 ml was attained [17, 18]. The tritium-enriched water samples were purified again by distillation and then mixed with low-tritium Ultimagold scintillation cocktail (Hewlett-Packard, HP Supplier) in vials of 20 ml capacity for counting the ^3H activity on a low background HP Liquid Scintillation Counter TriCarb TR 3770. The ^3H activity in the water samples was expressed in the Tritium Unit (TU, $1 \text{ TU} = 0.118 \text{ Bq L}^{-1}$). The limit of detection for ^3H by the procedure was estimated to be as low as 0.4 TU. The accuracy of the determination was checked by the participation in the inter-comparison exercises organized by the IAEA Isotope Hydrology Section in the years 2004 and 2008 [19, 20]. In the 2004 exercise, the Hanoi laboratory (No.74) produced results having Z-scores of -1.25 and 0.59 for the samples of 1.74 TU and 5.43 TU, respectively. In the 2008 exercise, the laboratory (No.27) produced results with Z-scores of 0.42 and 1.57 for the samples of 4.07 TU and 1.54 TU, respectively.

The carbon-14 activity in the TDIC used for dating the groundwater samples was measured in the Center for Nuclear techniques in HCM city. It was there that the BaCO_3 was first converted into CO_2 by decomposing it with concentrated H_3PO_4 (PA grade, Merck supplier), followed by the benzene synthesis [21]. The benzene obtained was mixed with the Ultimagold scintillation cocktail (HP Supplier) and then counted for the ^{14}C activity on the HP LSC TriCarb TR 3770. The ^{14}C content in the samples was expressed in percent of the modern carbon (pMC). This is a relative measurement of the ^{14}C activity in the samples and those in a standard supplied by the National Institute of Standards and Technology (NIST, USA). The ^{14}C NIST standard used in this study was oxalic acid II (ox-II) made from the molasses of French beet planted in 1977, which has a ^{14}C activity of 0.2147 Bq/g C and $\delta^{13}\text{C} = -25\%$ [22].

Groundwater transit time (the age) estimation

The age of the groundwater is defined as the transit time between the infiltration zone and the discharge point [5]. The aim of the age determination is to evaluate the flow direction of water in an aquifer. The groundwater age calculation was made based on the data of ^{14}C activity and $\delta^{13}\text{C}$ in the TDIC. The principle of the ^{14}C -dating method was the law of radioactive decay, and in the case of dating the groundwater, it was expressed by Equation (4).

$$^{14}\text{t} = 8268 \ln \frac{^{14}\text{a}_0}{^{14}\text{a}_{\text{sample}}} \quad (\text{a BP}) \quad (4)$$

where: ^{14}t denotes the age, in years Before Present (BP), of a groundwater sample estimated by the ^{14}C activity in TDIC; the number 8268 is the quotient of the half-life of the ^{14}C -isotope

(5,730 a) to $\ln 2$; $^{14}a_{in}^0$ is the relative initial content of ^{14}C in TDIC before entering the saturated zone in pMC; and $^{14}a_{sample}$ is the relative ^{14}C content in pMC in TDIC of the sample.

The estimation of the age of groundwater by the Eq. 4 requires corrections for the $^{14}a_{in}^0$, because before entering the saturated zone, the carbon in the bicarbonate would participate in the isotopic exchange with the carbon in the biogenic CO_2 that would be released from the plant root respiration on one hand, and, on the other hand, a new portion of bicarbonate could be formed there due to the oxidation of organic matters or the dissolution of the inorganic carbonates presented in the unsaturated zone. All these processes could modify the value of $^{14}a_{in}^0$. To do the correction, an isotope mixing model referred to as complete exchange with CO_2 in the unsaturated zone was proposed by Gonfiantini [23] for a closed system and was applied as follows:

$$^{14}a_{in}^0 = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{cc}}{\delta^{13}C_{CO_2,org} - \delta^{13}C_{cc} + \varepsilon_{CO_2/DIC}} \quad (5)$$

where: $\delta^{13}C_{DIC}$, $\delta^{13}C_{cc}$, and $\delta^{13}C_{org}$ are the content of carbon-13, respectively, in TDIC in a water sample, in calcareous materials, and in the biogenic carbon dioxide that originates from the decomposition of organic matters; $\varepsilon_{cc/DIC}$ is the fractionation coefficient for ^{13}C in the isotopic exchange reaction between carbon dioxide and TDIC and is temperature dependent [24].

$$\varepsilon_{CO_2/DIC} = \left(-\frac{9483}{T} + 23.89 \right) \% \quad (6)$$

where: T is the temperature of water sample in Kelvin.

In the study area, the $\delta^{13}C_{cc}$ was found to be ranging from

1‰ to 2‰, and the average value of 1.5‰ was taken in the correction for $^{14}a_{in}^0$. The $\delta^{13}C_{CO_2,org}$ in Equation (5) was taken as high as -23‰, as it was characterized by the carbon dioxide generated from the C3 plants in the tropical areas. Details for the procedure of $^{14}a_{in}^0$ calculation can be found in Fontes [25]. The data of the 3H activity were used just to confirm whether the studied water sample was old or modern.

Statistical treatment of isotopic data

To get an original isotopic signal, samples having water stable isotope data disturbed by evaporation or by mixing with seawater were eliminated. The mean of $\delta^{18}O$ and its standard deviation were calculated for each group of samples, i.e. for the river's water and groundwater from each aquifer qp_2^3 , qp_2^1 , n_2^2 , n_2^1 , and n_1^3 .

To compare the means of the groups, a non-parametric test, namely, the Mann-Whitney test, which allows the comparison of independent series of different size without any preliminary hypothesis was used. In our case, the sample size was large enough to consider that the variable built from the test, z, would follow a normal distribution. Therefore, the difference of means between the groups would be significant, if $z > 1.96$ (critical value at a 5% limit), and very significant, if $z > 2.58$ (critical value at a 1% limit).

Results

The isotopic composition of deuterium (δ^2H), oxygen-18 ($\delta^{18}O$) as well as the tritium concentration in water, and the composition of carbon-13 ($\delta^{13}C$) and the content of carbon-14 in TDIC are presented in Table 1 along with the sampling locations. The content of the major ionic constituents dissolved in water are presented in Table 2.

Table 1. Sampling locations, water isotopic compositions and ^{14}C -age of ground-water from different aquifers in the MKRD.

Middle Pleistocene aquifer (qp_2^3), Transect NE-SW: HCM-Ca Mau									
Sample code	Co-ordinate		Depth, m	$\delta^{18}O$, ‰	δ^2H , ‰	3H , TU	$\delta^{13}C$ (TDIC), ‰	^{14}C (TDIC), pMC	Age (TDIC), years
	X	Y							
V36	18676015	1193936	40	-6.2	-39.8	0.4	-24.4	73 ± 0.3	132 ± 20
V99	18495854	968776	130	-6.4	-44.8	<LOD*	-15.6	1.3 ± 0.5	34 900 ± 4 100
V126	18564782	1068665	117	-6.4	-44.5	<LOD	-12.0	9.3 ± 0.2	16 700 ± 1 200
Middle Pleistocene aquifer (qp_2^3), Transect W-E: Dong Thap-Tra Vinh									
V54	18661369	1065168	108	-6.7	-45.2	<LOD	-14.4	10.4 ± 0.5	17 200 ± 1 500
V76	18575206	1115425	95	-4.4	-37	<LOD	-14.8	12.2 ± 0.5	16 200 ± 1 800
V115	18517297	1187001	50	-6.0	-40.1	<LOD	-6.2	26.6 ± 0.8	3 200 ± 300
V178	18561605	1180746	78	-6.3	-40.5	<LOD	-5.8	23.6 ± 0.9	4 000 ± 400
Lower Pleistocene (qp_1), Transect NE-SW (HCM-Ca Mau)									
Sample code	Co-ordinate		Depth, m	$\delta^{18}O$, ‰	δ^2H , ‰	3H , TU	$\delta^{13}C$ (TDIC), ‰	^{14}C (TDIC), pMC	Age (TDIC), years
	X	Y							
V39	18681757	1212154	100	-7.3	-48.4	<LOD	-23.3	73.0 ± 1.6	2 600 ± 300
V152	18530684	1054018	132	-6.2	-41.6	<LOD	-15.9	7.6 ± 0.4	20 700 ± 2 300
V155	18533505	1076938	210	-6.2	-41.6	<LOD	-15.7	17.6 ± 0.7	11 400 ± 1 100
Lower Pleistocene (qp_1), Transect W-E: Dong Thap-Tra Vinh									
V77	18577871	1115588	98	-6.2	-44.1	<LOD	-15.0	16.9 ± 0.6	13 500 ± 900

V172	18517452	1187175	161			<LOD	-10.8	16.0 ± 0.7	13 900 ± 600
V176	18613774	1122479	371			<LOD	-7.6	6.1 ± 0.6	21 000 ± 2 100
V278	18620457	1111142	165	-5.5	-42.4	<LOD			
Upper Pliocene aquifer (n₂²), Transect NE-SW: HCM-Ca Mau									
Sample code	Co-ordinate		Depth, m	δ ¹⁸ O, ‰	δ ² H, ‰	³ H, TU	δ ¹³ C(TDIC), ‰	¹⁴ C(TDIC), pMC	Age (TDIC), years
	X	Y							
V9	18653687	1169165.9	195	-7.2	-47.1	<LOD	-21.1	11.5 ± 0.7	17 900 ± 1 400
V102	18615632	1118071	267	-4.9	-35.5	<LOD	-8.9	20.2 ± 0.2	12 900 ± 1 200
V153	18533043	1053242	210	-6.4	-43.1	<LOD	-12.9	3.4 ± 0.2	25 600 ± 2 100
V159	18566657	1117305	220	-5.5	-43.7	<LOD	-15.4	19.9 ± 0.5	12 400 ± 1 200
Upper Pliocene aquifer (n₂²), Transect W-E: Dong Thap-Tra Vinh									
V105	18522010	1185978.5	103	-5.8	-42.3	<LOD	-10.8	22.6 ± 0.3	7 200 ± 700
V108	18646466	1118006	261	-2.0	-13.7	-	-	-	-
V179	18561605	1180746	323	-7.4		<LOD	-8.5	9.8 ± 0.9	17 000 ± 2 200
Lower Pliocene (n₂¹), Transect NE-SW: HCM-Ca Mau									
Sample code	Co-ordinate		Depth, m	δ ¹⁸ O, ‰	δ ² H, ‰	³ H, TU	δ ¹³ C(TDIC), ‰	¹⁴ C(TDIC), pMC	Age (TDIC), years
	X	Y							
V31	18684831	1194150	100	-7.6		<LOD	-19.8	16.9 ± 0.4	15 900 ± 1 000
V35	18679045	1193786	200	-7.7	-52.4	<LOD	-19.6	17.3 ± 0.4	15 400 ± 1 000
V101	18621408	1114813	442	-2.42	-17.4	-	-6.3	-	-
V247	18565590	1115374	295	-7.0	-49.0	<LOD	-14.5	3.0 ± 0.4	27 400 ± 2 400
Lower Pliocene (n₂¹), Transect W-E: Dong Thap-Tra Vinh									
V104	18588283	1112838	366	-6.3	-42.0	<LOD	-9.0	0.9 ± 0.2	33 500 ± 2 600
V111	18583755	1138106	390	-7.3	-51.1	<LOD	-9.6	2.7 ± 0.7	24 600 ± 2 300
V122	18581619	1094903	462	-6.2	-42.4	<LOD	-8.0	2.1 ± 0.2	25 400 ± 2 700
Neogene aquifer (n₁³), Transect NE-SE: HCM-Ca Mau									
Sample code	Co-ordinate		Depth, m	δ ¹⁸ O, ‰	δ ² H, ‰	³ H, TU	δ ¹³ C(TDIC), ‰	¹⁴ C(TDIC), pMC	Age (TDIC), years
	X	Y							
V88	18500617	967772	360	-6.9	-40.8	<LOD	-11.9	4.1 ± 0.4	22 800 ± 2 200
V104	18591545	1113733	366	-6.3	-42.0	<LOD	-9.0	0.9 ± 0.2	33 500 ± 3 500
V111	18583755	1138106	390	-7.3	-51.1	<LOD	-9.6	2.7 ± 0.7	24 600 ± 2 300
V255	18602094	1145026.4	360	-7.6	-57.3	<LOD		10.5 ± 4.8	18 700 ± 1 800
Neogene aquifer (n₁³), Transect W-E: Dong Thap-Tra Vinh									
V104	18591545	1113733	366	-6.3	-42.0	<LOD	-9.0	0.9 ± 0.2	33 500 ± 3 500
V106	18577373	1136181	364	-6.7	-47.7	<LOD	-7.3	6.2 ± 0.4	15 800 ± 1 000
V111	18583755	1138106	390	-7.3	-51.1	<LOD	-9.6	2.7 ± 0.7	24 600 ± 2 400
V112	18574141	1138185	318	-6.8	-47.1	<LOD	-7.9	13.6 ± 0.4	10 100 ± 1 000

*LOD of ³H was 0.4 TU.

Table 2. Hydrogeochemical composition of groundwater in the MKRD.

Middle Pleistocene aquifer (pq₂³)												
Sample code	T, °C	pH	EC, mS cm ⁻¹	CO ₂	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻
V36	29.5	4.6	66		0.02	0.35		0.18	0.35	0.20		
V54	29.5	6.9	860	1.88	0.22	2.31	3.00	3.09	0.72	7.10		0.69
V76	28.0	6.8	1030	2.47	0.73	4.55	2.70	3.70	4.79	5.04	1.48	0.40
V115	29.0	6.5	2268	0.59	0.61	14.14	3.15	4.70	18.30	7.20		
V126	29.0	6.0	950	0.73	0.31	5.96	1.25	1.85	2.05	6.92		1.81
Lower Pleistocene aquifer (pq₁)												
Sample code	T, °C	pH	EC, mS cm ⁻¹	CO ₂	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻
V39	31.0	5.7	115		0.02	0.73	0.20	0.29	0.44	0.56		0.11
V72	31.0	7.4	1300	1.03	0.36	9.78	0.96	1.89	4.09	8.08	0.32	0.14
V278	28.5	6.5	593			5.83			7.28			
Upper Pliocene aquifer (n₂²)												
Sample code	T, °C	pH	EC, mS cm ⁻¹	CO ₂	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻
V8	31.5	6.5	1330	2.10	0.35	5.74	5	2.36	10.59	2.56		0.12
V42	28.5	4.6	139		0.06	1.03	0.08	0.25	0.10	1.34		

V70	35	7.4	1246	1.14	0.21	9.7	1.16	1.24	2.45	8.28	1.12	0.45
V71	36	7.8	1127		0.68	8.74	0.76	1.40	1.80	8.36	0.80	0.43
V98	36	8.2	2190	0.55	0.11	20.12	0.60	1.23	6.23	11.08	1.52	3.00
V125	30	7.9	752	0.14	3.80	255.65	24.80	52.65	312.56	11.52		12.45
V143	28.5	7.3	650		0.10	3.95	1.12	1.24	3.09	3.38		
Lower Pliocene aquifer (n_2^1)												
Sample code	T, °C	pH	EC, mS cm⁻¹	CO₂	K⁺	Na⁺	Ca²⁺	Mg²⁺	Cl⁻	HCO₃⁻	CO₃²⁻	SO₄²⁻
V35	33	6.1	233	4.78	0.15	0.81	0.72	0.66	0.21	1.92		0.26
V95	28	6.8	380	0.14	0.16	0.60	1.84	1.10	0.20	3.46		0.3
V102	31	7.8	33500	0.21	4.41	234.16	33.07	63.06	318.55	3.40		12.79
V108	29	6.5	35570	2.46	12.79	343.63	25.75	86.25	428.5	3.32		36.4
V113	29	8.4	977		1.05	8.09	0.25	0.35	2.50	5.60	0.60	1.02
Neogene aquifer (n_1^3)												
Sample code	T, °C	pH	EC, mS cm⁻¹	CO₂	K⁺	Na⁺	Ca²⁺	Mg²⁺	Cl⁻	HCO₃⁻	CO₃²⁻	SO₄²⁻
V88	38	8.1	760	0.27	0.12	7.25	0.4	0.17	0.75	6.60		0.23
V101	27	8.4	33587		1.67	358.18	3.82	2.31	356.96	6.04	0.20	2.38
V104	35	8.4	2730	0.50	0.26	23.88	1.38	1.67	18.12	6.79	0.40	1.96
V106	31	8.7	1910	0.41	0.51	16.87	1.00	0.58	5.50	6.50	0.80	6.28
V111	39	7.2	1120	0.30	0.10	10.54	0.55	0.32	3.91	7.44		0.31
V112	29	8.4	1250		0.17	11.22	0.76	0.82	3.52	7.52	1.20	0.68

Unit: meq L⁻¹.

Figure 6 depicts the regional meteoric water line (RMWL) determined in HCM and the water line for the Tien and Hau rivers. The RMWL in HCM could be considered to represent the whole MKRD, as the city is located at an elevation comparable to the average elevation of the region. The RMWL follows a model described by an expression as follows:

$$\delta^2\text{H} = 7.37\delta^{18}\text{O} + 5.15 \quad (R^2 = 0.966) \quad (7)$$

The isotopic composition of water from the Tien and Hau rivers did not differ from each other in the Mann-Whitney test at a 5% limit, and a model of the water line for the two rivers was as follows:

$$\delta^2\text{H} = 6.57\delta^{18}\text{O} - 3.36 \quad (R^2 = 0.875) \quad (8)$$

The slope of the water line for the rivers is lower than those for the RMWL in HCM (Eqs. 7 and 8), reflecting the

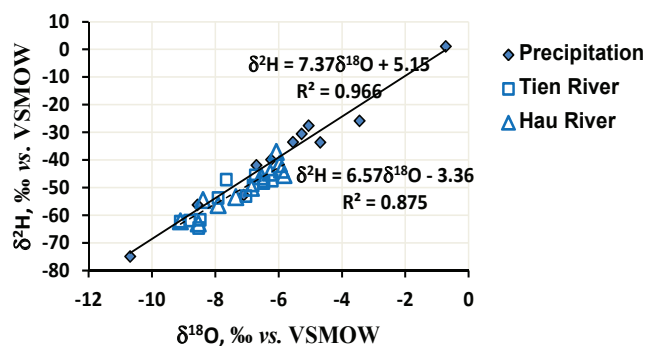


Fig. 6. Regional meteoric water line (RMWL) for HCM city and the water line for the Tien and Hau rivers in the Mekong river delta.

evaporative effect of the surface waters [5]. The RMWL in HCM is similar to that in Bangkok (Thailand) that was $\delta^2\text{H} = (7.35 \pm 0.08) \delta^{18}\text{O} + (5.33 \pm 0.50)$ ($R^2 = 0.96$) [26]. This is due to the fact that HCM city and Bangkok are located almost at the same latitude and at the same elevation and the mean annual air temperature in the two cities is in the same range of (28-30)°C.

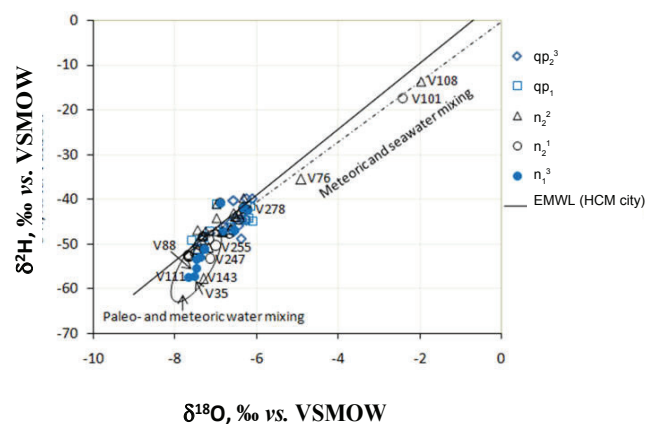


Fig. 7. Isotopic composition of groundwater in the deep aquifers of the MKRD along with the Regional Meteoric Water Line (RMWL, HCM city).

Figure 7 depicts the water line for groundwater from five aquifers as follows: qp_2^3 , qp_1 , n_2^2 , n_2^1 , and n_1^3 throughout the MKRD and sampled along the two transects.

Discussion

The age of groundwater from the five aquifers, namely,

middle Pleistocene (qp_2^3), lower Pleistocene (qp_1), upper Pliocene (n_2^2), lower Pliocene (n_2^1), and the Miocene (n_1^3) in the MKRD was older than 100 years as the tritium content in groundwater taken from these aquifers was found to be lower than the LOD of 0.4 TU of the analytical procedure. In the precipitation collected in HCM and water from the Tien and Hau rivers, the 3H content ranges from 0.6 to 3.5 TU (Table 1). This reflects the fact, that at present, the bomb tritium has already gone to the southern hemisphere, and the radioactive isotope of hydrogen in surface water in the region is mainly derived from the nuclear reactions in the atmosphere [27]. Unfortunately, in this study, no isotopic data for the Holocene (qh) and upper Pleistocene aquifers (qp_3) were available, so there is no idea about the hydraulic interaction of surface water with the water in the shallow aquifers. The water's isotopic composition can be used to judge whether the water from the two adjacent aquifers, e.g. surface water and water in aquifer qp_2^3 or water in aquifers qp_2^3 and qp_1 etc., do interact with each other hydraulically by performing the Mann-Whitney statistical test on the mean difference, based on the mean $\delta^{18}O$ or δ^2H and its standard deviation [4]. Table 3 shows the results of the test using the mean $\delta^{18}O$ for each pair of the aquifers along transects.

As seen from Table 3, in the Mekong river delta, the water from the Tien and Hau rivers (transect W-E, Fig. 5) did not interact hydraulically with those in the middle Pleistocene

(qp_2^3) aquifer, as the mean $\delta^{18}O$ in water from the rivers and the qp_2^3 aquifer was very significantly different from each other (z-value was 2.81 higher than the critical values of 2.58 at $\alpha = 1\%$, Table 3). In other words, the rivers do not recharge their water to the qp_2^3 aquifer, which also implies that the rivers do not recharge their water to deeper aquifers as well. Along the transect NE-SW (Fig. 4), it appears that all the studied aquifers were hydraulically connected with each other, as the mean $\delta^{18}O$ in the water of adjacent aquifers was insignificantly different from each other (z-value was lower than the critical value of 1.96 at $\alpha = 5\%$, Table 3).

In the study of Louvat and Ho Huu Dung [4], it was found that in the MKRD, there was no hydraulic connection between the pairs of adjacent aquifers. Probably, this was true for a time when the freshwater abstraction from those aquifers was not so intense like today. A recent survey showed that in the MKRD, at present, each day around 1,230,000 m^3 of groundwater is being abstracted, mainly, from the Pleistocene and Pliocene aquifers that were more than 240% of those freshwater production yield (510,761 m^3 day $^{-1}$) before 1990 [28]. It seems that the heavy freshwater mining in the region today has caused depression of the water table in the production aquifers, leading to inter-aquifer leakages, and as a result, the mixing of water from the upper aquifer with those in the lower aquifer has occurred. The inter-aquifer leakage has been observed in the Great Artesian basin in Australia and in the Canterbury plain in New Zealand

Table 3. The Mann-Whitney statistical treatment for the means $\delta^{18}O$ and its standard deviation to show the hydraulic interaction between the adjacent aquifers in the MKRD region.

Z-test of two sample for means					
Water group	$\delta^{18}O$ mean, ‰ vs. VSMOW	Standard error, ($\pm$)	Comparison	Value of z ($\alpha = 0.05$)	Difference between means
NE-SW Transect (Fig. 4)					
qp_2^3	-6.38	0.68			
qp_1	-6.75	0.76	qp_2^3 - qp_1	1.04	no
n_2^2	-6.70	0.65	qp_1 - n_2^2	-0.12	no
n_2^1	-7.07	0.51	n_2^2 - n_2^1	0.79	no
n_1^3	-6.87	0.61	n_2^1 - n_1^3	0.76	no
W-E Transect (Fig. 5)					
Rivers	-7.29	1.10			
qp_2^3	-6.46	0.16	Rivers- qp_2^3	-2.81($\alpha = 0.01$)	very significant
qp_1	-5.91	0.33	qp_2^3 - qp_1	-1.05	no
n_2^2	-7.44	0.75	qp_1 - n_2^2	2.66($\alpha = 0.01$)	very significant
n_2^1	-7.20	0.25	n_2^2 - n_2^1	-0.42	no
n_1^3	-6.74	0.41	n_2^1 - n_1^3	-1.07	no

[29, 30]. Inter-aquifer leakage in the MKRD could happen, as there the sediment primarily comprised the fluvial-marine type with high coarse sand content, making the conductivity high. Apparently, the inter-aquifer leakage has caused the water in the Pleistocene and the Pliocene aquifers in the Mekong river delta to mix with each other so that the isotopic composition of water in the two aquifers is insignificantly different from each other (transects NE-SW and W-E, Table 3).

As seen from Fig. 7, the groundwater in the deep (qp_1 , n_2^2 , n_2^1 , and n_1^3) aquifers in the MKRD displays a mixing of three water types, namely, paleo-water, regional meteoric water, and seawater. The mixing feature of the paleo-water with meteoric and seawater as depicted in Fig. 7 was similar to those characterized for groundwater in the Qatar city [31]. The Mann-Whitney statistical test showed that the mean of $\delta^{18}O$ in the recent precipitation during the rainy season was significantly different from that in the groundwater taken along the W-E transect (Fig. 5). This means that the recent local meteoric

water does not recharge the deep aquifers in the MKRD. From the data of stable isotopic composition and ^{14}C -ages (Table 1), it was thought that the groundwater in the deep aquifers of the MKRD was connate like those in the suggestion made by Nguyen Kim Cuong, et al. [2], or it was recharged from the remote areas at a slow speed.

The chloride concentration in most of the groundwater samples from different aquifers in the MKRD was lined up along a horizontal line in the graph of $\delta^{18}O$ vs. $[Cl^-]$ with a mean $\delta^{18}O$ around -7‰ as shown in the Figs. 8 and 9 for the transects NE-SW and W-E, respectively. The data that were taken to draw the Figs. 8 and 9 were from the Tables 1 and 2. In Figs. 8 and 9, the horizontal line characterizes the migration or diffusion of the saline water entrapped in the sediment pores into the fresh water present in the aquifer, whereas the dotted arrows (Figs. 8 and 9) characterize the salt intrusion [6, 32]. This result is consistent with those derived from the δ^2H vs. $\delta^{18}O$ relationship (Fig. 7) that was discussed above.

The salt intrusion and saline pores' water migration from the aquifer sediment (Figs. 8 and 9) resulted in a mixture of the freshwater and saline water, as it is evident from Figs. 10A and 10B, respectively, for the qp_2^3 , qp_1 , and n_2^1 , n_2^2 along the transect NE-SW (Fig. 4) as an example for the entire MKRD region.

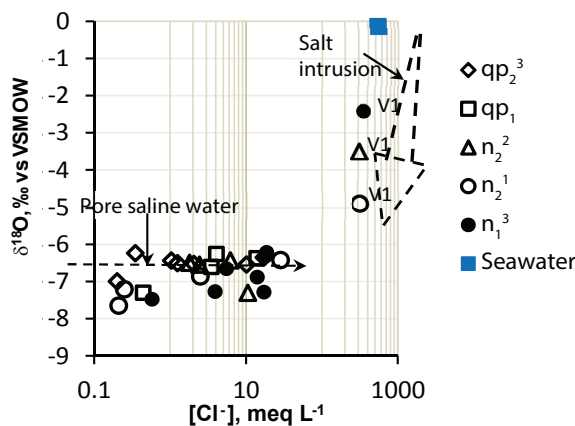


Fig. 8. Scatter plot of $\delta^{18}O$ vs. chloride concentration ($[Cl^-]$) in groundwater from the MKRD along transects NE-SW (Fig. 4). The concentration of chloride ion was expressed in the logarithmic scale.

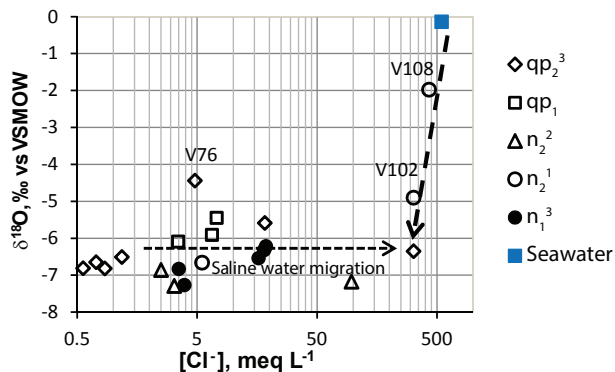


Fig. 9. Scatter plot of $\delta^{18}O$ vs. chloride concentration ($[Cl^-]$) in the groundwater in the MKRD along transect W-E (Fig. 5). The chloride concentration was expressed in the logarithmic scale.

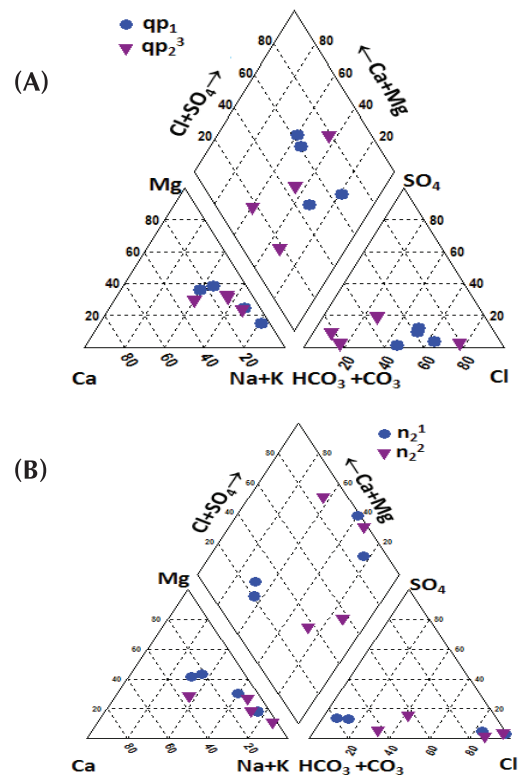


Fig. 10. Piper diagrams are showing the mixing of saline pore water with fresh water in the qp_2^3 and qp_1 (A) and seawater with fresh water in the n_2^1 and n_2^2 (B) along the NE-SW transect.

Apparently, the TDIC ($\text{HCO}_3^- + \text{CO}_3^{2-}$ in Figs. 10A and 10B) in the water samples was a mixture of the inorganic and biogenic carbonates. The inorganic source of TDIC could be from the calcite/dolomite dissolution. The biogenic source of TDIC could be from the oxidation of organic matters by sulfate and iron-oxy-hydroxide (FeOOH), following the reactions (9) and (10) [33-35].



The reactions (9) and (10) would lead the pH of the groundwater to be buffered within a range of 6.5-7.5 as it was seen from Table 2. The organic matters (CH_2O) participating in the reactions (9) and (10) are products of the bio-mineralization of the plant remnants co-deposited with sediment, and the FeOOH was an unavoidable constituent of the aquifer sediment. The source of sulfate in the groundwater could partly be from the seawater entrapped in the pores of the aquifer sediment, and partly from the gypsum dissolution (reaction 11).



The calculation of the saturation index (SI) for gypsum in all the studied aquifers showed that the mineral dissolves, as its $\text{SI} < 0$ (results of the calculation not shown here). Evidence for the sulfate reduction by organic matters in the aquifer sediment (reaction 9) is the trend of TDIC content increase with the increase of sulfate concentration in groundwater samples as shown in Fig. 11.

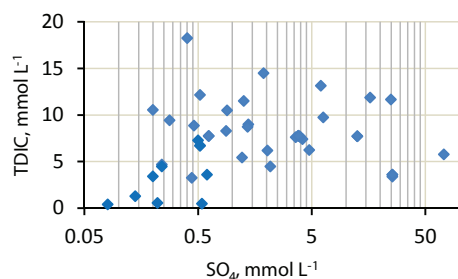
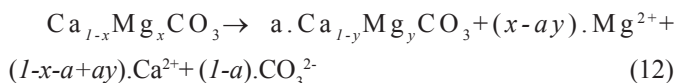


Fig. 11. A scatter plot of the TDIC content vs. $[\text{SO}_4^{2-}]$ showing the possible oxidation of organic matter by sulfate in groundwater (reaction 9) in the MKRD. The concentration of SO_4^{2-} was expressed in the logarithmic scale.

The oxidation of organic matters (reactions 10 and 11) in water would make the carbon in TDIC get depleted by the heavy ^{13}C isotope [36].

The aquifers' sediment in the MKRD was of fluvial-marine nature that could contain not only plant remnants but also biogenic carbonate, such as shells, skeletal debris etc. containing high Mg-calcite. Therefore, the incongruent dissolution [36] of the Mg-calcite could be expected to occur within aquifers as it was usually observed in marine sediments (reaction 12).



Reaction (12) would lead to the enrichment of $\delta^{13}\text{C}$ in the TDIC [6], because the carbon-13 signature in shells is more enriched compared with those in the organic matters. Gillikin, et al. [37] have found that the $\delta^{13}\text{C}$ in the shells of *Mytilus edulis* ranges from -3.0‰ to -7.7‰ vs. VPDB, independent of the temperature, that was much enriched compared with the $\delta^{13}\text{C}$ in C3 plant remnants (-23‰ vs. VPDB). The incongruent dissolution of Mg-calcite would also increase the Mg^{2+} concentration in water [6]. In fact, in this study, the concentration of a Mg^{2+} ion in most of the groundwater samples from the Mekong river delta was found to be higher than those of Ca^{2+} (Table 2).

Apparently, the contribution of carbonate from the reactions (9 and 10) and the reaction (12) to TDIC in groundwater in the MKRD was different in each sampling well, so the composition of carbon-13 ($\delta^{13}\text{C}$) in the TDIC ranged from -3.2‰ to -18.0‰ vs. VPDB as shown in Table 1 and Fig. 12.

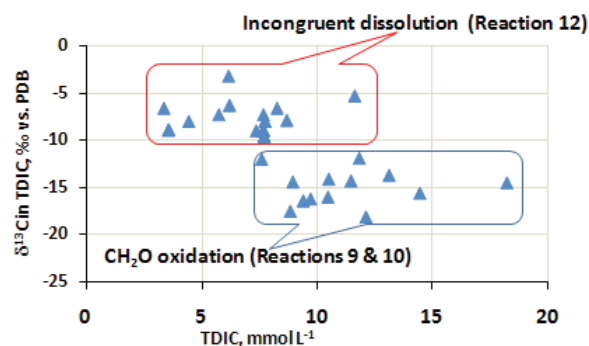


Fig. 12. A scatter plot of carbon-13 composition vs. TDIC content in groundwater throughout the MKRD: there are at least three geochemical reactions [(9), (10), and (12)] controlling the chemistry of groundwater in the MKRD.

As seen from Fig. 12, the trend of the $\delta^{13}\text{C}$ variation with the TDIC concentration in groundwater in the deep aquifers in the MKRD is that the more depleted the ^{13}C signature, the higher would be the concentration of TDIC in water. This indicates that the oxidation of organic matters by sulfate and iron oxyhydroxide, i.e. reaction (9) and (10) governs the TDIC content in the groundwater of the deep aquifers in the MKRD.

Conclusions

In the Mekong river delta, the groundwater in the Pleistocene, Pliocene, and Miocene aquifers was likely connate or very weakly recharged from the remote areas at a slow rate as it was evident from the ^{14}C -ages and water stable isotopic composition. This implies that the groundwater resource in that region is limited. The groundwater in the deep aquifers in the study region comprises the brackish, saline, and fresh types. The saline water in the deep aquifers could

result from the diffusion of saline pore water and salt intrusion into fresh water resources. The chemistry of groundwater is controlled by the oxidation of the organic matters and the incongruent dissolution of Mg-calcite. The heavy mining rate of groundwater today could cause inter-aquifer leakage and up conning of saline water, leading groundwater resources in the delta region to be deteriorated. This requires the development of appropriate measures for the better management of the groundwater resources in the entire MKRD region. Among others, artificial recharge with water from the Mekong river system could be considered to have a sustainable resource of freshwater for the region.

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Correlation between optical characteristics and NO₂ gas sensing performance of ZnO nanorods under UV assistance

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Abstract:

In this research, we present the ZnO nanorods synthesized through the simple route of the hydrothermal method. The ZnO nanorods were developed through the application of only zinc acetate Zn(CH₃COO)₂ and ammonia solution, NH₄OH, in the hydrothermal process at 150°C for 10 hours. The size of the ZnO nanorods was defined as approximately 300 nm in diameter and 1-2 μm in length. The fabrication of sensors was achieved through drop-coating of synthesized ZnO nanorods on Al₂O₃ substrates integrated with Au electrodes. Subsequent to the process of sintering done at 500°C for different durations, ZnO nanorod-based sensors were investigated when exposed to NO₂ gas (1.5, 2.5, and 5 ppm) at room temperature under continuous UV-LED (385 nm) illumination. The correlation between NO₂ gas sensing performance and the optical property of the ZnO nanorods is discussed in detail. Herein, the defect concentration, particularly in the surface region of the ZnO nanorods could be modified through sintering, and this indicates its importance in the reduction of response-recovery times and enhancement of high sensitivity to NO₂ gas.

Keywords: optical property, room temperature NO₂ gas sensors, ZnO nanorods.

Classification number: 5.1, 5.5

Introduction

Nitrogen oxides NO_x (NO₂, NO) are considered highly toxic gases, due to the adverse effects they have on human health as well as the environment. Thus, the analysis and control of NO_x gases is extremely crucial. The gas sensors with high response, fast response-recovery times, and high selectivity with regard to NO_x detection have attracted increased attention in recent times [1]. Nano metal oxide based NO_x gas sensors constituent promising candidates for realistic application in this regard due to advantages such as extremely low detecting level (even up to ppb), high resolution, and fast response. For example, the gas sensors that utilized metal oxides, such as WO₃ [2-4], ZnO [5-7], among others, were found to exhibit an extremely high sensing performance to NO₂ gas. However, the metal oxide based gas sensors usually operate at high temperatures, and subsequently, become unstable or less reliable due to the changing particle size and morphology structure [8]. Therefore, the development of metal oxide gas sensors that operate at room temperature has been emphasized.

Zinc oxide semiconductors with large band gaps ($E_g = 3.37$ eV) have been applied in many fields such as gas sensors [2-7], photovoltaic devices [9], optoelectronic devices [10], solar cells [11], among others. ZnO nanostructures such as nanosheets, nanorods, nanowires, nanotubes, and nanobelts are mostly utilized for gas sensing layers that operate at low temperatures. This is considered by the relation of their high surface to volume ratio, highly active center, along with other factors [12]. The application of ZnO nanostructures with respect to the detection of various gases such as NO₂ [5-7, 12], CO [13], H₂ [14], and ethanol [15, 16] has been widely investigated. Conversely, to effect a reduction of the operating temperature to room temperature, the application of metal oxide gas sensors with the assistance of UV light has been a mostly feasible approach [17, 18]. S.W. Fan, et al. [17] demonstrated that UV light strongly enhanced the H₂ sensing properties of polycrystalline ZnO at room temperature. Similarly, G. Lu, et al. [18] also indicated that gas sensors based on ZnO nanorods modified SnO₂ nanoparticles have high sensitivity

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and fast response-recovery times with regard to NO_2 gas at room temperature, illuminated by UV light. It was suggested that ZnO nanorods could generate photo-electrons into their conduction band under the exposure of UV irradiation. The photo-generated electrons could promote the adsorption of oxygen molecules on the surface of ZnO nanorods. Hence, the gas-sensing responses of the ZnO nanorod based sensors can significantly increase through the application of UV illumination at room temperature.

Recently, the significance of surface defects in ZnO nano oxides with regard to their gas sensing characteristics has been considered [1]. Liao, et al. have investigated that oxygen vacancies in ZnO nanorods dominated the electronic properties and adsorption behaviors, because they acted as donors to provide electrons to the ZnO conduction band [19]. Further, it was found that the defects (oxygen vacancies (V_{O}); oxygen interstitial (O_i); oxygen antisite (O_{Zn}); zinc vacancies (V_{Zn}); zinc interstitial (Zn_i)) influenced the sensing performance of ZnO-based gas sensors [1, 19, 20]. In general, ZnO nano-oxides' defects can be modified through annealing processes. However, the gas sensing mechanism of the ZnO nano-oxides at room temperature under UV irradiation has not been clearly verified with regard to the contribution of surface defects or bulk defects. Thus, in this paper, the correlation of optical characterizations with gas sensing properties was discussed in detail to provide further evidence related to the gas sensing performance of ZnO nanorods with the assistance of UV light.

Experimental

The ZnO nanorods were synthesized by a simple method. Specifically, zinc acetate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ salt (Sigma-Aldrich 1724703 USP) was dissolved in deionized water

water until the pH value of 7 was reached, and subsequently dried at 60°C for 24 hours to obtain the ZnO nanorods.

Crystalline structures and surface morphology of ZnO nanorods were characterized by X-ray diffraction (X'Pert Pro) using $\text{CuK}\alpha$ radiation, scanning electron microscope (FESEM, HITACHI S-4800). The optical characterization of ZnO nanorods was identified by photoluminescence (PL) emission spectra when excited by 325 nm light from a Cenon lamp at room temperature.

The ZnO nanorods were mixed with an organic (α -terpineol: antrox: ethyl-cellulose = 95:2:3) to obtain a paste. The ZnO nanorods paste was drop-coated on the Al_2O_3 substrates integrated with Au grid-electrodes. Fig. 1 illustrated the process from synthesizing the ZnO nanorods, fabricating sensor devices and illuminating UV-LED light to gas sensors. To measure gas sensing performance, these sensors were sintered at 500°C for different durations to obtain the devices for subsequent analyses. UV-LED light source (wavelength = 385 nm) was adjusted for the irradiation intensity via the applied currents (1, 5, and 15 mA) to investigate gas sensing performance of the sensors. The sensors were continuously irradiated with the UV light during the measurement of the gas sensing characteristics. The sensors were measured with the current source (Keithley, model 6220) and the voltage meter (Keithley, model 2700) for data acquisition of the sensor resistance when exposed upon NO_2 gas concentrations under UV irradiation. The response (S) of the ZnO nanorod sensors was calculated by the equation $S = (R_g - R_a)/R_a \times 100$, where R_g and R_a are the sensor resistances in the air containing NO_2 gas and in air respectively.

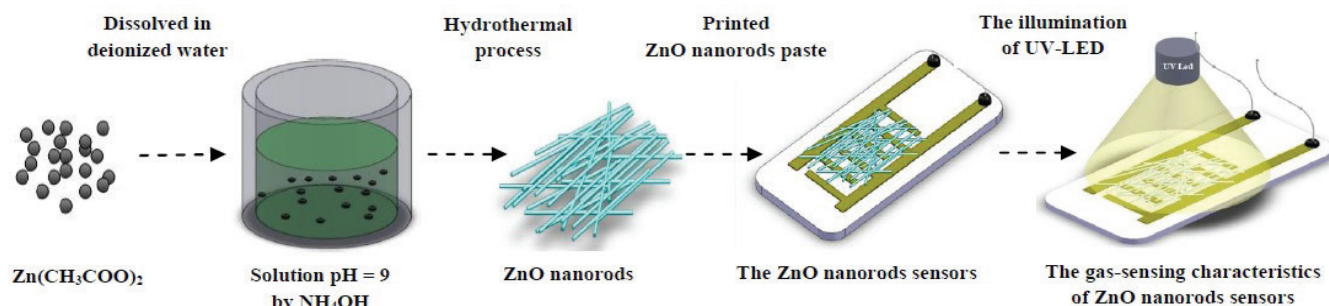


Fig. 1. Diagram illustrated procedure of synthesizing the ZnO nanorods, fabricating the sensor devices, and illuminating UV-LED to the ZnO nanorods sensors.

through stirring at 80°C for 15 minutes to obtain a homogeneous solution. Subsequently, the NH_4OH solution was gradually dropped into the solution until pH = 9 was attained and continuously stirred for 30 minutes to obtain a mixture that contained white precipitation. Thereafter, the mixture was transferred into a Teflon lined autoclave to grow ZnO nanorods at 150°C for 10 hours by hydrothermal condition. Finally, the precipitation mixture was filtered and washed with deionized

Results and discussion

Figure 2 displays the SEM image of the typical morphology of the synthesized ZnO nanorods sample. It can be observed that the sample contains uniform nanorods with 300 nm diameter and 1-2 μm length. It is found that the ZnO nanorods are hexagonal rod-shaped, as described in the inset in Fig. 2.

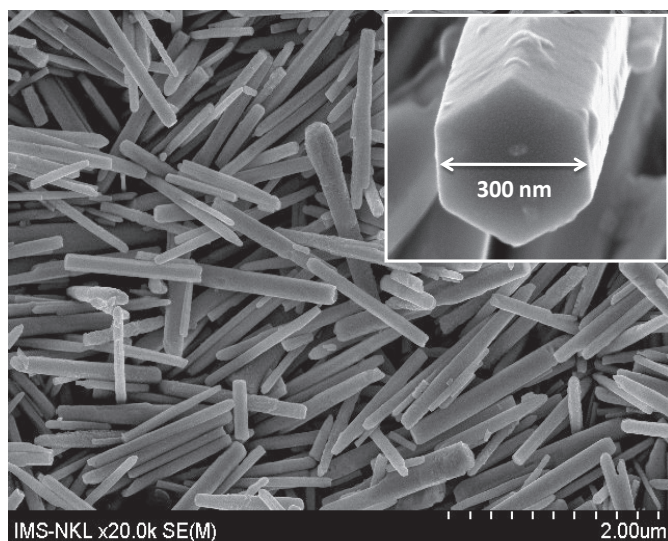


Fig. 2. SEM image of the ZnO nanorods synthesized through the hydrothermal process.

Figure 3 displays XRD patterns of the ZnO nanorod as-grown and after sintering at 500°C for 24 hours. All the diffraction peaks can be indexed to typical hexagonal Wurtzite structure, in accordance with the JCPDS card (No. 36-1451). No diffraction peaks for any impurity phases are found in the XRD patterns. In addition, the position and proportion of the diffraction peaks are found to be very similar when the as-grown and sintered samples are compared. This result suggests that crystalline structure and crystalline particle-size of the ZnO nanorods can be preserved even after the long sintering process conducted at 500°C.

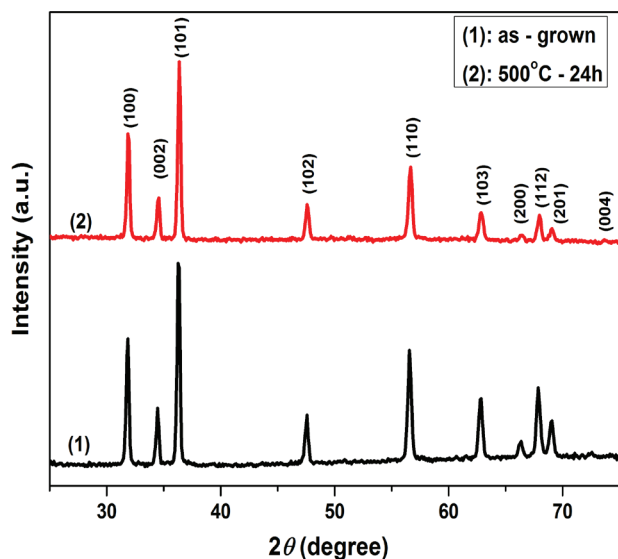


Fig. 3. XRD patterns of the ZnO nanorods as-grown and sintered at 500°C for 24 hours.

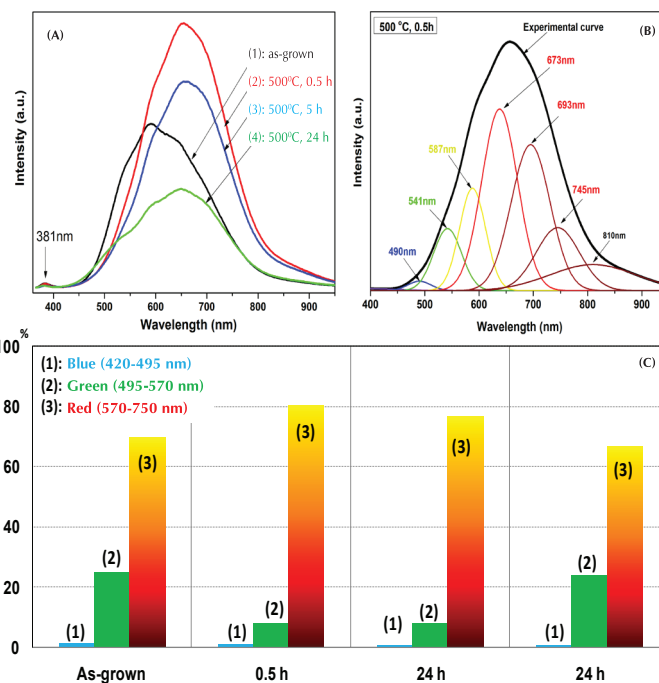


Fig. 4. PL spectra of the ZnO nanorods as-grown and sintered at 500°C for 0.5, 5, and 24 hours (A); the typical Gaussian deconvolution of the ZnO nanorods sintered at 500°C for 0.5 hours (B); the calculated percentage chart of blue (420-495 nm), green (495-570 nm), and yellow-red (570-750 nm) emissions of the samples (C).

It has been generally suggested that the five defects observed in the ZnO oxides include oxygen vacancies (V_O), oxygen interstitial (O_i), oxygen antisite (O_{Zn}), zinc vacancies (V_{Zn}), and zinc interstitial (Zn_i), in which V_O and Zn_i are donors and O_i , O_{Zn} and V_{Zn} are acceptors. These defects can be proofed through the photoluminescence properties. Fig. 4A shows the PL spectra of the ZnO nanorods sintered at 500°C for 30 minutes, 5 hours, and 24 hours. Evidently, all the samples have the two emission bands with a weak band of 381 nm (assigned to near band gap emission of the ZnO nanorods) and broad visible band of 400-750 nm. The visible emission band is assigned to the deep defects in ZnO nanorods [1, 19-21]. Fig. 4B displays the typical Gaussian deconvolutions of the PL spectra in the range of 400-950 nm of the ZnO nanorods sintered conditions at 500°C for 0.5 hours. The blue, green, yellow-red emissions are calculated in accordance with the assigned defects that occur in bulk and surface of the ZnO oxide. From the Gaussian deconvolution of the PL spectra, the calculated percentage of the emissions area is summarized for each wavelength ranges as described in Fig. 4C. The blue and green emissions band are considered in relation to oxygen antisite (O_{Zn}) or zinc vacancies (V_{Zn}) that is corresponded to the deep defects levels in the ZnO band-gap [22, 23]. Whereas, the yellow-red emissions are assigned for oxygen vacancies (V_O) that operate as donors, the behavior that has also been regarded with respect to the effect of the V_O^{++} surface defects [24-26].

These defects can be considered as important contributions to the electrical conductivity and gas sensing characteristics of the ZnO nanorods. The percentage of the yellow-red emissions are found to have maximum value for ZnO nanorods sintered at 500°C for 0.5 hours, and it gradually reduces with increasing sintering time (as seen in Fig. 4C). The result in Fig. 4C shows that the concentration of oxygen interstitial (O_i), oxygen antisite (O_{Zn}), zinc vacancies (V_{Zn}), which can be assigned as the bulk defects [26], decreased after sintering for short durations (0.5 and 5 hours), and then increased with the increase in sintering up to 24 hours.

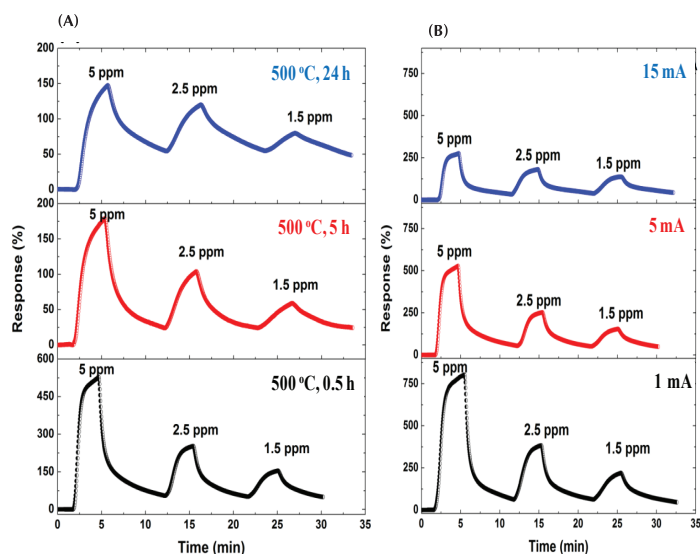


Fig. 5. Responses to NO_2 gas at room temperature of the ZnO nanorods based sensors with sintering for 0.5, 5, and 24 hours (A); with applied currents of 1, 5, and 15 mA to the UV-LED (B).

Figure 5A displays the NO_2 gas-sensing responses of the ZnO nanorod sensors sintered at 500°C for 0.5, 5, and 24 hours under UV-LED (385 nm) illumination with 5 mA applied current at room temperature. The results indicate that the responses of all the ZnO nanorod sensors increase when exposed upon NO_2 gas. This behavior is related to ZnO nanorods as n -type semiconductor. From the result, it is observed that the sensors with long sintering duration show the small responses to NO_2 gas.

Figure 5B presents the response to NO_2 gas at room temperature of ZnO nanorods sensor sintered 500°C for 0.5 hours when current values of 1, 5, and 15 mA are applied to the UV-LED. The result demonstrates that the response of this ZnO nanorods sensor reduces with increase in the currents applied to the UV-LED. To further analyze gas sensing performance, Fig. 6A presents the dependence of the response of the ZnO nanorods sensor on sintering time under measuring conditions of exposure to 5 ppm NO_2 gas and the application of 5 mA to the UV-LED. It was discovered that the NO_2 response

has maximum value for the ZnO nanorods based sensor for 0.5 hours sintering time, and it strongly decreases with the above given sintering time. The dependence of the response-recovery times of the ZnO nanorods sensor on sintering time under measuring conditions of exposure to 5 ppm NO_2 and application of 5 mA to the UV-LED can be observed in Fig. 6B. The response-recovery times of the ZnO nanorods based sensor increases with increase in the sintering time.

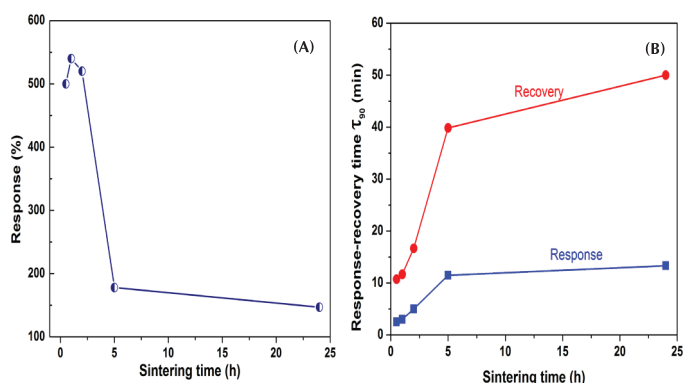
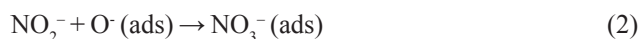


Fig. 6. Dependences of the response (A) and the response-recovery times (B) of the ZnO nanorods based sensors on sintering time under the measuring conditions of exposure to 5 ppm NO_2 and application of 5 mA to the UV-LED.

For gas-sensing mechanism, when the ZnO nanorods are illuminated by the UV-LED, electrons in the valence band or defect levels can move into the conduct band and simultaneously create holes in the valence band. The photo-induced electrons have highly chemical active. Therefore, when the ZnO nanorods exposed to NO_2 gas under UV irradiation, the chemical reactions between NO_2 gas and electrons can occur as following Eqs. (1-3):



From these reactions, it can be concluded that the resistance of ZnO nanorod sensors increases when exposed to NO_2 gas, as observed in Fig. 5, due to the electrons extracted from the conduction band. The gas sensing performance of the sensors can be governed by the photo-induced electrons that can move into the oxide surface and participate in the chemical reactions. This can be strongly affected by the surface-structure and surface defects of the ZnO nanorods. Thus, in this research, we have investigated the photoluminescence spectra of the ZnO nanorods sintered at 500°C for difference durations to examine the correlation between the optical properties and the gas-sensing characteristics. As the above results indicate, the sensor with the ZnO nanorods sintered for 0.5 hours exhibited high sensitivity and fast response-recovery times in comparison to others sintered for longer durations. The high concentration of the oxygen vacancies (as donors) can improve the interaction

with the oxidation/reduction gases (NO_2 and O_2 gases).

Conclusions

In conclusion, the ZnO nanorods were synthesized successfully by the simple hydrothermal method at 150°C for 10 hours. The nanorods were 300 nm in diameter and 1-2 μm in length. The ZnO nanorod-based sensors were fabricated to detect NO_2 gas at room temperature under UV-LED irradiation (385 nm) exposure. It was noticeable that when the sensor was sintered at 500°C for 0.5 hours, it exhibited high sensitivity and fast recovery-response times with regard to low NO_2 gas concentration. The correlation between the optical characterizations and the gas sensing properties depended on the concentration of oxygen vacancies in the ZnO nanorods. This sensor can be a promising device that offers room temperature operation for the detection of NO_2 gas in the air.

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Why does the river erosion situation become more complicated in the Mekong delta?

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Abstract:

Being a young river located in the delta that has been forming for a few thousand years now and developing during the several hundred years in the recent past under the pressure of socio-economic development, the impact of climate changes, rise in the sea level, and the Mekong upstream development, the riverbeds and coasts in the Mekong delta have currently transformed the erosion from an acceptable “chronic” and “essential” situation to a complicated, unpredictable, and alarming one. This is the cause behind the serious damages to local people and the infrastructures along the river banks and coastlines.

Understanding the basic causes, recognizing the continuous trends, or proposing the effective and feasible response solutions are the most important problems for the local people and the authorities, those of the Central Government and the those in the localities. Therefore, we must prepare for river banks’ or coastlines’ and valuable materials’ or entities’ protection, plan and stabilize the populated areas along the river banks and coasts, especially in the high-risk erosion areas. These are the major contents that would be presented as follow.

Keywords: *erosion, Mekong delta, sediment.*

Classification number: 6.2

Rivers and coastlines are considered to be living organisms. The living organisms always move. One of those movements results in siltation and erosion, generally known as the river metamorphosis. In addition, for living organisms, the metamorphosis is intermittent, rapid or slow, and strong or weak, from both the inside and outside elements. In the scope of this research, we would discuss the river bed and the coastal erosion sequences during the recent years in the Mekong delta.

Some major natural principles of river sequences in the Mekong delta

The Mekong delta river bed sequence principles by time and space are very diversified and complicated. The following are some of the typical principles:

Divided/incorporated rivers: right after entering the delta, both the Mekong and Bassac rivers start the division/incorporation process by forming a series of consecutive divided/incorporated nodes and end in all the distributaries that flow into the sea. The phenomenon of river shortcuts might have occurred several times in the past, on the segment from Phnom Penh to the Vietnam-Cambodia border and in the dead river segments that had formed in the current natural swamps and lakes (such as Bung Binh Thien and An Giang province). With tens of instances of river division and incorporation, the Mekong river might be laid on a less stable geological foundation. After many consecutive divided or incorporated nodes, from the Vinh Long province, the river starts its division process to constitute four separate distributaries flowing directly into the sea, namely, Cua Dai, Ba Lai, Ham Luong, and Co Chien. This process also happens at two other distributaries to separate the Cua Dai into Cua Dai and Cua Tieu, and the Co Chien into Co Chien and Cung Hau river mouths.

Located on the quite stable geological foundation and flowing parallel to the Mesozoic folds in the deep layer, the phenomenon of division/incorporation is fewer in the Bassac river. While approaching the sea, the river also splits into two mouths (formerly, the Bassac river had three mouths, but the middle one, namely, Bat That, the last in the nine mouths, disappeared about 100 years ago by sedimentation). Generally speaking, the continuous division/incorporation and formation of the distributaries when approaching the sea are the typical characteristics of the Mekong river system. This phenomenon can be assembled from various reasons, such as a sudden increase or decrease in the water flow velocity in the alternate wide or narrow river segments, which bring material sedimentation and form the alluvial grounds (in the middle of the Mekong and Bassac segments), or due to the non-coincidental dynamic axis of the flood/low-flow seasons, creating the slack velocity zones and the gradual sedimentation (in the upper Mekong and Bassac segments). In the strongly tide-affected zones, the river division process is formed by many combined elements. There exists a close relationship between the sediment/flow distribution and the cross-sectional area of each distributary. This allows us to explain the phenomenon of sedimentation on

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some branches along the river, such as the downstream of the Vam Nao distributary, Cao Lanh or the Cai Be creek (Sa Dec) on the Mekong river (Table 1, Fig. 1).

Table 1. Characteristics of morphology for the Mekong and Bassac rivers.

River segment	Distance from the estuary (km)	River	Cross sectional area (m ²)	Mean width of segment (m)	Mean depth of segment (m)	Hydraulic radius (m)
Estuary	0-60	Mekong	5,795	853	-10.0	6.87
		Bassac	17,870	1,860	-12.5	9.84
Middle	60-140	Mekong	6,722	882	-17.3	8.45
		Bassac	10,552	962	-16.6	11.20
Upper	140-220	Mekong	8,207	853	-15.5	10.30

(Sources: The data are summarized from [1] and a lot of other sources and at different moments).

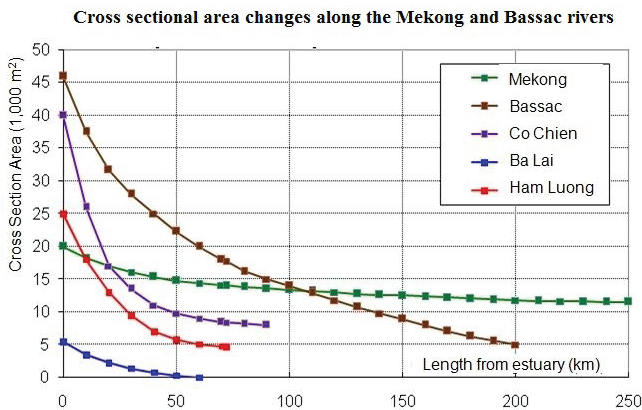


Fig. 1. The changes in the cross-sectional area along the Mekong and Bassac rivers (Sources: The data are summarized from [1] and a lot of sources and at different moments).

The formation of curved river segments: an important feature of the river flow and river bed mechanism is the formation of the curved river segments, of which, the most prominent is in the Mekong river. The curved form is ever better than straight to balance the kinetic energy between the flow and the bed. Consequently, the curved is the most sustainable form of rivers located in the land, which are easily eroded in the Mekong delta. Some typically curved segments are at Tan Chau, Sa Dec, and My Thuan on the Mekong river, and Khanh An (near the border), Vinh Thanh, and Long Xuyen on the Bassac river. However, due to the unformed balance state, some curved segments on the Mekong river are still strongly being dug and eroded. Meanwhile, some other river segments, most of which are on the Bassac river, have progressively advanced to the necessary stable state. The transformation of the curved segments is often associated with the process of

thalweg shifting, especially on the riverbeds. These thalwegs squeeze on the concave banks and increase the erosion ability, mainly in the flood season, to form the abysms close to the river banks, such as the abysms at Tan Chau, Hong Ngu, Sa Dec, and Vinh Long on the Mekong river (Table 2).

Table 2. The characteristics of the curved segments on the Mekong and Bassac rivers.

Curved segment	W_{max} (m)	W_{min} (m)	R (m)	L (m)	L' (m)	K (L/L')	Z_{min} (m)	Z_{mean} (m)
Mekong river								
Tan Chau	1,850	600	26.0	15,000	11,600	1.29	-45.1	-20.0
Sa Dec	1,500	800	15.5	24,000	21,600	1.11	-28.5	-10.3
Vinh Long	1,000	440	19.9	3,900	3,650	1.07	-35.0	-14.7
Bassac river								
Chau Doc	1,100	270	15.5	13,000	9,000	1.44	-25.8	-13.0
Chau Thanh	1,200	580	18.4	14,000	13,000	1.08	-21.0	-17.5

Notes: W_{max} : maximum width; W_{min} : minimum width; R: hydraulic radius; L: length of curved segments; L': length of the curved segment by straight; K: curved coefficient; Z_{min} : most depth; Z_{mean} : mean depth.

(Source: the data are summarized from [1] and a lot of other sources and at different moments).

The formation of alluvial grounds and islands: alluvial ground formation is associated with the river division/incorporation process, with the flow movement being ruled by the seasons and along the rivers, with the composition and size of suspended and bottomset bed materials carried by flows. At the same time, alluvial grounds have the opposite effect on the flows, such as by increasing the velocity before and after the division of the distributaries to form the eroded pits, causing the alluvial grounds to gradually shift to the downstream and change after each flood season. This phenomenon is often found in the small alluvial grounds along the Mekong river and in the downstream of the Bassac river. Islands are formed by the growth of alluvial grounds, which enables them to achieve the real stability. However, these kinds of islands are usually small in size. Another kind of islands, which are in larger size, are composed by the flow cutting and the establishment of a new flow process, such as in the islands of Cai Vung and Tay (Fig. 2) on the Mekong river, several islands on the Ham Luong and Co Chien rivers, the islands of Vinh Truong (Fig. 3), and Dung (Fig. 4) on the Bassac river. These islands are often quite stable. In the case of Dung island on the Bassac river, which is located between two large distributaries, it gets expanded significantly through time with a big amount of annual sedimentation. The formation of alluvial grounds and islands is one of the typical morphological characteristics of the Mekong and Bassac rivers.



Fig. 2. Islands formed by the flow cutting phenomena on the Mekong river.

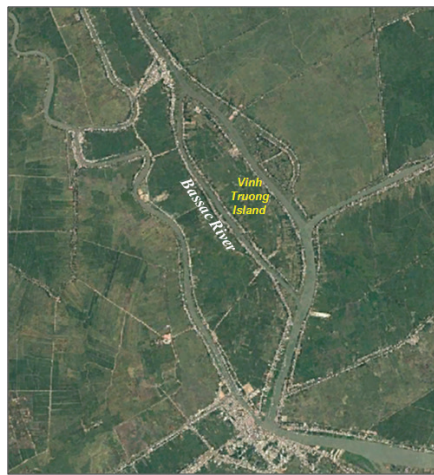


Fig. 3. Vinh Truong island formed by the flow cutting phenomena on the Bassac river.

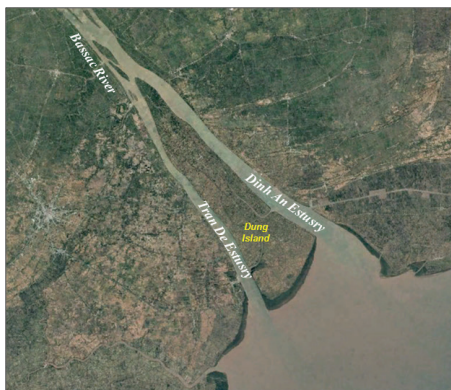


Fig. 4. Dung island formed by alluvial deposition phenomena on the Bassac river.

The formation of the grounds across the rivers: across ground is a type of relatively stable structure in the riverbed, often in the form of a diagonal edge across the river that is formed by the alluvium. The across grounds are formed on the quite stable and slightly wavy river segments, and so, in the Mekong river, these grounds are often found at about 100 km

from the estuaries.

The change of the depth along the rivers and the formation of abysms: in the delta, the depth of the river greatly depends on some flow factors. The river bottom is often raised in most of the rivers in the Mekong delta by approaching the estuaries. Within about 60 km from the mouths, the bottom depths are quite stable and leaned trend in the upstream on both the Mekong and the Bassac rivers. The river beds are wide and shallow (except the Ba Lai and the Ham Luong rivers, the bottom depth is only with the leaned trend from the mouth to the upstream, and there is no big change at river mouths). The deepest places and the big changes usually happen in the distance of 60 km from the estuary to the upstream. This is a complicated segment, as it is directly affected by the strong water flow in the flood season and the contrary between the upstream and the tidal flows during the dry season. At a distance from 60 to 140 km, both the rivers have the lowest average bottom depth, although there are several places of elevation at -25 and -35 m. The biggest abysms of the two rivers are found at a distance of 140 km to the upstream. On the Mekong river, that is where the curved segment at Tan Chau is present, with a depth of -45.1 m and on the Bassac river, that is present after the Vam Nao connection, with a depth of -40.6 m. In these segments, the bottom depth trend is gradually raised in both the rivers (Table 3).

Table 3. Characteristics of the bottom depth in the Mekong and Bassac segments.

River	Segment	Distance (km)	Maximum depth (m)	Minimum depth (m)	Average depth (m)
Mekong	Estuary	0-60	-16.3	-7.4	-10.0
	Middle	60-140	-35.3	-6.5	-17.3
	Upper	140-220	-45.1	-9.0	-15.5
Bassac	Estuary	0-60	-16.0	-8.4	-12.5
	Middle	60-140	-28.7	-9.6	-16.6
	Upper	140-220	-40.6	-5.1	-13.6

(Sources: The data are summarized from [1] and lots of other sources and at different moments).

Trend of river banks and coastlines changes during the past 100 years

Researches from the spatial images and the river and coastal topographic surveys in the Mekong delta show that the general trend of morphological change of the Mekong and Bassac rivers during more than 100 years are the flow shifts, island formation and accretion, flow division and incorporation, main stream swerve for the divided flows, estuary siltation, and gradual sea encroachment by alternation of the alluvial deposition and erosion process.

The flow shifts appear at many places on the river system,



Fig. 5. Changes of the islands between Dai and Tieu mouths on the Mekong estuary from 1906 to 2016 [Sources: Bibliothèque nationale de France (1906), U.S. Army (1972), and Google Maps (2016)].

such as the Mekong river at Cao Lanh (deviation of 3-4 km to the right), the Ba Lai river from 12-20 km to the estuary (deviation of 2.5 km to the right), the Bassac river at Long Xuyen-Thot Not segment (deviation of 1.0 km to the right), and the Vam Nao river at the segment closed to the Mekong river (deviation of nearly 1.0 km to the upstream). The formation and accretion of islands happen in most of the rivers, including the shift and the expansion of islands and the sedimentation and connection of small islands into the larger or with the major ones. Typically, this is applicable to the islands of Long Khanh, Gieng, the small islands from Cai Be to Vinh Long on the Mekong river, and the islands of Ong Ho, Cac, May, and Dung on the Bassac river. The swerve of the main streams is probably the biggest activity of the river system during the past 100 years and can be considered as the final stage of the flow division/incorporation process. This process is often correlated with the flow shifts, such as at Cao Lanh and Sa Dec on the Mekong river and Long Xuyen on the Bassac river. The alluvial deposition at the estuaries is also a special activity in the Mekong river system. The most typical alluvial deposition activities are at the entrances of the Co Chien and Ba Lai distributaries on the Mekong river and the Dung island on the Bassac river. During the past 100 years, there has also been a considerable variation in the coastline, with the general trend in sea encroachment being 2-4 km, even 7-8 km, on an average. The biggest changes are the connections of the islands between the Tieu and Dai estuaries with the Ilo Ilo island (in the offshore), 3 km far from each other, to create a new shoreline (Fig. 5), sedimentation and stretching out the Dung island toward the sea 2-6 km, along with the disappearance of the Bat That's mouth (Fig. 6), extended the shoreline between Ham Luong and Co Chien and the My Thanh river's right bank promontory, deeply eroding the shoreline up to 1-3 km, accompanied with the disappearance of a series of coastal small islands from My Thanh to Ganh Hao, stretching to Mui Ca Mau up to about 10-15 km to the sea.



Fig. 6. Changes of Dung island on the Bassac Estuary from 1863 to 2010 [Source: Bibliothèque nationale de France (1863-1906)/Department of Survey, Mapping and Geographic Information Vietnam (2010)].

Trend of river bank and coastal changes during the past 30 years and recent time

The general trend of the rivers' morphological course during the past 30 years was erosion and sedimentation along the rivers at different levels. This change has directly increased or decreased the cross-sectional area of the river. Such changes in accordance with the rules of the non-stop movement of the curved river segments, alluvial grounds, and deep channels. The cross-sectional area surveys for both the Mekong and Bassac rivers show that a general trend is increase in the area (0.1-0.4% per year) and decrease in the width (3-5 m per year). This conflict proves that the river bank becomes stable and the cross-sectional area is expanded only by digging deep the riverbed. However, the morphological course of the cross-sectional areas shows that the ability to deeply dig the stable bottom ground is harder than the eroding the river walls, leading the river bank to have an increase in the vertical trend.

In all the rivers' morphological characteristics, perhaps the depth along the rivers has little change than others, except for some extra tributaries. The sustainability of the riverbed proves that the flows have been dug to the deepest area by allowing the possibility at each location.

The biggest changes recorded by the spatial images and the actual measurements are the shifts or the connections to the islands on the Tu Thuong-Cao Lanh and Cai Be-Cho Lach segments. This includes the shift of a small island 2.0 km from the middle to the lower region of Tu Thuong, connecting the Ma island and another small island in the upper region with the Tay island, connecting two small islands with the Gieng island, and connecting the islands at the Cai Be-Cho Lach segment with the islands between the Tieu and Dai mouths. The morphology of the islands on the Bassac river from the upstream to Dai Ngai are quite stable, except for some small changes, such as the extension of the Thi Hoa island and the agglutination of the island at the Can Tho ferry into the right river bank. The most meaningful change on the Bassac river has been the development of the Dung island at the estuary and the continuing sea encroachment at an average speed of 20-50 m/year. The islands in the Ham Luong and Co Chien rivers seem to be stable. The Con Co island and another small one was merged with a bigger island between the mouths of Co Chien and Cung Hau. Some islands at the entrance of Co Chien on the Mekong river (opposite with Vinh Long province) were also interconnected to fill up quite a large mouth in the past (Fig. 7).

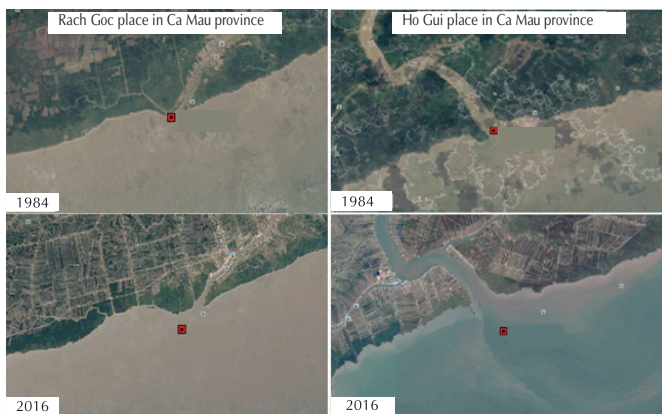


Fig. 7. The coastal erosion at Rach Goc and Ho Gui (Ca Mau province) from 1984 to 2016 (Source: Google Maps).

The general trend in coastal change is still the sea encroachment in the shoreline of the estuary and the alternation between the slow sedimentation and erosion processes in the other shorelines during the past dozens of years. The annual average sea encroachment velocity is about 10-20 m per year. The fastest sea encroachment happened from Mui Ca Mau to Bay Hap with an average speed of 30-50 m per year. The shorelines at Vam Cai Cung (Bac Lieu), Dong Hoa (U Minh Thuong), and Rach Gia also encroached to the sea at a speed of

5-10 m per year. In contrast, some shorelines of Ganh Hao-Mui Ca Mau and Rach Gia-Ha Tien were eroded at the same speed. The morphological change in the shallow territorial waters is quite large due to the move of the subterraneous sand dunes, which continuously occurred after the flood seasons and due to the strong wind spells (Fig. 8).

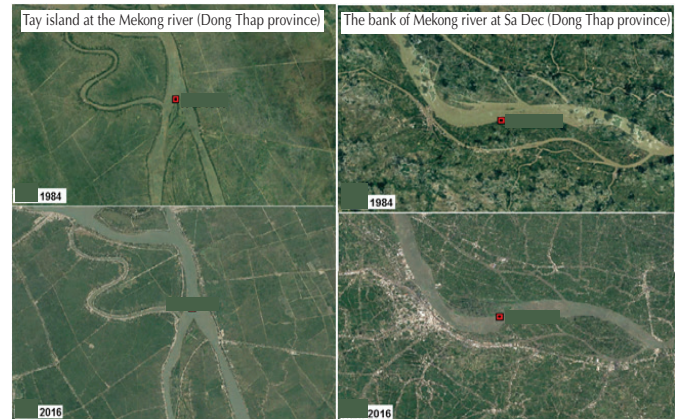


Fig. 8. The erosion at the Tay island and the Sa Dec bank on the Mekong river from 1984 to 2016 (Source: Google Maps).

In recent years, along with “salinity intrusion” and “drought”, the “erosion” has become the most “important and necessary” problem in the Mekong delta, whereas “flood and flooding” seem to be less interested.

During the recent 15 years, the erosion situation has become more complicated, occurring at many places in the river, for instance, in the canal systems and in most of the coasts in the Mekong delta. The most common is along the Mekong river banks (from Tan Chau-Hong Ngu to the estuaries) and in the island system (Long Khanh, Tay, Gieng, Dai, and Phung) in the provinces of An Giang, Dong Thap, Vinh Long, Tien Giang, Ben Tre, and Tra Vinh, along the Bassac river banks (from Long Binh to the estuaries) and the island system (My Hoa Hung, Tan An, and Dung) in the provinces of An Giang, Vinh Long, Soc Trang, Tra Vinh, and Can Tho, the coastlines in the provinces of Tien Giang, Ben Tre, Tra Vinh, Soc Trang, Bac Lieu, Ca Mau, and Kien Giang, in the canal systems in the provinces of Dong Thap, An Giang, and Ca Mau, in the connecting rivers/channels of the Mekong and Bassac rivers, especially the Vam Nao river (An Giang). According to the preliminary statistics, in the whole Mekong delta, there are about 1,000 places with erosion, including nearly 300 serious sites, more than half of which are on the main rivers [2].

Instability causes of riverbeds and the coasts, and the current erosion principal trend

Annually, the average discharge from the upstream of the Mekong river basin into the Mekong delta is about 13,700 m³/s [3], and it is quite stable from year to year. However, the seasonal changes in a year are somehow large. The differences

in the flow between the flood and the low-flow seasons are 7.42 times (24,500 m³/s and 3,300 m³/s) [3] and between the highest month (September) and the lowest month (April) are 18.0 times. This rate is not reduced significantly by the regulation of the Great Lake. In the flood season, the river banks are overwhelmed due to the overloading of the riverbed. In the low-flow season, all the rivers are strongly affected by the high tides due to a scanty water source. The early flood flow plays an important role in creating the river bed form, due to being maintained during a sufficiently long time and through stable erosion, which is only concentrated in the riverbed. In the middle of the flood season, especially during the high flood years, the deep pit digging ability and the erosion of the river banks (particularly in the curved river segments) are increased by the high velocity flood flow concentrated in the riverbed. Another major impact of the water flow is the conveyance of the sediment. If the strong flows at the beginning and middle

of the flood season (maximum velocity 2.0-2.5 m/s) are the principal causes of deep digging and sediment take away, then the flow reductions at the end of the flood season (average velocity of 1.0-1.5 m/s) are the major causes of siltation along the rivers, especially in the estuaries, so that there are many changes in the river form after a flood season.

The tide of the East Sea with a large amplitude is propagated very far to the upstream of rivers. In the low-flow season, the tidal fluctuation is still seen at Phnom Penh, more than 300 km away from the Mekong estuary. The tidal fluctuation makes the river bank always in wet or dry situations, creating favorable conditions for the river banks to have steep, porous, and crumbly soils and get easily eroded. Closer to the river upstream, in spite of the decreasing effects of tide, due to the river flow being operated by the accumulative/discharge phases of tidal flow, there have been certain effects on the process of erosion and siltation. In addition, a very strong velocity of the



Fig. 9. Some pictures of erosion at river banks and coasts in the Mekong delta (Source: individual information, e-newspapers, and the Internet).

opposite tidal flow at the nearly estuarine areas (0.7-1.5 m/s) also contributed to the instability of the riverbeds (Fig. 9).

The agglomeration of materials in the salt water environment is also a cause of sedimentation at estuaries.

Annually, a strong wind that blows from sea to inland, opposing the flow direction of the main rivers, is called the “Gio Chuong-strong wind”, which often appears from October to April in the Mekong delta. This strong wind usually appears frequently and strongest during February, then decreases until the end of the season. The average speed of Gio Chuong is from 4 to 6 m/s (at a frequency of 40-60%), sometimes reaching 9-10 m/s (at a frequency below 5%). When blowing into the wide and airy estuaries, the wind speed can reach up to 10-15 m/s, even 20 m/s. The estuarine water level rose due to the strong wind when combined with the high tide peak. According to surveys and calculations, the water level rise is about 20-30 cm, even up to 50 cm. With wider and airier estuaries, the winds in the Bassac and Co Chien rivers are stronger than others. Further inland, although the wind speed and appearance frequency decreased remarkably, but the strong wind still made big waves crash into the river banks that were always wet, causing strong erosion even in the dry season. Within a distance of 100 km from the mouth, the erosion of river banks by strong wind might be greater than that by flooding. At Sa Dec, the erosion of the river banks mainly occurs during the receding flood and wind strong period (from October to December). In addition, other impacts of strong wind are supporting for siltation and shifting submerged sand dunes move before the estuary, erosion and alluvial accretion along the coasts.

The ocean currents also have a certain role in the morphology of shorelines and shallow water. In the dry season, the Northern Hemisphere currents press onto the shores and at the end of the flood season carry the estuarine sediment to accrete in Mui Ca Mau. During the rainy season, the Southern Hemisphere currents take the opposite direction, causing most sediments during floods to be deposited right at the river mouths.

The sediment is a vital element of the flow characteristics. The amount and the size of the sediments play a major role in the alluvial deposition in rivers, estuaries, and along the coasts. Every year, the Mekong delta receives about 150 million tons of sediment, on which, 138 million tons is in the Mekong river and 12 million tons is in the Bassac river, mostly in the flood season [3]. The average sediment content of the flood season is about 500 g/m³ on the Mekong river and 200 g/m³ on the Bassac river, according to the measured data [3]. However, the sediment content changes largely by time and space. The analysis results have shown that the sediment size of the Mekong river is bigger and more uniform than that of the Bassac river. The average diameter of sand grain in the bottom of Mekong river is 0.23 mm at Tan Chau, 0.21 mm at Sa Dec, and 0.20 mm at Vinh Long. From Vinh Long (Mekong river) and Can Tho (Bassac river) to the estuaries, the alluvial sedimentation phenomena begin to occur very complex as forming newly emerged alluvial grounds, accreting, and extending the old islands to the estuaries. The rest would be

deposited to form estuaries with many sand dunes. For the finer particles, a part would be conveyed further in a high salinity water area, agglomerated and sunk down in shallow water before the estuary, whereas the other part would be shipped to the South for the consolidation of Mui Ca Mau. When going into the fields, both on the Mekong and Bassac rivers, most of the sediment is deposited at a distance of 10-20 km far from the river banks. This sedimentation made the river banks increasingly higher and formed the new soil dunes along the rivers.

The biggest changes of river morphology in the Mekong delta during the past hundred years, particularly in recent 30 years, have mainly been caused by human activities. The uncontrolled exploitation of the forests, construction of reservoirs in the upstream, digging and expansion of the canal systems, embankment along the rivers and canals, the construction of sluices and dams at the entrance of canals, dredging river channels to enhance the ability of ship traffic, and reinforcement of river banks for erosion protection have been the interventions, direct or indirect, in the morphological changes of rivers. In that, the exploitation in the upstream of the Mekong river basin is the most meaningful of all.

As mentioned above, the almost sediment yield of the Mekong delta is mainly generated by the upstream flood flow. In the past natural conditions, within an average of 10 years, there were 3-4 years of weak flood, 3-4 years of medium flood, and 3-4 years of high floods. During the weak flood years, due to the low sediment yield, the estuaries and shorelines often occur at the erosion rates of 5-20 m/year. During the medium flood years, the riverbeds and shorelines are quite stable by an insignificant erosion and accretion of tides, strong winds, and currents. During the high flood years, while the river affected by strong erosion, the coasts have a trend of accretion by a big amount of sediment to the estuaries, at a rate of tens of meters per year. Therefore, during the 10-year average, the upper parts of the rivers are not only accreted but also eroded at different levels; the estuaries and coasts even thought of an alternative accretion/erosion phenomenon but still are the general gradual sea encroachment trend (encroached about 100 m during 3-4 years of high flood and eroded about 30-40 m during 3-4 years of weak flood; during the 10-year average, still encroached to the sea about 60-70 m).

However, in the past 20 years, especially after three consecutive high floods in 2000, 2001, and 2002 in the Mekong delta, the changes in the flood sequences have some significant considerations, leading to huge impacts on the sedimentation and erosion of the riverbeds and coasts. In 13 years (from 2003 to 2016), except for the rather large flood in 2011, almost of the duration were only occurred with the medium floods (2004, 2005, and 2013), below the medium floods (2006, 2007, and 2009), weak floods (2008 and 2014), very weak floods (2010, 2012, and 2016), and extremely weak floods (2015). In 2011, the high amount of sediment was not enough to compensate for the accumulated consecutive shortage eight years before and five years after it [4].

According to the calculations, with the impacts of hydro-power system on the upstream of the Mekong river and the decrease in sediment due to weak floods, at an average of the past 10-15 years, the volume of the upstream sediment into the Mekong delta is around 60-70 million tons/year (40-50% compared with the previous average) [5]. Thus, the upstream river segments always have a shortage of sediment and imbalance of kinetic energy, which is the cause of the increased erosion phenomena. In particular, the medium and below medium floods with the flow of riverbed creation are maintained for long periods (3-4 months), causing a strong capacity for the erosion, respectively. This phenomenon is also spread into the canal system. At the estuaries and coasts, because of no sediment deposition, the erosion phenomena occur consecutively instead of alternating with sedimentation as before, conceiving the general trend of soil erosion, with an average speed of 2-5 m/year. In the past 10 years, some places were eroded inland not less than 100 m (Rach Goc, Ho Gui-Ca Mau) - some places have even turned from siltation before to erosion now (Mui Ca Mau).

In addition to that, the early flood (August) brings more sediment than the other periods in the Mekong delta. Sediment descends at the end of the flood season. About 60-70% of the total sediment into the Mekong delta is concentrated in the first two months of the flood season, namely, July and August [6]. At this moment, the flood water is needed to be stored early in the most of the upstream Mekong reservoirs to ensure its being fully filled from the end of August to early September. Therefore, the major part of the water flood and sediment is retained in these reservoirs. In the remainder of the sediment to the lower by flood flow, more than half of it flows back into the Great Lake. Until the Great Lake is filled with water (at the last September for medium and weak floods), the flood just starts from the Great Lake to complement into the Mekong delta, but almost all flood water has run out of sediment currently. Thus, it might be understood to be the reason behind why the erosion phenomenon has increased.

In addition, an important cause of the increased erosion is sand mining along the rivers from the lower region near the estuaries to the upper region near the Vietnam - Cambodia border, with a mass of millions of tons/year (according to the unofficial synthesis, the licensed exploitation of the sand can be up to 12-15 million m³/year, excluding the illegal exploitation). Thus, the total remaining amount of sediment for functions of "accretion" for rice fields and "stable" rivers and coasts in the Mekong delta is only 40-50 million tons (30-40% less than before) [5, 7].

Due to the multiple impacts from the nature and humans, the erosion in the Mekong delta in the recent years has begun to form the following notable trends:

Moving closer to estuaries for coastal erosion: if the erosion often occurred at the coasts about 100 km far away the estuaries before, nowadays, due to the limited amount of sediment, the erosion phenomenon is approaching following an asymptotic pattern toward the estuaries, such as at Binh Dai

(near the Dai estuary, Ben Tre), Duyen Hai (near the Cung Hau estuary, Tra Vinh) on the Mekong river, Vinh Chau (near the Tran De estuary, Soc Trang) on the Bassac river, and Dong Hai (Ganh Hao estuary, Bac Lieu) on the Ganh Hao river.

Erosion happening year-round, especially in the dry season: previously, erosion often happened from the middle of the flood season (September to October for the weak and medium floods) to the end of the flood season (November to December for the high floods), at a frequency of up to 90%. However, now, the erosion occurs almost year-round, with a trend leaning toward the dry season (due to more influence of the tide).

More serious erosion in the connecting rivers/canals of the Mekong and Bassac rivers: formerly, the erosion phenomenon happened almost rarely (or not too seriously) in the connecting rivers/canals of the Mekong and Bassac rivers. However, now, due to the changed hydraulic balance between the rivers, there is a trend of the flow moving from the Mekong river to the Bassac river, causing increased erosion in the almost river/canal system, especially in the Vam Nao river [6].

Ever-increasing serious level of erosion: some years ago, a serious erosion occurred once every 5-10 years (on the Mekong river in 1991 at Hong Ngu, in 2000 at Tan Chau, and on the Bassac river in 2012 along the National Road No. 91 from Long Xuyen to Chau Doc). However, nowadays, almost every year, a serious erosion occurs, from the coast at Ganh Hao (Bac Lieu), Duyen Hai (Tra Vinh), Ho Gui (Ca Mau), and Go Cong (Tien Giang) to the river banks at Cho Moi, Tan Chau (An Giang), Thanh Binh, Hong Ngu, Sa Dec (Dong Thap), and at the infield canals at Thoi Binh, Dam Doi, Cai Nuoc (Ca Mau), Hong Ngu, Thap Muoi, Thanh Binh, Lap Vo (Dong Thap), Tri Ton, Phu Tan, Tinh Bien (An Giang), O Mon, and Phong Dien (Can Tho) (Fig. 10) [5].

General trend of the erosion phenomenon is to continue developing, both in terms of width and depth in the coming years: this general trend might be dominated from the coasts to along the rivers and canal systems year-round, from the flood season to the low-flow season, expanding from the flood to the tidal area, getting distributed from the large rivers to the small canals, happening on the whole Mekong delta, from the Plain of Reeds (Dong Thap Muoi), Long Xuyen Quadrangle, and between the Mekong and Bassac rivers, to the Ca Mau Peninsula and in the entire coastal strip. The level of erosion can be slight, medium to serious, or even very serious.

The basic solutions for the erosion problem of rivers and coasts in the Mekong delta

To attain effective and sustainable responses for the existing erosion situation of rivers and coasts in the Mekong delta, the following basic solutions should be considered and implemented:

1) Close cooperation with the riparian countries situated at the upstream of the Mekong river basin on river basin management, especially in the fields of hydro-power

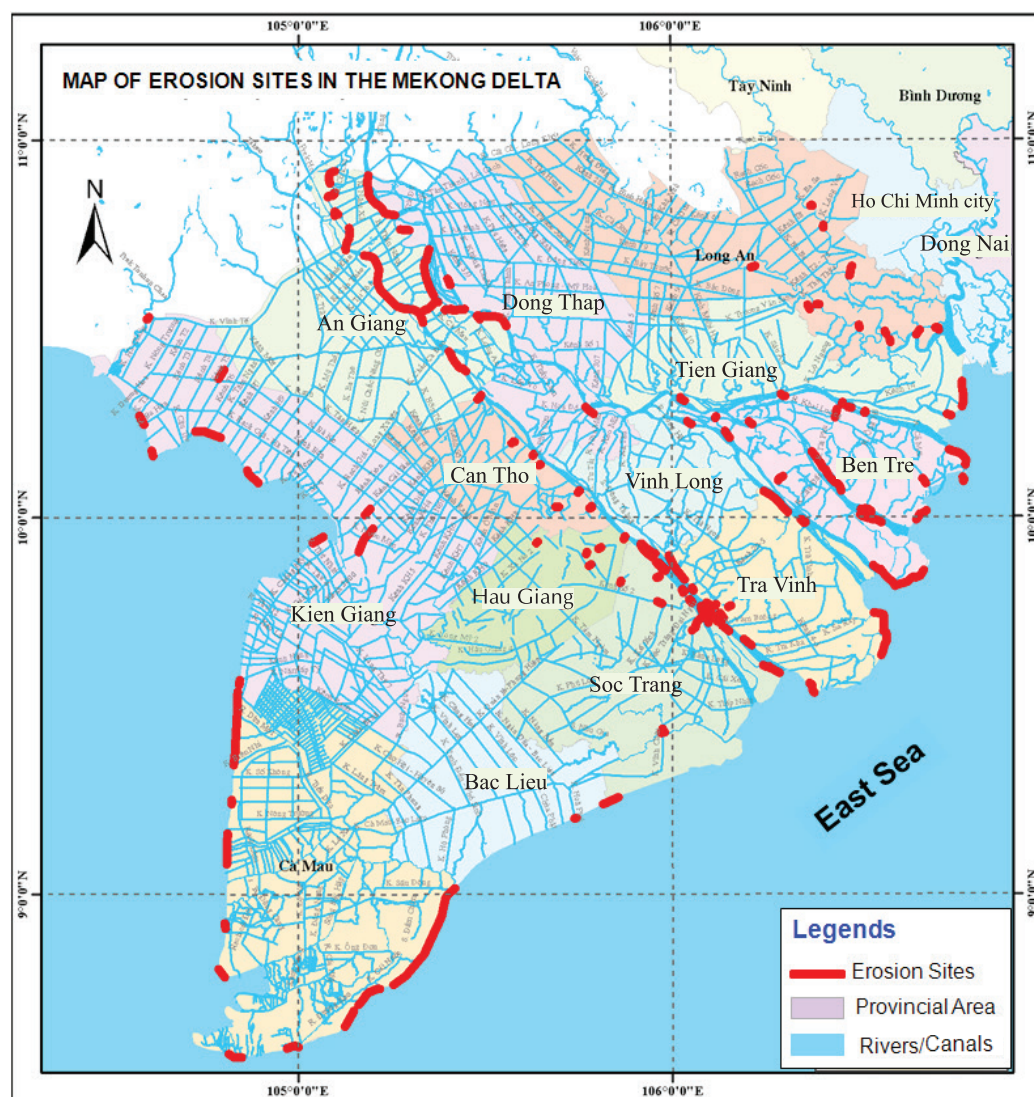


Fig. 10. Map of erosion situation in the Mekong delta during 2016-2017 (Sources: Southern Institute for water resources planning, 2017).

development (size determining, designing, constructing, and operation processing for reservoirs), management and development of forests, agriculture, and infrastructures.

2) Management and licensing restrictions on sand mining in rivers. The rigid prohibition and prevention of illegal and contraband sand mining activities.

3) The rivers and canal banks should be reinforced by traditional measures with local materials (melaleuca pile and bamboo) and trees should be planted for wave protection, which can be an early initiative for the protection activities of all the rivers and canal banks, that would constitute planting mangroves to protect sea dykes and the coasts, including the uneroded places. In the coasts, depending on the nature and the characteristics of the erosion areas, we can apply the traditional and inexpensive structural solutions, such as creating the grid layers of wave prevention or soft embankment by melaleuca

or bamboo piles (according to the form of the alternate wave preventive layers, T-shape, and improved T-shape) for the erosion protection or sedimentation increase.

4) The erosion situation should be surveyed and comprehensively evaluated to gauge the stability of rivers, canals, and coasts. The development trend of rivers, canal banks, and coasts with the changes in the flow and sediment content in flood and low-flow seasons under the impacts of sea-level rise, climate changes, upstream development, and other related disasters should be researched.

5) The strategies for river, canal bank, and coast management and protection should be built. Henceforth, reasonable and feasibility solutions for the relocation, strengthening, and protection activities (according to different measures) for the entire river, canal, and coast system should be proposed, based on the overall and harmonious perspective on the economic,

social and investments, capital allocation for each stage, each region, and each river segment.

6) Consideration to balance for all the problems (capital source, technical feasibility, importance level, impacts of upper/lower, and the entire system) to define the number of priority-protected sites/segments on the river/canal banks and coasts.

7) Solutions for housing along rivers, canals, and coasts by different materials, forms, and structures should be researched to enhance the sustainability and stability, both in the building structures and shoreline stabilization.

8) A safe corridor for the inhabitants, welfare structures, and infrastructures along the rivers, canals, and coasts should be established to closely manage the use and socio-economic development related to the rivers, channels, and coasts.

9) The welfares and socio-economic development programs should be combined to layout and relocate inhabitants along the rivers, canals, and coasts.

10) Solutions should be proposed to protect or relocate the initiative infrastructural structures (especially roads) in the high-risk erosion areas.

11) Establishing river treatment planning, river and coast space organizing, and zoning river and coastal functions to management, exploitation, rational and sustainable use of rivers and coasts should be conducted.

Conclusions and recommendation

Erosion of the rivers and the coasts is a natural phenomenon, especially with a young river and an accretive coast as the Mekong delta. Under the impacts of human activities, the erosion becomes more and more complicated. Though there exist many causes of the river and coastal erosion, however, the most fundamental cause is flood flow and the amount of sediment in the rivers. The changes in the upstream of the Mekong river basin in the last 20 years have been the main causes of the flood flow and sediment concentration fluctuations in the Mekong delta. This is also the basic and direct cause for increase in the erosion phenomenon of the rivers and the coasts during the recent years. In addition, sand mining on a large scale and unreasonability about space and

time is also a cause of serious erosion in the river segments. In addition, the sea-level rise, increase in the peak tide, strong winds, and high waves are also some of the root causes behind the more complicated erosion processes in many river segments and coasts. In certain structures of natural disaster protection, the erosion preventive structure has the highest cost and risk. Consequently, the economic, social, engineering, and environmental factors should be considered satisfactorily before making an investment decision for the river and coast protection constructions. The combination or separation between the structural and non-structural measures, between the works of local materials, between the inexpensive and the temporary with the constructions of strong, high investment capital and durable structures are considered to be reasonable solutions. For the coast, even planting mangroves is a good solution to protect the banks, but it cannot be implemented to achieve the desired effects anywhere or at any time. Careful survey of each of the coastal section, during each appropriate period, as well as the effective preventive solutions of the ocean waves must be considered importantly before planting.

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Study on sensitivity of CCAM model to the sea surface temperature boundary conditions

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Abstract:

The ability of simulation on large-scale global circulation, as well as temperature and rainfall over Vietnam area with different sea surface temperature (SST) boundary conditions by the Conformal-Cubic Atmospheric Model (CCAM) is presented in this paper. CCAM is a global circulation model, which may be used in the variable resolution mode to function as a regional climate model. That is, the model may be integrated with high horizontal resolution over the area of interest, with the resolution gradually decreasing as one moved away from the area of interest. The results show that model has well predicted large global circulation all over the global compared to Climate Forecast System (CFS) analysis data, two experiment of CCAM model were not too different with CFS model. For detailed forecasts in Vietnam region, the CCAM model will capture surface temperature compared to observed data with correlation coefficient above 0.85. Forecast temperature of CCAM tends to be lower than observed data, but the magnitude of error is not so much. Comparing the two experiments, forecast skill of CCAM_IRI is slightly better than CCAM_CFS. For rainfall, CCAM generally tends to forecast rainfall higher than observation data in summer and lower in winter. The predictive skill of rainfall in short lead times is better than others and skill of CCAM_CFS is significantly better than CCAM_IRI.

Keywords: CCAM, forecast SST, global model, region Vietnam, seasonal forecasting.

Classification number: 6.2

Introduction

Seasonal climate prediction is currently one of the top concerns because of its benefits and has been applied widely in many sectors like agriculture, construction and socio-economic activities. Seasonal prediction information plays an important role in making plans and decisions for upcoming activities like, crop production and disaster response. Seasonal prediction usually provides information on seasonal statistical features, with lead times from 1 to 9 months. The two main approaches used in seasonal forecasting are statistical and dynamical methods [1]. The dynamical method has been shown to have more advantages, as it can capture the nonlinearity of the climate variables. Along with the development of science and technology, especially in computing and storage capabilities, dynamical models have been used more commonly, with dynamic processes described in more detail on both global and regional scales. In Vietnam, there have been many studies on regional models such as RegCM and cIWRf [2-4]; the results are positive in forecasting temperature, but still have significant error in rainfall prediction. However, the initial boundary conditions for these regional models are mainly collected from forecast products of meteorological agencies in the world. To be more active in data sources for operational forecast system, the study of constructing global model for Vietnam is very necessary. In this study, we firstly apply a global model to simulate climate for Vietnam. The main purpose of this paper is to investigate sensitivity of CCAM model to SST boundary conditions, both on global scale and downscaling for Vietnam area. The paper is organised as follows: Section 2 outlines the model description and experimental configuration. In Section 3, the ability of CCAM to simulate large-scale global circulation, as well as temperature and rainfall over Vietnam area is presented and discussed. Summary and conclusions can be found in Section 4.

Methodology and data

The conformal-cubic atmospheric model and experimental configuration

CCAM is a variable-resolution global atmospheric model, developed at the Commonwealth Scientific and Industrial

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Research Organisation (CSIRO). This model uses the conformal cubic grid. The application of conformal cubic grid in CCAM derives from Sadourny's idea [5]. Then, through much research, experimentation, and development of Rancic, et al. [6] and McGregor [7-10] in construction and incorporation of primitive equations into the grid, it was basically completed and is being applied so far. The remarkable advantage of this grid is that it can solve problems in the polar and sub-polar regions, where the resolution of grid is uneven and narrowed down; this may lead to serious limitations on integration time steps or require special filtering techniques. Although CCAM is a global model, it also can simulate or predict with high resolution for specific areas. The concept of "stretched grid" was introduced to do this [11]. In "stretched" state, the grid system is shaped like a square frustum, with a small face corresponding to higher resolution region, and the remaining faces in other regions have coarser resolution. Due to this feature, even when downscaling for a given region, simulations or predictions of CCAM are always global, allowing CCAM to avoid some complicated processes when calculating in a domain's boundaries, different from other regional models.

CCAM can either be used as a global model, or be downscaled for a specific area such as other regional models. On the other hand, beside initial conditions, CCAM just requires boundary condition of monthly average SST. This is an important advantage of CCAM, making it easier to add different inputs than other models. Additionally, CCAM is a global model, so output from CCAM can be used as input for other regional models.

In this study, CCAM includes GFDL SEA/ESF radiation scheme (Fels and Schwarzkopf [12]; Schwarzkopf and Fels [13] vertical mixing scheme of Holtslag and Boville [14] CABLE biosphere-atmosphere exchange model consisting of 6 layers for soil temperature, 6 layers for soil moisture and 3 layers for snow [15], cumulus convection scheme described by McGregor [16] and some schemes developed specifically for this model, see more detail in McGregor's description [17].

To evaluate effects of SST boundary condition on CCAM's seasonal prediction for the global and Vietnam region, CCAM will be run with two different SST data. One is from the output of CFS and another is from the SST forecast of International Research Institute for Climate and Society (IRI). Experiments began from January 2008 until September 2014. The CCAM

configuration used in the experiment was as follows:

1) Global forecast: Use C96 grid with 96 x 96 grid points (horizontal resolution of about 100 km) and 27 vertical levels.

2) Regional forecast: CCAM itself is also a regional model, so in this experiment, CCAM was used to downscale for Vietnam area, the domain centre was 108°E and 17°N, horizontal resolution of 25 km, and vertical levels same as the global. The terrain elevation and the domain size are shown in Fig. 1 (left).

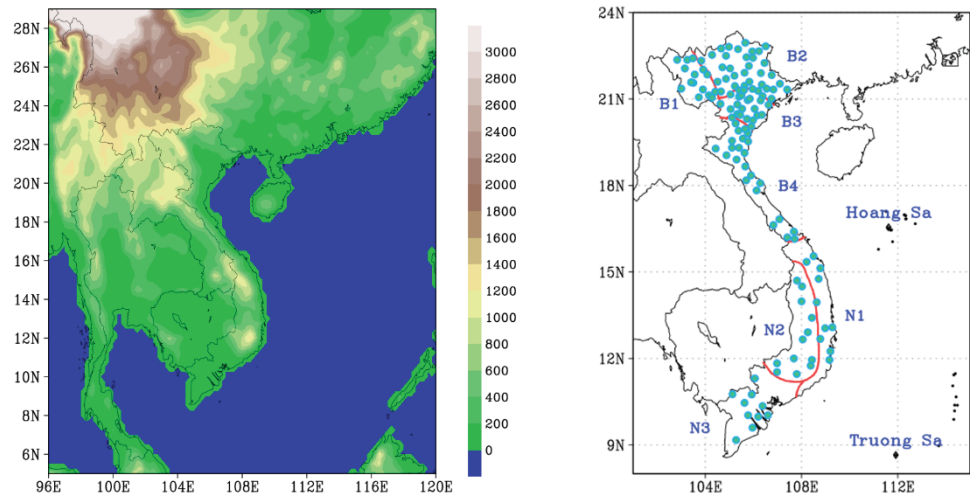


Fig. 1. Topography and domain of Vietnam (left); location of observed station (right).

Data

Initial condition data for the model included atmospheric (0.5 degree horizontal resolution) and surface variables (0.3 degree resolution) from CFS analysis data (CFSnl). The boundary condition data is monthly SST, with 6-month forecasts from CFS and IRI. In which, CFS is operational forecasting data of the National Oceanic and Atmospheric Administration (NOAA), with 1 x 1 degree resolution, and lead time up to 9 months. IRI is forecast data of anomaly of SST, 2.5x 2.5 degree resolution, with a 7-month forecast. When using IRI data, it is necessary to add to average climate period of IRI, combined from Reynolds' SST data from 1961 to 1981 and the NOAA optimum interpolation SST V2 from 1982 to 1990 [18, 19]. For convenience, CCAM_CFS is represented for CCAM run with CFS SST and CCAM_IRI is for CCAM with SST input from IRI.

As CFSnl is assimilation data from observations, so in this study, CFSnl data is also used to evaluate forecast results of global circulation from CCAM. The regional prediction of CCAM for temperature and rainfall will be compared to observed data at 128 stations all over Vietnam (The location of the stations is shown in Fig. 1, right). Statistical indicators used in the paper included mean error (ME), mean absolute error (MAE), and correlation coefficient.

Results and discussions

Evaluating global forecasts

Firstly, the results of CCAM's global prediction at 850 mb from CCAM_CFS and CCAM_IRI will be compared with the CFS model and CFSnl data for January and July of 2008-2014 period, according to 1, 3 and 5 month lead times.

In January, overall, CCAM_CFS and CCAM_IRI both predicted geopotential height and winds at 850 mb, quite similar to CFS and CFSnl with all of lead times (1, 3 and 5 months). For more detail, CCAM predicts geopotential height higher than CFS and CFSnl in most of the tropical and subtropical regions, especially in Atlantic region. However, geopotential height of CCAM tends to be lower than CFSnl in northeastern Russia. For wind at 850 mb level, CCAM can capture very well the main wind direction in January in most parts of the globe, the predicted wind speed of the model also is not too

different from CFSnl. Comparison of two CCAM experiments shows that there is not significant difference, but CCAM_CFS result tends to be better than CCAM_IRI in the Pacific region.

In July, similar to January, CCAM in both experiments also forecasts relatively well, the spatial distribution of geopotential height, as well as wind at 850 mb level compared to CFSnl. CCAM still predicts geopotential height higher than CFSnl in tropical and subtropical regions, but the difference is clearer than in January. In the Northern Hemisphere's high latitude region, the geopotential height predicted by CCAM tends to be significantly lower than CFSnl. Wind at 850 mb in July of CCAM is still well suited to CFS and CFSnl in most parts of the globe. However, the predicted wind speed tends to be stronger than CFSnl. Comparing two CCAM model experiments, there is not much difference between CCAM_CFS and CCAM_IRI (Figs. 2-4).

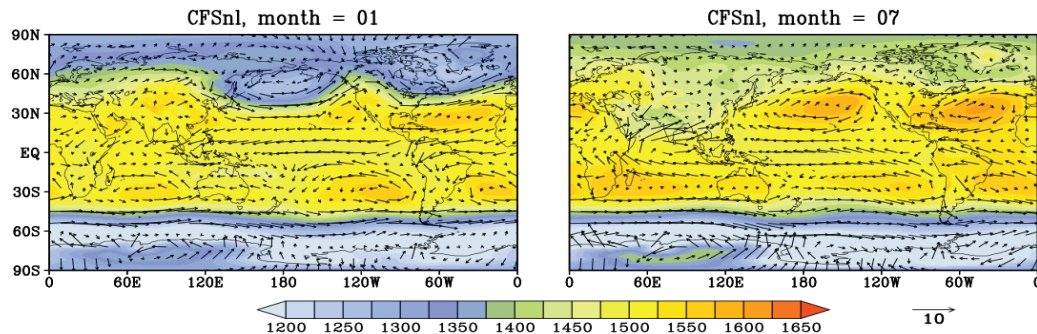


Fig. 2. Geopotential height (m) and wind (m/s) at 850 mb level, for January (left) and July (right), average of 2008-2014 period, from CFSnl analysis data.

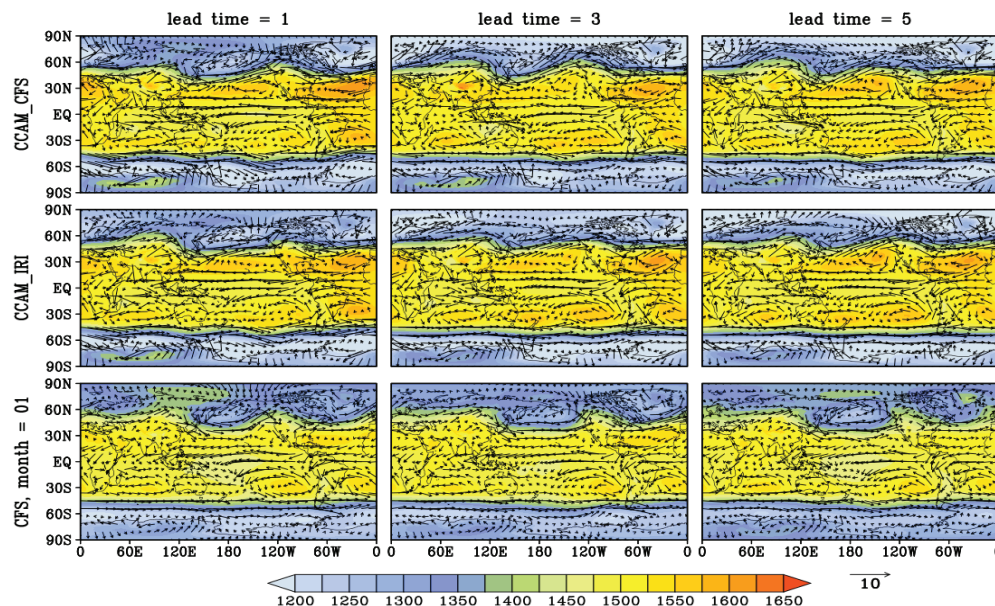


Fig. 3. Prediction of geopotential height (m) and wind (m/s) at 850 mb level, for January with lead times of 1, 3 and 5 months (from left to right), average of 2008-2014 period. CCAM_CFS (top), CCAM_IRI (middle) and CFS (bottom).

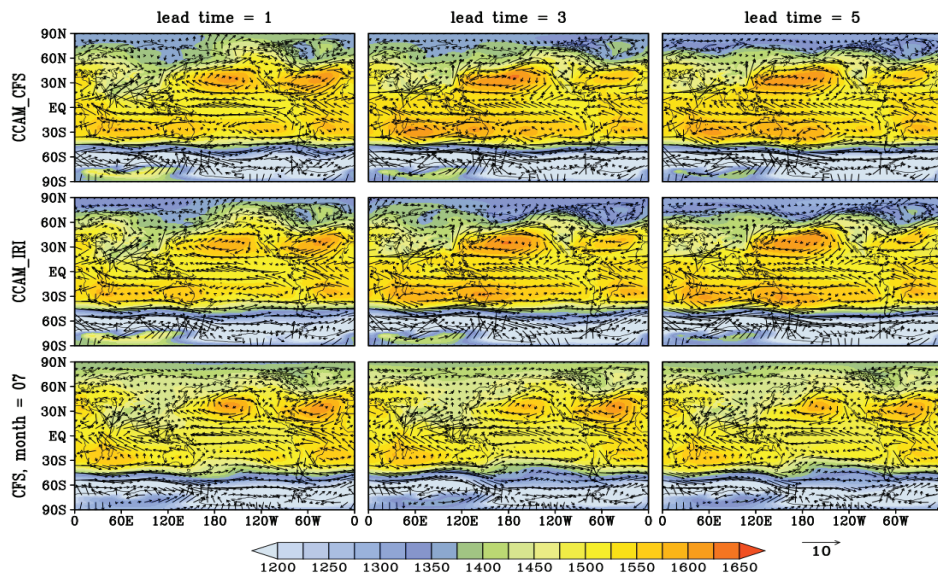


Fig. 4. Prediction of geopotential height (m) and wind (m/s) at 850 mb level, for July with lead times of 1, 3 and 5 months (from left to right), average of 2008-2014 period. CCAM_CFS (top), CCAM_IRI (middle) and CFS (bottom).

Evaluating regional forecasts

Next, regional forecast of CCAM will be assessed through temperature and rainfall at 128 stations in the Vietnam area.

Figure 5 shows errors (ME and MAE) of temperature from CCAM_CFS and CCAM_IRI with observation data for 1-month, 3-month and 5-month lead times. In general, ME value is negative, indicating that forecast temperature of CCAM tends to be lower than observed data in most climatic regions across the country with three lead times. Forecasting temperature is higher than observed data in spring in Northern Delta and Northern Central areas, especially with 3-month and 5-month lead times. With MAE error, CCAM's results are quite good with magnitude of error not exceeding 2-3°C; October, November and December have maximum error value, which may be up to 5°C in Northern regions. Error for 1-month lead time is greater than 3-month and 5-month lead times.

Comparing two experimental options, CCAM_CFS could be found to have a larger error than CCAM_IRI in October, November and December with 5-month lead time.

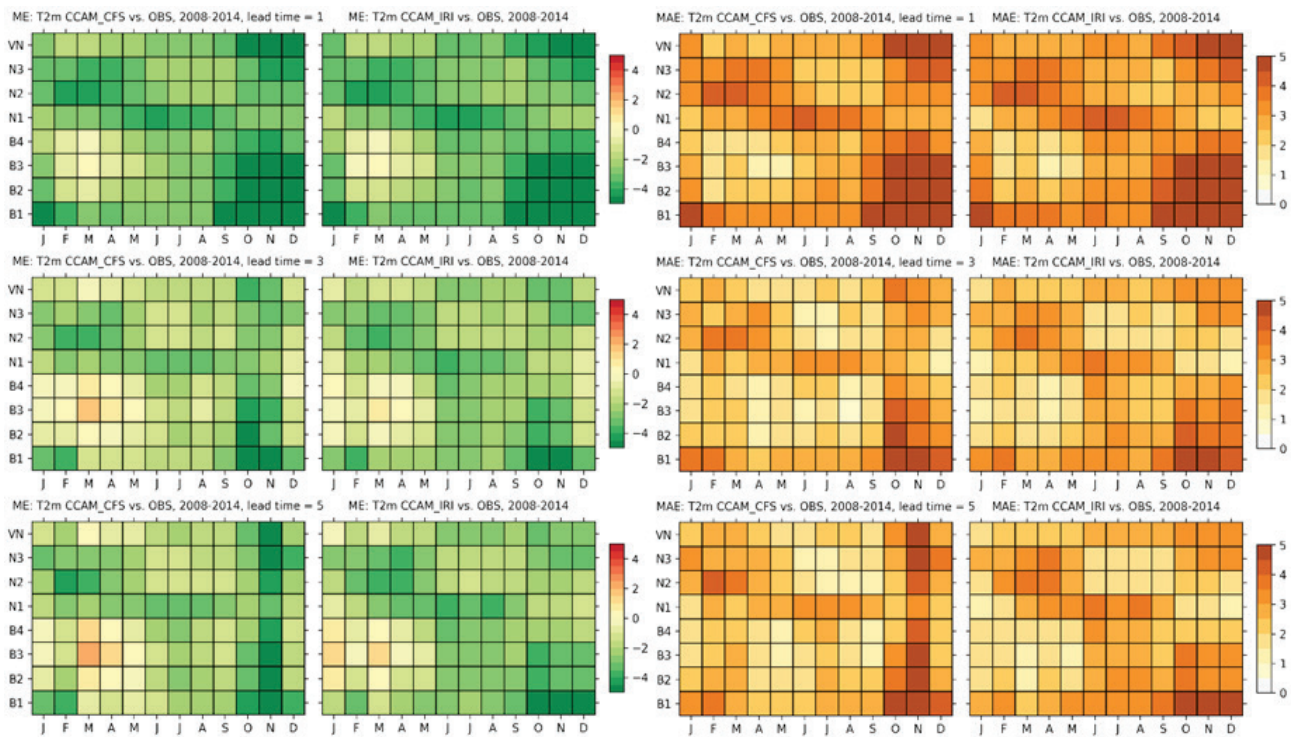


Fig. 5. The monthly ME error (°C, left) and the MAE error (°C, right) of temperature from CCAM_CFS and CCAM_IRI compared to observed data, average for 7 climatic regions and Vietnam, with lead times of 1, 3 and 5 months (order from top to bottom), period of 2008-2014.

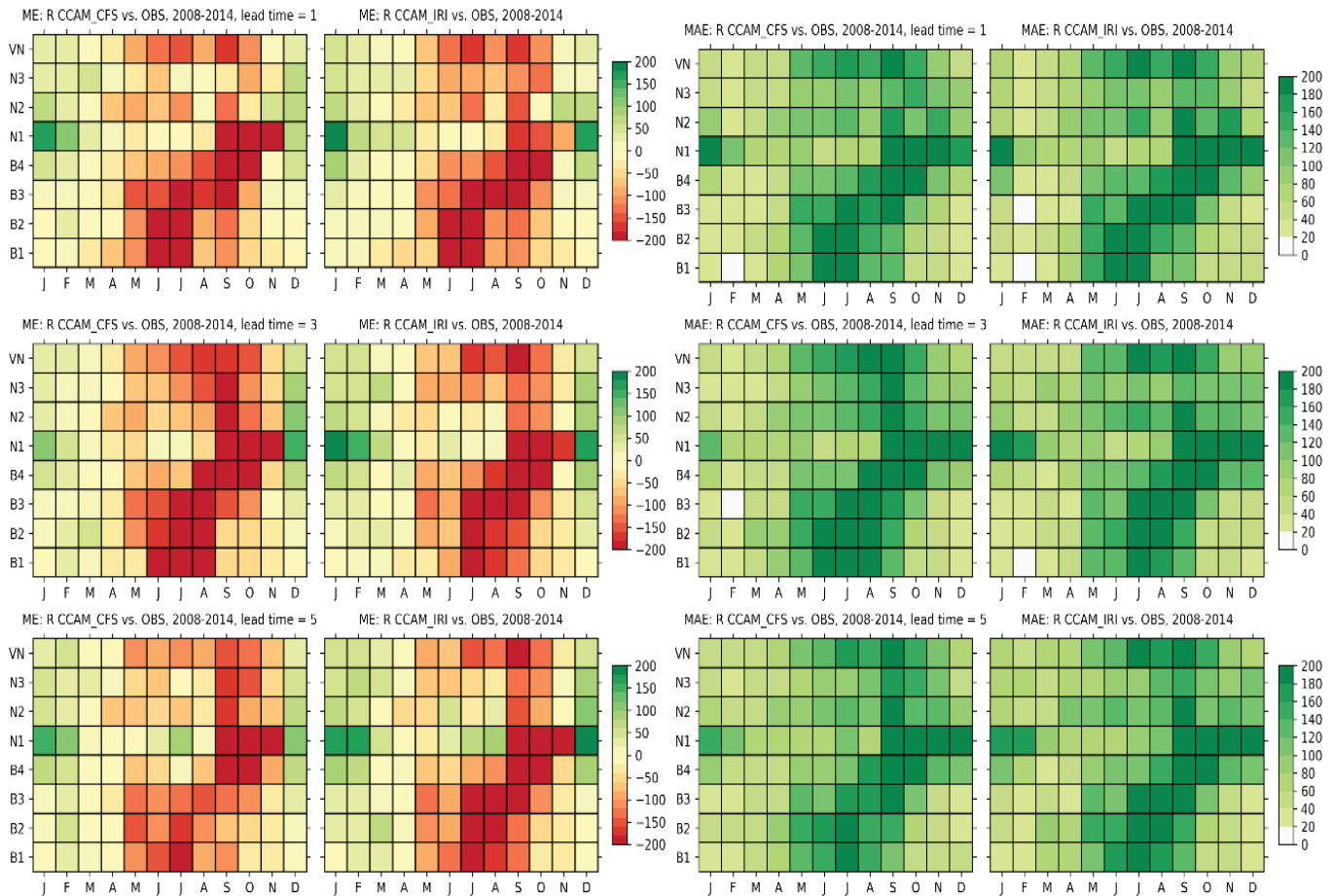


Fig. 6. The monthly ME error (mm, left) and the MAE error (mm, right) of rainfall from CCAM_CFS and CCAM_IRI compared to observed data, average for 7 climatic regions and Vietnam, with lead times of 1, 3 and 5 months (order from top to bottom), period of 2008-2014.

For rainfall, CCAM generally tends to forecast rainfall higher than observation data in summer and lower in winter. In the summer months, the error of rainfall is about 80 to more than 200 mm/month, southern regions have smaller errors than northern ones, results of 1-month lead time is better than 3-month and 5-month lead times in southern part of Vietnam with two cases. For the winter months, error of rainfall varies 20-80 mm/month, South Central region has larger errors than the rest of Vietnam. There is not significant differences in two experimentations, however, with the 5-month lead time, error of CCAM_CFS is smaller than CCAM_IRI in summer months (Fig. 6).

Figures 7-8 show the scatter graph of temperature and precipitation from two experimental options of CCAM compared to observed data at the stations across Vietnam, and for 1-month, 3-month and 5-month lead times. With temperature, the correlation coefficient between CCAM and observation is very high, above 0.85 for all lead times. For rainfall, CCAM_CFS with 1-month lead time has best correlation (0.497); the correlation coefficient for 3-month lead

time is lower than others. In general, the correlation coefficient of rainfall from CCAM_CFS is higher than CCAM_IRI.

In order to evaluate the predictive skills of CCAM with two input data and be able to give a conclusion on which one is better, this study applied model assessment method based on the Taylor diagram [20]. The model's skill is evaluated based on the combination of correlation coefficient and standard deviation; the skill measure is the distance from model point to observation point on the diagram. The Taylor diagram of forecast temperature and rainfall from two CCAM cases, with lead times ranging from 1 to 5 months compared to observed stations across Vietnam, was shown in Fig. 9. The results show that with temperature, the model's forecasting skill in lead times is not much different. However, it can be pointed out that skills of short and long lead times are lower than the medium, and CCAM_IRI skills are slightly better than CCAM_CFS. For rainfall, it is easy and better seeing predictive skill in short lead times and skill of CCAM_CFS is significantly better than CCAM_IRI.

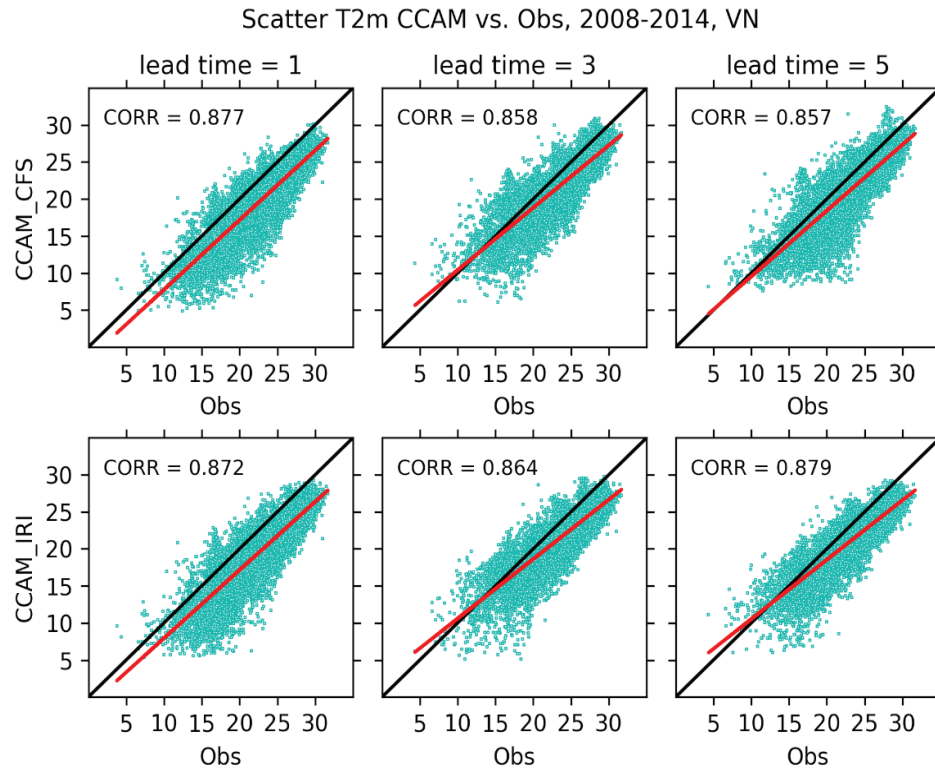


Fig. 7. Scatter graph of the temperature (°C) predicted by CCAM_CFS (top) and CCAM_IRI (bottom) compared to observations, with lead times of 1, 3 and 5 months (from left to right), for the period of 2008-2014, throughout-Vietnam.

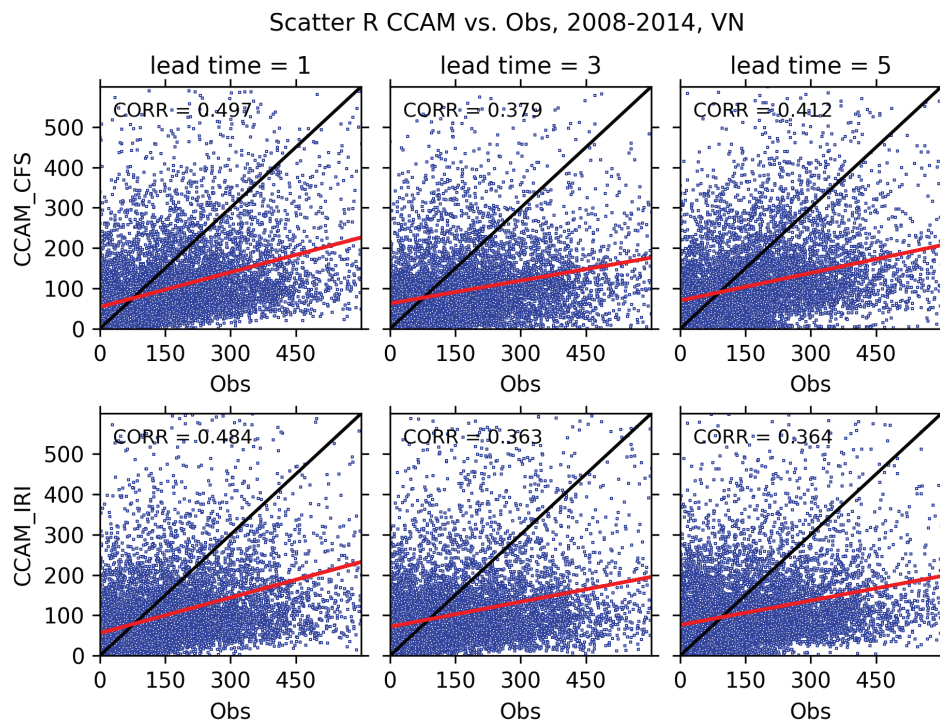


Fig. 8. Scatter graph of the rainfall (mm) predicted by CCAM_CFS (top) and CCAM_IRI (bottom) compared to observations, with lead times of 1, 3 and 5 months (from left to right), for the period of 2008-2014, throughout Vietnam.

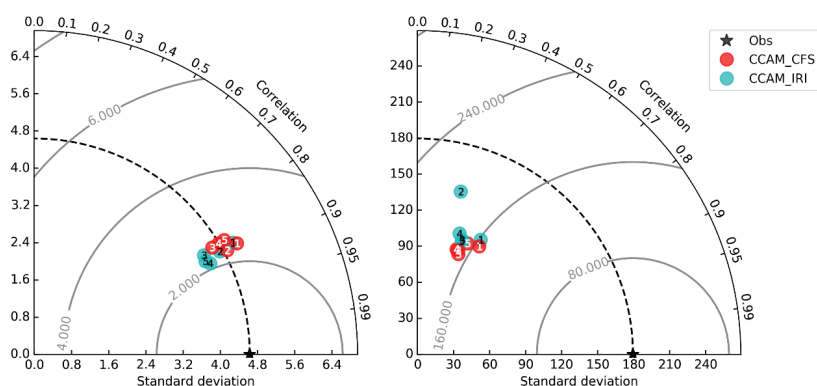


Fig. 9. The Taylor diagram of CCAM_CFS and CCAM_IRI with observation of monthly temperature ($^{\circ}\text{C}$, left) and rainfall (mm, right), with 5 lead times from 1 to 5 months, for the period of 2008-2014.

Summary and conclusions

This research has illustrated the applicability and development of a global model for seasonal climate prediction in Vietnam. CCAM has modern advantages on conformal cubic grid and “stretched grid” technique, which makes it possible to run for both global and regional forecasts with boundary conditions from monthly SST. The study ran CCAM with two SST sources, for global and regional prediction in Vietnam, with lead time up to 5 months, for the period of 2008-2014. The purpose of this study is to show the sensitivity of CCAM with SST on seasonal prediction, as well as to evaluate which CCAM option is better to construct climate period from the model, and initially orientating the use of SST sources for future studies with CCAM. From above results, the following conclusions can be made:

CCAM can capture quite well large-scale circulation including geopotential height and wind at 850 mb level compared to CFS and CFSnl. In which, the geopotential height of CCAM tends to be higher than the CFS and CFSnl in the tropics and subtropics, but lower in the Northern Hemisphere, although the difference is not significant. The January forecast for CCAM is better than in July. The two experiments of CCAM_CFS and CCAM_IRI were not much different.

The prediction of temperature and rainfall of CCAM were evaluated with observed data at 128 stations all over Vietnam. The results show that forecast temperature of CCAM tends to be lower than observed data in most climatic regions across the country, but the magnitude of error is not so much. The correlation coefficient between CCAM and observation is very high, above 0.85 for all lead times. Comparing the two experiments, forecast skill of temperature of CCAM_IRI is slightly better than CCAM_CFS. CCAM generally tends to forecast rainfall higher than observation data in summer and lower in winter; southern regions have smaller errors than northern ones. The predictive skill of rainfall in short lead times is better than others and skill of CCAM_CFS is significantly better than CCAM_IRI.

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[2] T. Binzoni, T.S. Leung, D. Boggett, D.T. Delpy (2003), “Non-invasive laser Doppler perfusion measurements of large tissue volumes and human skeletal muscle blood RMS velocity”, *Phys. Med. Biol.*, **48(1)**, pp.2527-2549.

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